

A DICTIONARY
OF
APPLIED CHEMISTRY

VOL. VII

A DICTIONARY OF APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

REVISED AND ENLARGED EDITION

VOL. VII.

*WITH AN INDEX TO THE WHOLE WORK BY
FRANCES M. G. MICKLETHWAIT*

WITH ILLUSTRATIONS.

LONGMANS, GREEN AND CO. LTD.

CALCUTTA, BOMBAY AND MADRAS

1927

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Amer. Min.</i>	American Mineralogist.
<i>Anal. Fis. Quím.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Annalen der Chemie (Justus Liebig).
<i>Ann. Appl. Biol.</i>	Annals of Applied Biology.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur.</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik.</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Ann. Report</i>	Annual Reports of the Chemical Society.
<i>Annali Chim. Appl.</i>	Annali di Chimica Applicata.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arch. exp. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Astrophys. J.</i>	Astrophysical Journal.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Bentl. a. Trim.</i>	Bentley and Trimen. Medicinal Plants.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Brewers J.</i>	Brewer's Journal.
<i>Brit. Assoc. Rep.</i>	Report of the British Association for the Advancement of Science.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Asso. Chim. Suçr.</i>	Bulletin de l'Association des Chimistes de Suçrerie et de Distillerie.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. Biol.</i>	Bulletin de la Société de chimie Biologique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Chem. and Met. Eng.</i>	Chemical and Metallurgical Engineering.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Soc. Abstr.</i>	Chemical Society of London. Abstracts.
<i>Chem. Soc. Proc.</i>	Journal of the Chemical Society of London. Proceedings.
<i>Chem. Soc. Trans.</i>	Journal of the Chemical Society of London. Transactions.
<i>Chem. Umschau.</i>	Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse, und Harze.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.
<i>D. R. P.</i>	Deutsches Reichs-Patent.
<i>Färber-Zeit.</i>	Färber-Zeitung.
<i>Flück. a. Hanb.</i>	Flückiger and Hanbury. Pharmacographia.
<i>Frdl.</i>	Friedländer's Fortschritte der Teerfarbenfabrikation.
<i>Gazz. Chim. Ital.</i>	Gazzetta Chimica Italiana.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>J.</i>	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
<i>Jahrb. Min.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
<i>Japan J. Phys.</i>	Japanese Journal of Physics.

ABBREVIATIONS OF THE TITLES OF JOURNALS AND PUBLICATIONS

<i>J. Agric. Res.</i>	Journal of Agricultural Research.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Bact.</i>	Journal of Bacteriology.
<i>J. Bd. Agric.</i>	Journal of the Board of Agriculture.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Chem. Soc. Japan</i>	Journal of the Chemical Society of Japan.
<i>J. Chim. Phys.</i>	Journal de Chimie Physique.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i>	Journal of General Physiology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i>	Journal of the Institute of Brewing.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Soc.</i>	
<i>Japan</i>	Journal of the Pharmaceutical Society of Japan.
<i>J. Phys. Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Kolloid Zeitsch.</i>	Kolloid-Zeitschrift.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Met. & Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshette für Chemie und verwandte Theile anderer Wissenschaften.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeit.</i>	Pharmaceutische Zeitung.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society.
<i>Phot. J.</i>	Photographic Journal.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i>	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Sci. Abstr.</i>	Science Abstracts.
<i>Sci. Proc. R. Dublin Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzb.</i>	Sitzungsberichte der K. Akademie zu Wien.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Swiss Pat.</i>	Swiss Patent.
<i>T.</i>	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>U.S. Pat.</i>	United States Patent.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Krist.</i>	Zeitschrift für Kristallographie.
<i>Zeitsch. Krist. Min.</i>	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i>	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. Physik.</i>	Zeitschrift für Physik.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Electrochemie.
<i>Zeitsch. ges. Brauw.</i>	Zeitschrift für das gesamte Brauwesen.

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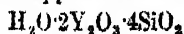
A

DICTIONARY

OF

APPLIED CHEMISTRY.

THALENITE. Silicate of yttrium (Y_2O_3 , 58·64 p.c.) with the approximate formula



Several other constituents are present in small amount, including 1·4–2·5 p.c. of gas (nitrogen and helium) liberated when the mineral is heated or treated with acids. It is yellow to flesh-red and translucent with a greasy lustre; sp.gr. 4·11–4·23; H. 6½; readily decomposed by dilute hydrochloric acid with separation of gelatinous silica. Monoclinic crystals and massive material occur with fluorite, gadolinite, and allanite in quartz at Osterby in Sweden.

L. J. S.

THALLIUM, sym. Tl., at.wt. 204·0, was discovered spectroscopically by Crookes in 1861 (Chem. News, 1861, 3, 193) in a seleniferous deposit from a sulphuric acid manufactory. It occurs in many iron and copper pyrites, in some micas, in zinc blendes, in the minerals *marcasite*, *hematite*, *crookesite* ($CuTlAg_2Se$, *lorandite* ($TlAsS_2$), *urbaitite* $TlAs_2SbS_6$, and in various other iron and manganese ores (Igelström, Z. Krist. Min. 1895, 25, 94; Antipoff, J. Russ. Phys. Chem. Soc. 1896, 28, 384; Hartley and Ramage, Chem. Soc. Trans. 1897, 533). It also occurs in small quantities in various mineral springs, and has been found in volcanic exhalations.

Its presence has been observed in crude zinc (Kosmann) and in platinum and its ores (H. N. Warren, Chem. News, 1887, 55, 241).

Thallium is prepared from flue dust by boiling it with dilute sulphuric acid and precipitating the chloride or iodide by treatment with hydrochloric or hydriodic acid, after which the metal can be obtained by electrolytic deposition, by the action of potassium cyanide or by electrolysis (Bunsen, Phil. Mag. 1865, [iv.] 29, 168; Foerster, Zeitsch. anorg. Chem. 1897, 15, 71). Traces of lead, tin, copper, and aluminium occur as impurities in commercial thallium (Pollock, Sci. Proc. Roy. Dublin Soc. 1909, 11, 338).

Thallium is a bluish-white, lead-like, crystalline, extremely soft metal, malleable, but of

low tenacity. It exists in two modifications, the transition temperature being 226° (235·3°, Richards and Smyth). Its sp.gr. is 11·85, its m.p. 303° (Potrenko, Zeitsch. anorg. Chem. 1906, 50, 133), its b.p. in vacuum 818° (Krafft and Knocke, Ber. 1909, 42, 202); at ordinary pressure 1515±2° (Isaac and Tammann, *ibid.* 1907, 55, 58); but its b.p. should be 1462° at 760 mm. It gives a monatomic vapour. For its absorption spectrum, see W. Grotrian, Zeits. f. Physik. 1923, 12, 218–231; Narayan, Gunnaiya and Rao, Proc. Roy. Soc., 1914, A., 106, 596. It commences to volatilise at 174° in vacuo. At a high temperature it may be distilled in a current of hydrogen. When heated it burns with a beautiful green flame, and its flame spectrum is characterised by a single green line. The heat of solution of thallium in thallium amalgams of 0·0–11·17 p.c. thallium has been determined by Theodore W. Richards and Charles P. Smyth by the adiabatic method (J. Amer. Chem. Soc. 1923, 45, 1435–1460). The following values of the heat of solution in joules at 20° of 1 gram-atom of thallium in amalgams of the composition stated are recorded: 0·92 p.c., 2706; 2·49 p.c., 2265; 3·81 p.c., 1917; 5·21 p.c., 1590; 5·80 p.c., 1975; 8·76 p.c., 486; 10·43 p.c., 45; 11·81 p.c., 234. These values are compared with those obtained by Richards and Daniels for concentrated amalgams, and found to be consistent with them (A. 1920, ii. 34). A short extrapolation of the composition-heat of solution curve above 0·92 p.c. gives a value for the heat of solution of thallium in an infinite quantity of mercury of 2970 joules, a value which is in fair agreement with 3220 joules, the value obtained by Lewis and Randall (Chem. Soc. Abstr. 1921, ii. 241) by calculation from the E.M.F. measurements of Richards and Daniels (*l.c.*) of thallium amalgam concentration cells (Abstr. J. Chem. Soc. 1923, 123, 124, ii. 536).

The temperature of transformation of α - into β -thallium was found by Asahara (Chem. Soc. Abstr. 1925, ii. 463, 645) to be 232°.

Thallium oxidises before the blowpipe. It dissolves readily in dilute nitric and sulphuric

THALLIUM.

acids, but more slowly in hydrochloric acid, and at a red heat decomposes water.

Thallium and its salts are very poisonous (Curci, Chem. Zentr. 1895, ii. 999; Swain and Bateman, J. Biol. Chem. 1910, 7, 137). Thallium forms alloys with a large number of metals, and an amalgam with mercury, which has been proved to be useful in thermometry (McIntosh and Johnson, J. Amer. Chem. Soc. 1912, 34, 910; Pavlovitch, J. Russ. Phys. Chem. Soc. 1915, 47, 29; Hildebrand and Eastman, J. Amer. Chem. Soc. 1915, 37, 2452). The existence of a solid compound Tl_2Hg has been established by Richards and Daniels (J. Amer. Chem. Soc. 1919, 41, 1732), who have studied the electro- and thermo-chemical behaviour, densities and freezing points of thallium amalgams (cf. Richards and Smyth, J. Amer. Chem. Soc. 1922, 44, 524). For references to alloys, see Masumi Chikashigé (Zeitsch. anorg. Chem. 1912, 78, 68); Kurnakov, Shemtschushin, and Tatarin (J. Russ. Phys. Chem. Soc. 1913, 45, 300); Rolla (Gazz. chim. ital. 1915, 45, i. 185; Di Capua, Chem. Soc. Abs. 1925, ii. 787). For the electric resistance of thallium in the temperature field of liquid helium, see H. K. Onnes and W. Tuyn (K. Akad. Amsterdam, Proc. 25, 1923, 9 and 10, pp. 443-450, Comm. No. 160A, from the Phys. Lab. Leiden).

Compounds.—Thallium forms two series of compounds—

(1) **Thallic (TlX_3) compounds** in which the metal is trivalent, corresponding to its position in the aluminium group. Like the compounds of aluminium, the thallic salts undergo hydrolysis in aqueous solution and form complex salts more readily than the corresponding thallous compounds (Spencer and Abegg, Zeitsch. anorg. Chem. 1905, 44, 379). Metallic thallium reduces the thallic salts to the thallous condition. They are also reduced by hydroxylamine in acid or alkaline solutions, by acid solutions of ferrous sulphate, by sodium arsenite solution and, on boiling, with finely divided copper (Berry, Chem. Soc. Trans. 1922, 394). In the absence of oxidising agents, even in the presence of thallous salts, thallic salts give the blue coloration of indophenols when α -naphthol and dimethyl-*p*-phenylene-diamine are added to an alkaline solution of the salt (Marigo, Gazz. chim. ital. 1907, 37, i. 55).

(2) **Thallous (TlX) compounds** in which thallium is monovalent. The thallous salts closely resemble the salts of the alkali metals; thus the hydroxide and carbonate are readily soluble and give an alkaline aqueous solution. Many of the thallous salts, like the sulphate, phosphate, &c., are isomorphous with the corresponding potassium salts and give double salts with platinum chloride Tl_2PtCl_6 . The alum $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and other double sulphates are also closely analogous to the corresponding potassium salts. The thallous halides and sulphides, on the other hand, resemble the corresponding lead and silver salts. Thallous salts react with a clear aqueous solution of antimony chloride and potassium iodide, giving a characteristic voluminous orange precipitate of the compound $3TlI \cdot 2SbI_3$ (Eppraim, Zeitsch. anorg. Chem. 1908, 58, 353).

Thermal studies of the systems formed by thallous nitrate with mercuric chloride, bromide,

and iodide show that no double decomposition occurs, but the following compounds are formed: $TlNO_3 \cdot HgCl$, m.p. 202.5° ; $2TlNO_3 \cdot HgCl$, m.p. 105° ; $TlNO_3 \cdot HgBr$, m.p. 152° (A. G. Bergmann, T. A. Henke, and F. M. Isakson, J. Russ. Phys. Chem. Soc. 1922, 54, 466; see also J. Russ. Phys. Chem. 1922, 54, 200).

Oxides.—Thallium trioxide (thallic oxide) Tl_2O_3 is formed when an alkaline solution of a thallous salt is treated with 3-5 p.c. solution of hydrogen peroxide. When the precipitation is made in the cold, the oxide is brown, is readily soluble in acids, and has sp.gr. 8.65 at 21° , but when the solutions are hot, the oxide is black, is sparingly soluble in acids, and has the sp.gr. 10.19 at 22° . The brown oxide is partly reduced when boiled with water, but the black oxide remains unchanged. At 100° the brown slowly changes into the black variety, and at 529° this change is complete within 24 hours (Rabe, Zeitsch. anorg. Chem. 1906, 48, 427; *ibid.* 50, 158; *ibid.* 1907, 55, 130). Thallic oxide may also be made by acting upon thallous sulphate with an alkaline solution of potassium ferricyanide (cf. Berry, Chem. Soc. Trans. 1922, 394). The crystalline oxide obtained by heating the nitrate has sp.gr. 9.97 (Thomas, Compt. rend. 1904, 138, 1697; see also Fortini, Gazz. chim. ital. 1905, 35, ii. 450). Thallous hydroxide is readily obtained in good yellow, micro-crystalline powder by adding to thallous ethoxide in the cold an equal volume of water, and drying the precipitate on porous plates out of contact with air. A determination of the heat of hydration of thallous oxide by finding the difference in the heat of solution of the oxide and hydroxide in dilute hydrofluoric acid gave a value 3.117 cal., compared with 3.331 cal. found by Thomsen. The heat of hydration is therefore very far removed from that of the oxides of the alkali metals, but thallous hydroxide is nevertheless an equally powerful base, and towards feeble acids, phenols, &c., shows even stronger basic properties than the alkali hydroxides. It can be estimated acidimetrically using phenolphthalein as indicator (R. de Forcrand, Compt. rend. 1923, 176, 873-876; J. Chem. Soc. 1923, 124, ii. 420).

The oxide dissolves in concentrated hydrochloric acid without evolution of chlorine, forming thallic chloride.

Thallium monoxide (thallous oxide) Tl_2O is obtained by shaking fine turnings of the metal with cold water in a current of oxygen or by heating the corresponding hydroxide at 150° - 200° in nitrogen. It is a black powder, m.p. 300° , readily dissolving in water with formation of the hydroxide $TlOH$, which crystallises with 2 molecules of water in yellow needles. The hydroxide is darkened by light, turns turmeric brown, and finally destroys the colouring matter.

With phenolphthalein, thallous hydroxide gives a yellow colour which is slowly discharged by moderately concentrated aqueous solutions, especially on warming. It dissolves isatin to form a deep purple liquid, the colour of which on warming with slight excess of the reagent changes to yellow, due to the formation of a salt of isatinic acid. Thallous salts are generally isomorphous with the salts of the alkali metals (Thorpe, J. 1876, i. 859).

Thallous salts of mono- and di-basic normal

aliphatic acids have been prepared. The *valerate* described by Kuhlmann (Annalen, 1863, 126, 78) is prepared by adding thallous hydroxide solution to valeric acid until the reaction is faintly alkaline to litmus, evaporating the solvent, and recrystallising the residue from benzene. The salt, m.p. 145° – 147° , is very soluble in water, ethyl alcohol, or hot benzene, readily soluble in amyl alcohol, and sparingly soluble in boiling ether, hot light petroleum, or cold benzene. It is not readily thrown out of solution in ethyl alcohol by addition of ether.

The *palmitate*, prepared by adding 33 p.c. thallous hydroxide solution to a hot alcoholic solution of palmitic acid until the reaction is neutral to litmus, crystallises from alcohol in feathery aggregates. It is readily soluble in hot alcohol, insoluble in ether, and soluble in water, the solution being opalescent when dilute. On shaking a warm dilute aqueous solution a froth forms on the surface, which disappears on cooling, and is not formed on shaking the cold solution. It softens on heating at 116° – 118° , but does not melt completely at 170° .

The *oleate* is prepared by adding the theoretical amount of thallous hydroxide solution to oleic acid, dissolved in alcohol, and evaporating the solution to dryness in a vacuum desiccator. The residual soap separates from ethereal solution in white needles, which are soft and can easily be bent. On drying they cohere to a solid, soap-like mass. The salt is also soluble in perfectly dry ether free from alcohol. It forms an opalescent solution and, on shaking, a froth permanent in the cold (distinction from the palmitate). It forms a jelly below the main bulk of the solution, the volume of the jelly being many times greater than that of the oleate left undissolved.

The normal *adipate* is prepared by accurately neutralising adipic acid with aqueous thallous hydroxide solution, using phenolphthalein as indicator. The solution is evaporated to small bulk and the crude adipate precipitated with ethyl alcohol. The salt is dissolved in ethylene glycol, in which it is very soluble, and butyl alcohol added with continued heating until a faint cloudiness is apparent in the boiling mixture; on cooling, the salt separates out in crystalline leaflets.

The normal *pinelate* is obtained by neutralising an aqueous solution of pimelic acid with thallous hydroxide solution, using phenolphthalein as indicator and evaporating the solution to dryness. It is much more soluble in water than the normal adipate, and is almost insoluble in ethyl alcohol, but can be recrystallised from amyl alcohol, in which at the boiling-point it is sparingly soluble, separating on cooling in long needles. The acid *pinelate* is readily soluble in water, almost insoluble in ethyl alcohol, and crystallises from amyl alcohol in prisms.

Thallous salt of ethyl acetonedicarboxylate.—Minute needles, melting at 125° (decomp.), readily soluble in cold ethyl or methyl iodide, thallous iodide being deposited on standing or on heating. This property is shared by thallous acetylacetonate (Kurowski, Ber. 1910, 43, 1078; Morgan and Moss, J. 1914, 106, 195).

Thallous salts of fumaric, maleic, succinic and

tartaric acids, and also of cresol, resorcinol, guaiacol, naphthol and vanillin are described by Christie and Menzies (J. Chem. Soc. 1925, 127, 2369).

Qualitative reactions of aqueous thallous hydroxide solutions with sugars.—In concentrated aqueous solution, fructose, glucose, and xylose give with thallous hydroxide solution in the cold yellow precipitates which, on heating, become reddish-yellow, and finally very dark; under suitable conditions mirrors are formed. With dilute solutions no precipitates are formed with glucose and fructose, but the same colour changes are observed on heating, and again on heating thallium mirrors are formed, provided only the thallous hydroxide is present in sufficient excess. Sucrose and mannitol can be boiled with 10 p.c. thallous hydroxide solution without change other than the appearance of a faint yellow colour, but after hydrolysis of sucrose with dilute sulphuric acid mirrors are formed on subsequent heating with thallous hydroxide solution. The formation of mirrors is favoured by addition of ammonium or sodium hydroxide. Good results are obtained by heating a mixture of N-glucose and thallous hydroxide with addition of 4 or 5 drops of N-sodium hydroxide solution in a clean test-tube for 2 minutes in a water-bath. The mirrors obtained can readily be removed from the glass by boiling with tap-water, but are permanent for some weeks under cold air-free distilled water. On adding tetra-methyl- γ -fructose to thallous hydroxide solution, a brown colour is developed in the cold, a small amount of a dark flocculent precipitate being also formed; on boiling this brown colour becomes darker and the precipitate dissolves. No mirror is formed. A standard solution of thallous hydroxide may be used for the titration particularly of organic acids. The thallous salts of organic acids are considerably less soluble than those of the alkali metals, are readily crystallised, and hence can be used as a convenient means of isolation and purification (Menzies and Wilkins, Chem. Soc. Trans. 1924, 125, 1148).

The *oxide* (TiO_2), probably $\text{Ti}_2\text{O}_3 \cdot \text{Ti}_2\text{O}_5$, is prepared by adding 175–200 grms. of 20 p.c. potassium hydroxide to 15 grms. of a 10 p.c. aqueous solution of thallous sulphate. The solution is filtered, cooled to -15° , and 3.5 grms. of a 3 p.c. solution of hydrogen peroxide is added with constant shaking. The oxide forms a bluish-black, lustrous precipitate, is quickly decomposed into thallic oxide and thallous hydroxide by cold water and by dilute acids. It readily absorbs carbon dioxide, and, unlike thallous salts, is oxidised by a current of oxygen at ordinary temperature to thallic oxide (Rabe, Zeitsch. anorg. Chem. 1908, 58, 23).

When a mixture of thallous sulphate and oxalic acid is electrolysed at the ordinary temperature with a current of 3–4 volts and 0.15–0.2 ampère, the oxide Ti_2O_3 or $\text{TiO}_2 \cdot \text{Ti}_2\text{O}_5$ is deposited on the anode. When the deposit is dissolved in dilute hydrochloric acid, chlorine is evolved and a yellow salt $\text{TiCl}_3 \cdot 3\text{TiCl}$ is formed (Gallo and Cenni, Atti R. Accad. Lincei, 1906, [v.] 17, 276).

The following complex salts of copper and thallium are described by G. Cannori (Gazz. chim. ital. 1922, 52, ii, 206), viz: $\text{Ti}_2\text{Cu}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

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blue crystals; $\text{Ti}_2\text{Cu}(\text{SO}_4)_2$, a yellow powder; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Cu_2SO_4 , Ti_2SO_4 , cinnabarised crystals soluble in aqueous ammonia to a blue solution; $\text{Ti}_2\text{Cu}(\text{S}_2\text{O}_8)_2$, a yellow, microcrystalline powder (Chem. Soc. Abstr. 1923, 124, ii. 74).

For the halogen and mixed halogen compounds of thallium, see Wells and Penfield (Zeitsch. anorg. Chem. 1894, 6, 312); Meyer (*ibid.* 1900, 24, 321; *ibid.* 1902, 32, 72); Thomas (Compt. rend. 1900, 131, 892, 1208; *ibid.* 1901, 132, 80, 1487; *ibid.* 1902, 133, 735; *ibid.* 1902, 134, 545; *ibid.* 1903, 135, 1051; *ibid.* 1906, 142, 838; *ibid.* 1907, 143, 282; Ann. Chim. 1907, [viii.] 11, 204); Cushman (Amer. Chem. J. 1900, 24, 222; *ibid.* 1901, 26, 505); Maitland and Abegg (Zeitsch. anorg. Chem. 1906, 49, 341); Stolzenberg and Huth (Zeitsch. physikal. Chem. 1910, 71, 641). Thallium halides form double salts with many other metals (Meyer, *l.c.*; Thomas, *l.c.*; Pratt, Zeitsch. anorg. Chem. 1895, 9, 19; Wells and Foote, Amer. J. Sci. 1897, 3, 466; Ephraim and Heymann, Ber. 1909, 42, 4456; Ephraim and Barteczko, Zeitsch. anorg. Chem. 1909, 61, 238; Gewecke, Annalen, 1909, 366, 217; Delépine, Compt. rend. 1909, 149, 1072; Gewecke, Zeitsch. anorg. Chem. 1912, 75, 272; Sandonini, Atti R. Accad. Lincei. 1913, [v.] 22, ii. 20; Scarpa, *ibid.* 1912, [v.] 21, ii. 719; Lunde, Chem. Soc. Abstr. 1925, ii. 941; Randall and Vanselow, *ibid.* 1925, ii. 33). Thallous chloride darkens on exposure to light and becomes blackish-brown, due to the formation of a photo-thallous chloride and thallous-thallic chloride (*cf.* Renz, Helv. Chim. Acta, 1919, 2, 704). When thallium is dissolved in hot dilute hydrofluoric acid, H_2TlF_6 is obtained crystallising in white prisms. On heating it evolves hydrofluoric acid; its aqueous solution is acid, but does not attack glass, the fluorine ion being masked. It forms two types of salts, KHTlF_6 and K_2TlF_6 (Barlot, Compt. rend. 1920, 171, 1143).

Thallic sulphide Ti_2S_3 is formed when the metal is fused with excess of sulphur. It is black and above 12° is plastic, but below 12° it is hard and brittle. When sulphuretted hydrogen is passed into a solution of a thallous salt, thallous sulphide Ti_2S is formed as a black precipitate, which can be obtained in a crystalline form (Staněk, Zeitsch. anorg. Chem. 1898, 17, 117; see also Loczka, Chem. Zentr. 1898, i. 657; Hawley, J. Amer. Chem. Soc. 1907, 29, 1011). According to Pélabon, (Compt. rend. 1907, 145, 118) the sulphides Ti_2S_7 , Ti_2S_8 also exist (see Hofmann and Höchtlein, Ber. 1903, 36, 3090). Double sulphides with copper and tin are also known (Bruner and Zawadzki, Bull. Acad. Sci. Cracow, 1909, 312; Hawley, J. Phys. Chem. 1906, 10, 654).

Thallium sulphates and their double salts are described by Stortenbeker (Rec. trav. chim. 1902, 21, 87); Kohn (Zeitsch. anorg. Chem. 1908, 59, 111); Piccini and Fortini (*ibid.* 1902, 31, 451); Locke (Amer. Chem. J. 1902, 27, 280); Marshall (Proc. Roy. Soc. Edm. 1902, 24, 306); Meyer and Goldschmidt (Ber. 1903, 36, 238). Many double salts of thallic and thallous sulphates have been described, but according to Benrath and Espenschied (Zeitsch. anorg. Chem. 1922, 121, 361), only two exist, viz. $\text{Ti}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3$ and $5\text{Ti}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3$, all others being regarded as mixtures of these. For

the reduction of thallic sulphate in presence of ferrous sulphate, see Berry (Chem. Soc. Trans. 1923, 123, 1109).

The solubility of thallic oxide, the basic sulphate, $\text{Ti}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and the acid sulphate, $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, has been determined in sulphuric acid of various concentrations from 10 p.c. to 90 p.c. at various temperatures and the stability diagram constructed. It is shown that no other thallic sulphate exists under the above-named conditions, and that the other thallic sulphates described in the literature are mixtures, the formation of which is due to the slowness of the change from one salt to another. The transition point of the two sulphates mentioned above lies at about 40° . The corresponding selenates have also been investigated, and are found to be very similar to the sulphates; the main point of difference between them is that the transition point lies at 45° (Julius Meyer, Rec. trav. chim. 1921, 43, 614-619; J. Chem. Soc. 1923, 123, 124, ii. 637).

Thallium sulphite is a white granular crystalline powder (Seubert and Elten, Zeitsch. anorg. Chem. 1892, 2, 434; *ibid.* 1893, 4, 44).

Thallium selenides Ti_2Se and TiSe , are known. The existence of a third Ti_2Se_3 (Pélabon), or Ti_2Se_5 (Murakami) is doubtful.

Thallium telluride is described by Brukl (Monatsh. 1924, 45, 471, (Chem. Soc. Abstr. 1925, ii. 895).

Thallium nitrates are described by Wells and Beardsley (Amer. Chem. J. 1901, 26, 257); Meyer (*l.c.*); Thomas (Compt. rend. 1904, 138, 1697); van Eyk (Zeitsch. physikal. Chem. 1906, 51, 721).

Thallium mercurous nitrate, m.p. 76° , sp.gr. 5.3, gives a clear mobile solution miscible with water and not reacting with sulphides. It forms a useful liquid for the separation of mineral sulphides (Retgers, Jahrb. Min. 1896, ii. 183).

Thallium nitrite forms double salts with cobalt and other metals (Przibylla, Zeitsch. anorg. Chem. 1898, 18, 448; Cunningham and Perkin, Chem. Soc. Trans. 1909, 1569; Tanatar and Petroff, J. Russ. Phys. Chem. Soc. 1910, 42, 94).

For nitrous-nitric complexes of thallium, v. Gazz. chim. ital. 1919, 49, ii. 217.

Thallous tetraborate $\text{Ti}_2\text{B}_4\text{O}_{10}$, hexaborate $\text{Ti}_2\text{B}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$, octoborate $\text{Ti}_2\text{B}_8\text{O}_{22} \cdot 4\text{H}_2\text{O}$, decaborate $\text{Ti}_2\text{B}_{10}\text{O}_{26} \cdot 8\text{H}_2\text{O}$, dodecaborate $\text{Ti}_2\text{B}_{12}\text{O}_{28} \cdot 7\text{H}_2\text{O}$, have also been prepared. Thallous perborate is also known.

Thallium azoinide or nitride TIN , remains unchanged when heated to 340° , but explodes when heated more strongly or when struck (Curtius and Risson, J. pr. Chem. 1898, [ii.] 56, 261; also Dennis and Doan, J. Amer. Chem. Soc. 1896, 18, 970; Franklin, J. Phys. Chem. 1912, 16, 682).

Thallium oxalate $\text{HTl}(\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ is prepared by treating the freshly precipitated hydroxide at 25° with a large excess of a cold saturated solution of oxalic acid. When suspended in absolute alcohol, cooled to 0° , and treated with dry ammonia, the compound $\text{Ti}(\text{CO}_2)_2 \cdot \text{NH}_3 \cdot (\text{NH}_3)_2$ is formed; at a higher temperature the compound $\text{Ti}(\text{CO}_2)_2 \cdot \text{NH}_3$ separates. The pyridine salt $\text{Ti}(\text{CO}_2)_2 \cdot \text{HC}_5\text{H}_5\text{N}$ and the salt $\text{Ti}(\text{CO}_2)_2 \cdot (\text{NH}_3)_2$, as well as other oxalates $\text{Ti}(\text{CO}_2)_2 \cdot (\text{C}_6\text{H}_5)_3$, $3\text{H}_2\text{O}$ and $\text{Ti}_2(\text{CO}_2)_4 \cdot 3\text{H}_2\text{O}$

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have also been obtained (Rabe and Steinmetz, Ber. 1902, 35, 4447).

Thallous alkyl oxides (Chem. Soc. Abstr. 1923, i, 84).

Thallous carbonate, nitrite, and cyanide are also known.

Thallous chromate is practically insoluble in dilute alcohol and may be employed for the quantitative separation and estimation of thallium (see Cuttice and Canneri, Gazz. chim. ital. 1921, 51, 2, 189).

Thallous picrolonate, see Giua (Gazz. chim. ital. 1924, 54, 204; Chem. Soc. Abstr. 1924, 126, i, 770).

For a number of other thallium salts, see Georgis, Gazz. chim. ital. 1894, 24, ii, 474; Stavenhagen, J. pr. Chem. 1895, [ii.] 51, 1; Joly, Compt. rend. 1894, 118, 640; Mauro, Real. Accad. Lincei, 1893, ii, 382; Hofmann, Zeitsch. anorg. Chem. 1896, 12, 55; Piccini, *ibid.* 1897, 13, 441; Piccini and Marino, *ibid.* 1901, 27, 62; Marino, *ibid.* 1909, 62, 173; Glauser, *ibid.* 1910, 66, 437; Dennis and Doan, *l.c.*; Wyruboff, Bull. Franc. Min. 1896, 19, 219; Hawley, J. Amer. Chem. Soc. 1907, 29, 300; Kurowski, Ber. 1910, 43, 1078; Buchala, J. pr. Chem. 1913, [ii.] 88, 771; Franklin, J. Amer. Chem. Soc. 1915, 37, 2279; Benrath, Zeitsch. anorg. Chem. 1915, 93, 161; for photochemical reactions of compounds of thallium, see Benrath, Zeitsch. wiss. Photochem. 1915, 14, 217; Renz, Helv. Chim. Acta, 1919, 2, 704; 1921, 4950; 1923, 1161; Goddard, Chem. Soc. Trans. 1921, 672; 1922, 36, 256, 482.

Thallium dimethyl fluoride TiMe_2F and the corresponding thallium diethyl fluoride and thallium diphenyl fluoride and similar compounds are described by Krause and von Grosse, Ber. 1925, 58 [B], 272, 1933; Chem. Soc. Abstr. 1925, i, 378, 1252.

For the constitution of aqueous solutions of thallium salts, see Drucker, Zeitsch. Electrochem. 1922, 28, 463-467.

Thallium may be determined by the electrolytic deposition of thallous oxide as follows: A solution containing 0.1-0.5 gram of thallous nitrate and 0.1 gram of free nitric acid is placed in a roughened platinum dish, diluted to 100 c.c., and either 10 c.c. of absolute alcohol or 5-10 c.c. of rectified acetone added. The dish is made the anode in the electrolysis, and the cathode is a disc of iridio-platinum of 12 sq. cm., which is rotated at 300 revs. per minute. The electrolysis is carried out at 60°-62°, directly from a single accumulator. After 10 hours the voltage is raised to 2.5-3.0 volts and a current of 0.05 amp. passed for a short time. The deposit, which is firm, is washed with water and dried at 160°-170°, preferably in an electrically heated oven; in any case reducing gases must not come into contact with the deposit. When dry the dish is cooled in a desiccator and weighed rapidly, since the deposit is somewhat hygroscopic. The method is good, the results being accurate to within ± 0.2 p.c. (W. Dieterle, Zeitsch. Elektrochem. 1923, 29, 493; J. Soc. Chem. Ind. 1924, 43, B, 79).

THALLOCHLORE. A name given by Knop and Schneidermann to the green colouring matter of lichens (Annalen, 56, 147).

THAPSIC ACID $\text{C}_{11}\text{H}_{18}\text{O}_4$. Obtained from the dried roots of *Asperula* (Linn.)

(Canzoneri, Gazz. chim. ital. 13, 514; 24, ii, 437); m.p. 123°-124°. The anhydride melts at 71°.

Thapsic acid is identical with tetradecane dicarboxylic acid obtained by the electrolysis of potassium ethyl azelate (Carmichael, Chem. Soc. Trans. 1922, 121, 2545).

THAUMASITE. Hydrated silicate, carbonate, and sulphate of calcium, crystallised in the hexagonal system. This mineral is of interest in containing three acid radicles, and the existence of such a compound, which has not been prepared artificially, may possibly have some bearing on the setting of plasters. The formula is $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$. Since $13\text{H}_2\text{O}$ is expelled at 150°, and the remainder in four stages below a red-heat, corresponding to four hydroxyl groups, the formula may be written $[(\text{CaOH})\text{CO}_3][(\text{CaOH})\text{SO}_4][\text{CaOH}]\text{HSiO}_3 \cdot 13\text{H}_2\text{O}$. The mineral forms snow-white, alabaster-like masses or loose aggregates of small transparent hexagonal prisms. It is very light, sp.gr. 1.88; H. 3½; readily decomposed by dilute hydrochloric acid, and slightly soluble in water. It is known from two mines in Sweden, and has been found in considerable quantity with pectolite ($\text{HNaCa}_2(\text{SiO}_3)_2$) and apophyllite in cavities in basalt at West Paterson in New Jersey. Another occurrence is as a filling of small fissures in metamorphosed dolomitic limestone in Beaver Co., Utah.

Wilkeite is a similar complex combination of calcium salts, but containing in addition phosphate and a surplus of oxide, the formula being $3\text{Ca}_3(\text{PO}_4)_2 \cdot 3\text{Ca}_2\text{SiO}_3 \cdot 3\text{CaSO}_4 \cdot \text{CaCO}_3 \cdot \text{CaO}$. The hexagonal crystals have characters near those of apatite, sp.gr. 3.234. They are pink in colour and are found embedded in the blue calcite of a contact-metamorphic limestone at Crestmore in Riverside Co., California.

L. J. S.

THEBAINE v. OPIUM.

THEINE or *Caffeine* v. **CAFFEINE.** For the extraction of caffeine by various solvents, see H. E. Watson, K. M. Sheth, and J. J. Sudborough, (J. Ind. Inst. Sci. 1922, 5, 177-207).

The fact that theine (caffeine) exists in the leaves of the coffee plant has long been known, but it is only since the war that they have been commercially exploited to produce this drug. The idea originated in Sumatra, where under the present system of cultivation coffee is frequently attacked by insects of the genus *coccus*. With the failure of the berry crop, the growers, seeking a substitute for the ordinary caffeine-containing product, collected the leaves from which pure theine was prepared. With the war the demand for theine so greatly expanded that the process of extracting it from the leaves was resorted to on an extensive scale by the Dutch factories, which purchased them by the ton from the native growers and pickers. So far, the process of preparation has been kept secret, but there is no gainsaying the purity of the product. On the western side of the island of Sumatra the producers, and, in fact, the general public, have long used an infusion of torrefied coffee leaves as a beverage, the berries themselves all being reserved for export. The use of the leaves for this purpose has grown to such an extent that

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it is now looked upon as an absolute necessary of life.

During the past four years Germany has been importing enormous quantities of coffee leaves from Sumatra and utilising them in the same way; and in some parts of Germany the infusion from the leaves has quite taken the place of the berry, the price of which has been an obstacle to its ready sale. Careful research work has resulted in proof that the extract obtained from the leaves has undoubted nutritive properties. In addition, a vast number of analyses have been taken which furnish data practically guaranteeing its safety as an article of diet, with an entire absence of deleterious effects. With a little boiled rice and infusion of the coffee leaf a man will support the labours of the field in rice-planting for days and weeks successively up to the knees in mud, under a burning sun or drenching rains, which he could not do by the use of simple water, or by the aid of spirituous or fermented liquors. Planters in Sumatra had opportunity of observing for twenty years the comparative use of the coffee leaf in one class of natives, and of spirituous liquors in another, the native Sumatrans using the former, and the natives of British India (imported labour) the latter. Records show, while the former expose themselves with impunity for any period to every degree of heat, cold and wet, the latter can endure neither wet nor cold for even a short period without danger to their health. Although the coffee berry can only be produced in certain climates and on soils containing marked peculiarities, the plant itself will flourish in any tropical country where the soil is sufficiently fertile, and in consequence the field for production of the leaves is almost unlimited. As a means, therefore, of providing caffeine for general consumption, free from deleterious qualities, and yet containing great nutritive properties, the leaves appear to be eminently suitable.

Samples of the leaves grown in North Queensland have already been shipped to Hamburg, where they have been most favourably commented upon. The shippers' withstood the long voyage well. They disclosed fairly regular fragments of shining leaves mixed with small pieces of stalk, all of deep brown colour. The odour is described as exceedingly fragrant and something like a mixture of tea and coffee. An infusion in boiling water produced a transparent, dark-amber to brown-coloured liquid, which, used in the same way as ordinary coffee, with the addition of milk and sugar, was pronounced by experts as excellent. The price of the leaves is only about one-half that of the berries for which they are proposed as a substitute (Pharm. J. 1924, 113, 59).

For the determination of theine in coffee, see Lucas (J. Soc. Chem. Ind. 1924, 43, B, 489).

THENARDITE. A mineral consisting of anhydrous sodium sulphate (Na_2SO_4), crystallised in the orthorhombic system. It is found as large crystals, 6 ins. or more in length, on the shores of salt, soda, and borax lakes in arid regions, and sometimes forms beds of considerable extent, together with glauberite, &c. Sp.gr. 2.68-2.69; H. 2-3. The water-clear crystals absorb water from a moist atmosphere and become cloudy. Localities are: Borax

Lake in San Bernardino Co., California; on the Rio Verde in Arizona; Rhodes Marsh in Nevada; Tarapaca and elsewhere in the Chilean nitrate deposits; Espartinas near Madrid; the oasis of Bilma in French Sudan; and the salt lakes north of the Caspian. It is of rare occurrence in the German abraum-salts and in the fumaroles of volcanoes. I. J. S.

THENARD'S BLUE. Cobalt blue v. PIGMENTS.

THEOBROMA CACAO v. *Coçôa*.

THEOBROMIC ACID $\text{C}_{19}\text{H}_{33}\text{COOH}$ is obtained from cocoa bitter and melts at 72° ; it is apparently identical with arachidic acid (q.v.).

THEOBROMINE v. **CAFFEINE**, Vol. I., 726. For the estimation of theobromine in cocoa and its products v. Wadsworth, Analyst, 1921, 32. The theobromine content of nibs from 21 different producing areas varied from 2.2 to 3.9 p.c. calculated on dry, fat-free material, the variation depending upon the variety of the bean and on the degree of fermentation, a process which considerably reduces the theobromine content. In the shell the theobromine varied from 0.19 to 2.89 p.c., the alkaloid being carried by the sweatings from nut to shell. No theobromine was lost from nibs or shells during roasting. In order to determine the amount of theobromine in cocoa, the cocoa is heated in a dry Kjeldahl digestion flask until the theobromine is sublimed and the cocoa completely carbonised. The theobromine is extracted with hot water, the solution filtered, and the filtrate evaporated to dryness on the water-bath. The residue is purified by extraction with absolute alcohol, treated with aqueous ammonia, and dissolved in chloroform. The chloroform solution is filtered and evaporated to dryness, the residue extracted three times with 3 c.c. of hot water, filtered, and the filtrate evaporated to dryness on a watch glass, dried at 100° - 105°C ., and weighed. The whole determination takes about $2\frac{1}{2}$ hrs. The percentage of theobromine in various samples of commercial cocoa varied from 0.45 p.p. to 1.17 p.c. (T. Ugarte, J. Pharm. Chim. 1923, 27, 420-423; J. Soc. Chem. Ind. 1923, 42, 675A).

Theobromine may be distinguished from caffeine by the differences in the colorations produced when the respective bismutho-iodides are reduced by hydriodic acid. For the distribution of theobromine during the fermentation of cacao, see Knapp and Wadsworth (J. Soc. Chem. Ind. 1924, 43, 124 T).

THEOBROMOSE, THEOCIN, THEOLACTIN, THEOPHORIN, THEOPHYLLIN, v. SYNTHETIC DRUGS.

THEOCYLENE. Compound of theobromine and aspirin.

THEOFORM. A condensation product of theobromine and formic acid.

THEOPHYLLINE v. **CAFFEINE**.

THEOPHYSEM. Iodoethylallylthioxy-urea.

THEOSALIN. Trade name for an addition product of theobromine sodium, and sodium sulphosalicylate.

THERMAL PROPERTIES OF GASES. In J. Phys. Chem. Feb., 1924, 28, 97, Pickering reviews the constants of the more common gases

THERMIT PROCESS.

and gives the following values as the most probable:—

Gas	Critical Temperature °C. abs.	Critical Pressure atm.	Critical Density gr. per c.c.
Acetylene	300.0 ?	16.6	0.231
Air	132.4	37.2	0.355
Allylene	401.0	—	0.31c
Ammonia	405.5	112.0	0.236
Argon	350.7	48.0	0.52
Butane (iso)	406.8 ?	36.5 ?	—
Butane (n)	426.3 ?	35.7 ?	—
Carbon dioxide	304.1	72.9	0.460
Carbon monoxide	134.4	34.6	0.311
Chlorine	417.0	76.0	0.573
Cyanogen	401.4	59.7	—
Ethane	305.2	48.8	0.21
Ethyl chloride	456.0 ?	54.0 ?	—
Ethylene	282.6	50.7	—
Helium	5.20	2.26	0.066
Hydrogen	33.18	12.8	0.031c
Hydrogen bromide	363.5	—	—
Hydrogen chloride	321.5	83.0 ?	—
Hydrogen iodide	423.9 ?	—	—
Hydrogen sulphide	373.5	89.0	—
Krypton	210.6	54.3 ?	—
Methane	190.6	45.7	0.162
Methyl chloride	416.2	65.9	0.37 ?
Neon	44.7	26.9	—
Nitric oxide	180.0 ?	71.0 ?	—
Nitrogen	126.0	33.5	0.3310
Nitrous oxide	309.6	71.7	0.45 ?
Oxygen ozone	268.0 ?	92.3 ?	—
Phosgene	456.0 ?	—	—
Propane	368.7	45.0	—
Propylene	364.5 ?	45.3 ?	—
Sulphur dioxide	430.3	77.7	0.52 ?
Xenon	289.7	58.2	1.155

(Sci. Abstr. 1924, 27, 531).

Determination of the normal boiling-points of oxygen, nitrogen, and hydrogen.—Henning and Heuse's (Zeits. f. Physik. 1924, 23 1, 105) final results reduced to the thermodynamic scale of temperature are:

Oxygen	—183.00±.02
Nitrogen	—195.81±.02
Hydrogen	—252.78±.02

Over the range —183° to —205° the variation of the boiling-point of oxygen with pressure is given by the equation

$$\log p_{mm} = -379.95/T - 0.0096219T + 1.75$$

$$\log T + 4.53939 \text{ (where } T = 273.20 + t)$$

and for nitrogen by

$$\log p_{mm} = -301.91/T - 0.0090272T + 1.75$$

$$\log T + 4.17643$$

The resistances of two Pt thermometers used over a period of twelve years in this work were again measured at these fixed-point temperatures. The values have remained practically constant, the greatest observed alteration only corresponding to a change of temperature of 0.02° (Sci. Abstr. 1924, 27, 645).

THERMIOL. Trade name for sodium phenylpropionate.

THERMIT PROCESS. 'In a thermit reaction a metallic compound (e.g. an oxide) is reduced by one or several metals or metallic alloys in such a way that when the mixture is ignited at one place, the reaction continues to go on spontaneously with complete oxidation of the reducing element, a fluid slag being formed, whilst the reduced metal is obtained as a compact

uniform regulus; if the oxide is used in excess, the reduced metal is free, or practically free, from the element used as reducing agent' (H. Goldschmidt, *Electrochem. and Metall. Ind.* 1908, 6, 360).

In 1898 Goldschmidt (Stahl and Eisen, 1898, 18, 408; J. Soc. Chem. Ind. 1898, 17, 543, 584, 649; Zeitsch. für. Elektrochem. 1898, 4, 494; 1899, 6, 53) succeeded in reducing the oxides of chromium, manganese, iron, copper, titanium, boron, tungsten, molybdenum, nickel, cobalt, zirconium, vanadium, columbium, tantalum, cerium, thorium, barium, calcium, sodium, potassium, lead, and tin very conveniently by means of aluminium. Such reduction processes had been anticipated, owing to the fact that measured with respect to the same quantity of oxygen, aluminium has a greater heat of oxidation than almost any other metal. Earlier attempts to carry out such experiments had, however, proved very unsatisfactory; either the reactions would not begin, or they occurred with explosive violence. Goldschmidt overcame the difficulty by mixing the finely-divided oxide intimately with powdered or granulated aluminium, and starting the action at one point by raising its temperature sufficiently high. The reaction being once initiated, the enormous heat developed causes it to spread quickly throughout the entire mass, the time of reaction not varying appreciably with the quantity of material employed, and being about 30 seconds in the case of iron oxide and aluminium. To start the reaction at one spot, Goldschmidt placed a small heap of a mixture of powdered aluminium (or magnesium) and barium peroxide on top of the mixture to act as a fuse, and inserted therein a strip of magnesium ribbon. On lighting the latter, the fuse ignites, and the thermit reaction is started.

Owing to the heat developed in these reactions and the rapidity with which they occur, an enormous temperature is produced, second only to that of the electric arc. It has been estimated at 2600°–3000°, and direct observation with a Fery radiation pyrometer has shown that the temperature of a stream of steel produced from iron oxide and aluminium, as it was poured from the crucible, was 3200° (the melting-point of steel is approximately 1350°). At such temperatures the entire contents of the crucible remain liquid; the reduced metal sinks to the bottom, covered with a layer of molten alumina.

Other metals have been tried for the reduction of metallic oxides. Perkin (Faraday Soc. Trans. 1907, 3, 115, 179), and also Goldschmidt have tried calcium, but the reactions are too violent to be of much use, whilst the slag is difficultly fusible. Silicon (made in the electric furnace) has also been tried; but the reactions are too slow. The so-called mixed-metal, which consists essentially of cerium, has, however, been successfully employed in the preparation of pure vanadium, columbium, and tantalum (Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, 355, 58; Weiss and Aichel, *ibid.* 1904, 337, 370).

A number of mixtures may be used in place of aluminium, and some have been patented. A mixture of equal parts of calcium-thermit and silicon-thermit, so that the active elements,

THERMIT PROCESS.

calcium and silicon, are in the ratio of 2 to 1, is especially effective (Fr. Pat. 361197, 1905). It reacts like an ordinary aluminium-thermit, yielding a thin fluid having approximately the composition $4\text{CaO} \cdot 3\text{SiO}_2$, and melting at 1425° (Boudouard, Iron and Steel, 1905, 352). The active mixture may be prepared either by mixing or alloying calcium with silicon (v. Fr. Pat. 388638, 1908). A mixture of magnesium and silicon may also be used to replace aluminium, giving a reaction like ordinary thermit (Eng. Pat. 3089, 1906; Fr. Pat. 364313, 1906; U.S. Pat. 902871, 1908), whilst magnesium itself acts similarly to calcium in its reactions with metallic oxides. *Magnesium-silicon* thermit is best mixed in proportions which yield a slag of the composition $7\text{MgO} \cdot 4\text{SiO}_2$. A third mixture, viz. *aluminium-thermit* and *calcium-thermit*, gives very good results. The proportions may vary between wide limits, avoiding too large an excess of calcium, and the calcium aluminate slag is more fusible than alumina. A mixture containing 40 p.c. calcium-thermit produces a very fluid slag $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and has a heat effect greater than that of aluminium-thermit (Fr. Pat. 361197, 1905; addn. Jan. 1906; U.S.A. Pats. 875345, 1907; 875666, 1907; 906009, 1908; Eng. Pat. 926, 1906). See also Watts and Breckenridge, *Electrochem. & Metall.* Ind. 1908, 6, 237; Weston and Ellis, *Faraday Soc. Trans.* 1907, 3, 170; 1908, 4, 60, 130; 1910, 6, 144; and Skinder, *Chem. Zentr.* 1909, i, 629.

Technical applications.—Although the thermit reaction (Goldschmidt's reaction only dates from 1898, it has acquired great technological importance, and the subject of 'aluminothermics' has been extensively developed.

Preparation of metals and alloys.—The following are obtained by reducing the requisite metallic oxides (or mixtures of oxides) with a slight deficit of aluminium; chromium, manganese, molybdenum, ferro-titanium, ferro-vanadium, ferro-boron, manganese-copper, manganese-zinc, manganese-tin, manganese-titanium, chromium-manganese. They are of great value in the iron and steel and other metallurgical industries; chromium, in particular, is largely employed in the manufacture of high-speed tool steel and armour plate. The metals and alloys produced are *carbon-free*. The crucibles in which the preparations are carried out must be lined with magnesia (Eng. Pat. 9610, 1905; Fr. Pat. 354597, 1906), one of the few oxides that aluminium is unable to reduce. The best method of procedure to ensure a maximum yield of chromium or manganese consists in mixing 1-4 p.c. of higher oxide with the bulk of lower oxide to be reduced to metal (Eng. Pat. 20004, 1905; Fr. Pat. 358071, 1905; U.S. Pat. 895628, 1908).

For experimental purposes, steel of any grade can be made by the thermit process, since the heat developed is sufficient to melt thoroughly small portions of even the most refractory metals. The thermit steel is free from carbon, but may be converted into high carbon steel by the addition of cast-iron shot.

The slag produced is also of commercial value. It may be employed in the preparation of aluminium, or used in place of natural corun-

dum. It is especially valuable for use in the manufacture of pottery, for which purpose it is mixed with clay and burned (D. R. P. 160780, 1901). *Corubin*, an abrasive material for making emery wheels, emery cloth, &c., is prepared by crushing the slag obtained as by-product in the manufacture of chromium.

Welding iron and steel, and repairing broken steel castings.—The advantages of the thermit process for these applications are, that it is simple, rapid, requires no special skill, and enables repairs to be made *in situ*, when any other process would necessitate a dismantling of apparatus.

The mixture employed is composed of powdered aluminium and magnetic iron oxide, and when ignited yields half its weight of molten steel. Its registered trade name is 'thermit.' The reaction



indicates that approximately 3 parts of aluminium powder require 10 parts of magnetic oxide, and produce 7 parts of iron. Early literature on the subject gives the reaction as



but examination of thermit with a magnet will show that the magnetic oxide is now employed. It is added in the form of granulated rolling-mill scale.

The firing of a charge of thermit produces a pure mild steel of the following average composition—

Carbon	. . .	0.05-0.10
Manganese	. . .	0.08-0.10
Silicon	. . .	0.09-0.20
Sulphur	. . .	0.03-0.04
Phosphorus	. . .	0.04-0.05
Aluminium	. . .	0.07-0.18

Two methods of welding are in use, (a) the reaction serving merely as a source of heat (Eng. Pat. 19328, 1899), and (b) the steel produced by the reaction being utilised as well (Eng. Pat. 10859, 1901; 20894, 1900; U.S. Pat. 729573, 1903). In process (a) pure materials need not be used, and, if necessary, the thermit may be diluted with a cheap oxide, e.g. iron ore or sand, to lower the final temperature reached. This process is used in the butt-welding of pipes and bars. The ends are cut square, smoothed, and clamped together. A mould is then clamped round the junction. A charge of thermit is fired in an ordinary magnesia-lined crucible, allowed to stand half a minute so that slag and steel may separate (the volume of the molten slag is three times that of the iron produced), and then poured out so that the slag comes first. As the slag is poured in the mould on to the pipe, it forms a hard casing around the metal, and the liquid which follows distributes its heat uniformly through this casing to the metal. In about a minute the pipes have been raised to welding heat. The ends are then pressed tightly together by means of screws arranged in position beforehand. The mould is then removed, the slag collar carefully knocked off, and the red-hot joint allowed to cool. Process (b) has been largely employed in welding together tram and railway line sections. The ends are brought together and clamped accurately in position. A refractory clay mould is clamped

round the ends and the requisite charge of thermit fired in a crucible placed over the pouring gate of the mould. At the end of the reaction, the crucible is tapped from the bottom (see Fig. 1), and the liquid steel flows into the mould, passes upwards from the bottom of the mould, surrounds the base and web of the rail, with which it fuses on account of its enormously high temperature, and on cooling makes a solid steel joint.

The welding of rails is a typical instance of the application of process (b) above, which is also employed for all kinds of repairing work, e.g. mending broken engine frames, driving rods

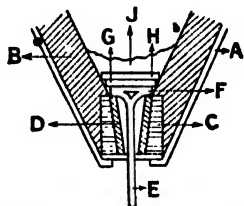


FIG. 1.—TAP-HOLE OF THERMIT CRUCIBLE.

A, iron casing; B, magnesia lining; C, hollow cylindrical magnesistone; D, conical magnesia thimble; E, iron tapping pin, with flattened end F; G, asbestos washer; H, iron washer; J, layer of sand.

and spokes, crank shafts, rudder and propeller shafts, stern-posts, &c., in fact, in the majority of cases where it is cheaper to repair than to replace. Where necessary, the fracture is opened out by drilling holes. A wax matrix is then built up over the break of the exact shape that the thermit steel collar to be fused into the casting is to have. Over this, in a sheet iron box, is constructed a mould, having a pouring gate, a preheating gate, and a large riser (Fig. 2). A gasoline torch, fed with compressed air, is then directed through the preheating gate. It melts out the wax, dries the mould, and heats

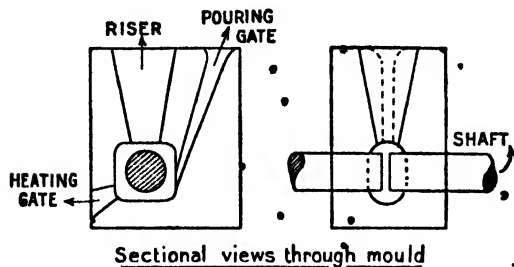


Fig. 2.

the junction to be repaired to a bright red heat. Meanwhile, the crucible containing the thermit is arranged over the pouring gate. The quantity of thermit required is given by the rule: take 32 times the weight of the wax used, or 18 times as many ounces of thermit powder as there are cubic inches of surplus space in the mould. The crucible (Fig. 1) is designed so as to be tapped from the bottom (Goldschmidt, *Zeitsch. Elektrochem.* 1901, 7, 935; Cohn, *J. Gasbeleucht.* 1901, 44). The gasoline torch is withdrawn when the junction is red hot, the preheating gate plugged with a sand core held in readiness, and the thermit fired without delay. After the reaction is over, and the molten liquid

has stood 30 seconds to allow the slag to rise, the crucible is tapped. The molten steel passes down the pouring gate, around the fractured joint, and up into the riser. The ends of the casting melt into the liquid steel, and on cooling one homogeneous mass is formed. The projecting collar of thermit steel around the joint is left on whenever possible.

The average tensile strength of a thermit steel joint is about 30 tons per square inch cross-section. If the projecting collar of thermit steel has to be planed off, and the tensile strength of the joint is less than that of the body of the casting, the weld may be made stronger by introducing nickel into the composition of the thermit; 1 p.c. of nickel increases the tensile strength of the weld about one-third. For a 1 p.c. alloy, 2 p.c. of nickel thermit may be added to the usual steel thermit, or 5 oz. of metallic nickel may be added to each 100 lbs. of thermit.

Thermit powder is supplied in 50 or 100 lb. drums. For use in repair work, about 2 p.c. of manganese and 5 p.c. of mild steel punchings are added. The former acts as a purifier of the steel produced; the latter serves to lower the final temperature of the reaction and so prevent the contents of the crucible from boiling over.

Use of thermit in foundry practice.—(a) The thermit reaction provides a ready means of introducing in an iron ladle a material which will stir up or pole the entire contents of the ladle, and at the same time produce an increase of temperature. For this purpose, the thermit is contained in cylindrical cans with a sleeve in the middle, suitable for passing on an iron rod. The can is held by the iron rod under the surface of the metal, where the reaction takes place. This procedure prevents the iron from becoming too dull to pour (U.S. Pat. 733957, 1903).

(b) A convenient means of purifying the iron in the ladle, by reducing the presence of harmful nitrogen in the molten metal, consists in holding a can of titanium-thermit under the surface as described in (a). This thermit is a mixture of pulverised aluminium and a titanium-iron oxide. The titanium set free in the reaction is sufficient to combine with the nitrogen in the ladle, titanium cyanonitride being produced. During this formation, the entire contents of the ladle are stirred up, to give the gases an opportunity of escaping. The iron is thereby rendered hotter and distinctly more fluid, and castings made from it are distinguished by their closeness of grain, being especially well adapted for withstanding pressure, e.g. cylinders, valves, &c.

(c) The enormous heat developed may be utilised to decrease the size of the risers of steel castings. The thermit, contained in suitable cans, is held in the neck of the riser, which is thus kept in the liquid state for a longer time than would otherwise be the case, thereby facilitating the proper feeding of the casting. The same principle is successfully applied to reduce the size of lost heads of steel ingots.

(d) In foundries where it is of importance to occasionally make a steel casting in a hurry, burning down the requisite quantity of thermit with an admixture of steel punchings affords by far the easiest method of procedure.

See also Hart's *Welding* (McGraw-Hill Book Co.).

THERMODIN. An acetyl derivative of *p*-ethoxy-phenylurethane. Used as an anti-pyretic.

THERMOMETERS. Changes of temperature are measured by the corresponding alterations produced in one or other of the physical properties of a substance. Thus the expansion of solids, liquids, and gases, the vapour pressures of liquids, the electrical resistance of metals, and other properties have been utilised for the determination of temperature.

In nearly every case the amount of change produced by a given rise or fall of temperature depends on the nature of the substance, and must therefore be carefully determined beforehand for the particular material employed.

There is, indeed, only one known method of measuring temperature which is theoretically perfect, that is to say, which is entirely independent of the nature of the substance; this method, proposed by Lord Kelvin, depends on the ratio of the work done by a reversible heat engine to the heat supplied to it, and the temperature, reckoned from absolute zero, may be defined as the reciprocal of Carnot's function. The method is not one, however, that is capable of practical application.

It has been found that within certain limits of temperature and pressure the expansion of all gases is very nearly the same for equal changes of temperature. Hence it is possible to devise a method of measuring temperature which, while practically independent of the nature of the (gaseous) substance employed, is at the same time fairly convenient for many purposes. It is important also to remark that the values given by an air or gas thermometer are in very close agreement with Lord Kelvin's thermo-dynamical temperatures.

The relation of the volume of a gas to its temperature and pressure may be stated simply as follows: The volume of a gas varies inversely as the pressure and directly as the absolute temperature, or $p \propto 1/v$, where p is the pressure, v the volume, T the absolute temperature, and c a constant depending on the units chosen. If the volume remains constant the pressure varies directly as the absolute temperature, or $p \propto T$, while if the pressure is kept constant the volume varies directly as the absolute temperature, or $v \propto T$.

It is true that the co-efficients of expansion of different gases are not absolutely identical, and that the law holds good only within certain limits of temperature and pressure; but under pressures not greatly exceeding that of the atmosphere the deviations are extremely small in the case of nitrogen, hydrogen, helium, and some other gases, except at very low temperatures. Very accurate investigations of the properties of gases at extremely low temperatures have been carried out by Kamerlingh Onnes and his collaborators at Leiden, and their results show that the constant volume hydrogen thermometer gives nearly accurate results down to -250° and the helium thermometer to still lower temperatures.

An 'air' thermometer may be so constructed that (1) the pressure remains constant and the alteration of volume is measured; (2) the volume remains constant and the change of pressure is observed; (3) both pressure and volume are

allowed to alter, and both are measured. The air or other gas is contained in a bulb of glass, or for very high temperatures of some other material, connected by means of a capillary tube with a mercury or sulphuric acid manometer. The bulb is heated to the required temperature while the other parts of the apparatus remain at the temperature of the room. If the pressure be kept constant the gas will expand, and at high temperatures a considerable portion of it will pass into the cold part of the apparatus and must be measured at the ordinary temperature; it is therefore usually considered better to raise the pressure so as to keep the volume of gas as nearly constant as possible. The vessel containing the gas expands, however, when the temperature rises, and a correction on account of this expansion must be introduced.

There are also three sources of error which are difficult to estimate, but they may be almost entirely eliminated by taking suitable precautions. The first depends on the fact that at ordinary temperatures air condenses to a slight extent as a sort of film on the surface of glass, while at high temperatures this condensed air is converted into gas, so that the apparent expansion is a little greater than the real. If, however, the bulb, after thorough exhaustion at a high temperature, is filled with air from which all moisture and carbon dioxide have been removed, the error becomes practically negligible (Callendar, Phil. Trans. 178A, 161).

The second is due to slight changes of volume which a glass vessel is liable to undergo after being strongly heated and allowed to cool again. The magnitude of the possible error becomes extremely small, however, if the bulb is heated for some hours to at least the highest temperature which is to be registered, before its volume is determined. This point will be more fully discussed when dealing with mercurial thermometers. The third source of error is due to the deformation of the bulb or to leakage of gas through it when the temperature and the internal gaseous pressure are greatly raised. This difficulty has been overcome by Day and Clement (Amer. J. Sci. 26, 1908), who employed a platinum-iridium bulb containing nitrogen, by surrounding the bulb with nitrogen at the same pressure as that within the bulb. Further precautions are described by Day, Sosman and Allen, Carnegie Inst. of Washington, Geophys. Lab. 1; Day and Sosman, Amer. J. Sci. 33, 517; and Ezer Griffiths, Methods of Measuring Temperature, 1918.

Of the numerous forms of air thermometer which have been devised, the three shown in the diagrams may serve as examples. The first (Fig. 1) represents a form of instrument employed by Regnault in his classical researches. The bulb A of the thermometer is connected by a capillary tube (passing through a perforation in the screen B) with the mercury manometer mm' , a front view of which is shown in Fig. 2. By addition of mercury to the open limb m' , or by its removal by means of the stopcock s , the mercury in the limb of the manometer connected with the air thermometer may be always kept at the same height, so that there is no alteration of the volume of air except that due to the expansion of the bulb when heated.

The calculation of the temperature is based on the fact that the mass of air remains constant, although its temperature, its pressure, and, to a small extent, its volume undergo change. Let

V = volume of bulb A at 0° ;

v = volume of capillary tube, together with the small portion of the manometer above the mercury in m , also at 0° ;

α = coefficient of increase of pressure of dry air at constant volume;

κ = coefficient of expansion of glass;

D = mass of 1 c.c. of air at 0° and 76 cms. pressure;

P = observed pressure—that is to say, the barometric pressure, plus or minus the difference of level of the mercury in m and m' .

When the bulb is placed in melting ice, while the capillary tube and manometer are at the

	p_0
Hydrogen	760 mm. 0.0036627
Helium	700 „ 0.0036626
Nitrogen	760 „ 0.0036714
Oxygen	663 „ 0.003674

If the volume of air be allowed to vary, the limb m of the manometer must be graduated, and should be surrounded by cold water of known temperature. In this case the additional volume v' at the temperature of the water must be brought into the equation.

Sulphuric acid may be employed with advantage in place of mercury, since it moves more freely in a narrow tube, and, being lighter, allows of more delicate readings; or a small sulphuric acid gauge may be interposed between the thermometer and the mercury manometer. An apparatus which can be employed either as a constant volume or constant pressure manometer has been described by Callendar (*l.c.*)

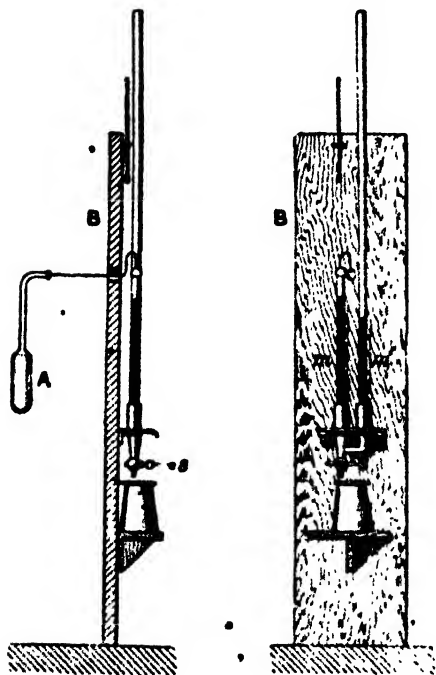


FIG. 1.

FIG. 2.

temperature t' of the room, the total mass of air will be

$$D.P. \left\{ V + \frac{v(1 + \kappa t')}{1 + \alpha t'} \right\}$$

When the bulb is heated to the unknown temperature x , the temperature of the capillary tube and manometer being now t' the mass of air will be

$$D.P. \left\{ \frac{V(1 + \kappa x)}{1 + \alpha x} + \frac{v(1 + \kappa t')}{1 + \alpha t'} \right\}$$

Therefore

$$P \left\{ V + \frac{v(1 + \kappa t')}{1 + \alpha t'} \right\} = P' \left\{ \frac{V(1 + \kappa x)}{1 + \alpha x} + \frac{v(1 + \kappa t')}{1 + \alpha t'} \right\}$$

an equation in which everything is known but x .

Values of α for several gases for the temperature range 0° to 100° are given below, p_0 being the initial pressure (at 0°).

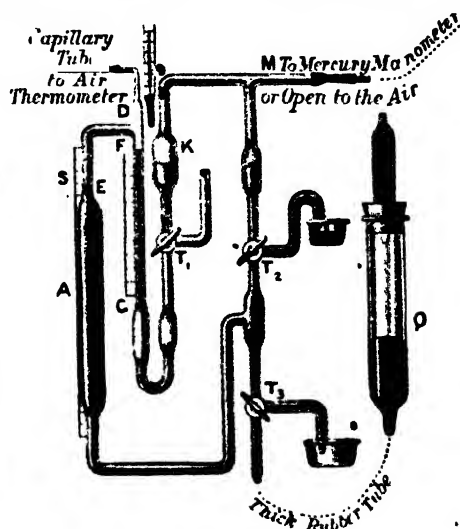


FIG. 3.

and more fully by Callendar and Griffiths (*Phil. Trans.* 1824, 119). It is represented in Fig. 3.

When the measurement is to be made at constant volume the mercury in A is brought up to the zero point, and the stopcocks T_1 and T_2 are closed. The level of the sulphuric acid in the gauge is then regulated by means of an ordinary mercury manometer, not shown in the diagram, and the pressure is the algebraical sum of the barometric pressure, that registered by the mercury manometer, and the slight difference in level, if any, of the sulphuric acid in the two limbs of the gauge FK , divided by the specific gravity of mercury compared with that of sulphuric acid.

If the pressure is to be kept constant, the tube A is first filled from the reservoir Q until the level of the mercury stands at some point in the tube DE , recorded by the scale S , the pressure of the air in the bulb being equal to that of the atmosphere, as shown by the sulphuric acid gauge. (In this case the tube M is not connected with the mercury manometer, but is open to the air.) When the bulb is heated, mercury is allowed to escape by the three-way tap T_3 into the weighed beaker, the tap being closed as soon as the sulphuric acid gauge indicates that the pressure is again equal to that of the

atmosphere. The increased volume is calculated from the weight of mercury expelled. The narrow tubes DE and FG are calibrated and provided with scales. For the advantages of the sulphuric acid gauge see also Bottomley (Phil. Mag. 1888 (Aug.), 149).

Callendar has (Nature, 1891, 45, 212) described a modified constant-pressure air thermometer which appears to possess marked advantages over those previously devised, and gives extremely accurate results. The pressure of the air in the thermometer is not adjusted to equality with that of the atmosphere, but always with the same constant pressure, obtained by connecting the outer limb of the sulphuric acid gauge to a glass bulb filled with air and kept in melting ice.

The effect of changes of temperature of the connecting tubes on the readings is entirely eliminated by the employment of compensating tubes of the same size, and thus the troublesome and somewhat uncertain correction hitherto necessary is obviated. The compensation is perfect when (1) the two sets of connecting tubes are of equal volume and at the same mean temperature; (2) the mass of air inclosed in the standard pressure-bulb is equal to that in the thermometric and mercury bulbs; (3) the pressures are adjusted to equality. Under these conditions, the temperature of the thermometer bulb (on the air-thermometer scale) is given by the simple equation $\theta_1 = V_1 \theta_0 (V_0 - V_m)$, where V_1 is the volume of air in the thermometer bulb at θ_1° , V_0 and V_m are the volumes of air at 0° in the standard pressure bulb and the mercury reservoir (this being also surrounded by melting ice), and θ_0 is the temperature of melting ice on the air-thermometer scale.

For moderate ranges of temperature, and when extreme accuracy is not required, the apparatus may be greatly simplified, and may be so constructed that the temperatures are read directly on the sulphuric acid gauge; it is stated that such thermometers can be made to read to the tenth of a degree at 450° . This form of direct reading thermometer has been patented and is recommended for technical purposes.

Other forms of air thermometer have been described by Balfour Stewart, Phil. Trans. 153, 425; Codazza, Dingl. poly. J. 210, 255; Jolly, Pogg. Jubelband, p. 82; Mitscherlich, Annalen, 12, 146; Crafts, Ann. Chim. [v.] 14, 409; Andrews, Ber. 14, 2116; Pettersson, J. pr. Chem. [ii.] 25, 102; Caillaet, Compt. rend. 106, 1055; Berthelot, Ann. Chim. [iv.] 13, 144; Murray, J. Phys. Chem. 1897, i. 714; v. also Ezer Griffiths, *l.c.* A platinum bulb was recommended by Pouillet (Compt. rend. 3, 782), but it was pointed out by Becquerel (Ann. Chim. 58, 49) that at high temperatures air passes through the platinum. A porcelain bulb was employed by Weinhold (Pogg. Ann. 149, 188), by Deville and Troost (Ann. Chim. [iii.] 58, 265), and others. According to Holborn and Day (Wied. Ann. 68, 817; Amer. J. Sci. 8, 165; 10, 171), however, porcelain does not give satisfactory results at high temperatures. They recommend bulbs of Jena boro-silicate

No. 59m, containing hydrogen for temperatures up to 500° , and bulbs of a platinum-iridium alloy (10 p.c. Ir) with pure nitrogen gas from 500° to 1300° . The Pt Ir bulbs

should be heated electrically or else protected from gaseous combustion products, which are liable to pass through the alloy. Holborn and Henning (Ann. d. Physik. 35, 4, 761) used Jena glass No. 59m for nitrogen, hydrogen, and helium, and quartz for nitrogen. Day and Sosman (Amer. J. Sci. 1910, 20) have measured temperatures to 1550° . They describe special precautions required to obtain a uniform temperature about the bulb (*ibid.* 1912, 33, 517). Harker proposes to make bulbs of rare earths such as those used for Nernst filaments.

For very low temperatures, the glass bulbs should contain hydrogen or helium. A very complete account of the hydrogen thermometer in use at the cryogenic laboratory at Leiden is given by Kamerlingh Onnes and Clay (Comm. No. 95e), and of the helium thermometer by K. Onnes and Weber (Comm. No. 147b, 1915), and Cath and K. Onnes (Comm. 152a, 1918).

As regards the theory of the subject and the comparison of the temperatures registered by different gas thermometers with each other and with the thermodynamical scale, reference may be made to the following memoirs and papers: D. Berthelot, Sur les thermomètres à gas, Paris, 1903; Anh. d. poids et mesures, 1907, 13b, 3; Chappuis, Phil. Mag. 1900, 50, 433; 1902, 3, 234; Phil. Trans. 1900, 191, 37, 131; J. Phys. 1904, 3, 833; Ann. d. poids et mes. 1907, 13a, 3; Kamerlingh Onnes, Comm. 97a and b, 102b and d; Holborn, Ann. Physik. 1901, [vi.] 2, 242; Buckingham, Bureau of Standards, 1907, 3, 237; Phil. Mag. 1908, 15, 526; Rose-Innes, *ibid.* 1908, 14, 301; Kamerlingh Onnes and Holst, Comm. 141a; Report by Kamerlingh Onnes at Third International Congress of Refrigeration, 1913, section for Physics, Chemistry and Thermometry; Ezer Griffiths, *l.c.*; Cath and K. Onnes, Comm. No. 156a, 1922.

Air thermometers for technical purposes are generally provided with scales which are calibrated empirically by heating the bulbs to two or three known temperatures, so as to obtain a certain number of fixed points. The scales are then constructed by interpolation.

Thermometers of this class have been described by P. Schoon, D. R. P. 20345, 1882; Witz, Compt. rend. 91, 164; Beilby, J. Soc. Chem. Ind. 1885, 41; Coleman, *ibid.* 1885, 43; Heisch and Folkard, and by Bristol (Mech. Eng. 1900, 6, 916). They consist of a porcelain bulb, a copper capillary, and a pressure gauge constructed with two spiral tubes on the Bourdon principle. They can be constructed as recording instruments. The thermometer of Heisch and Folkard is very simple, and has been found by Hurter (J. Soc. Chem. Ind. 1886, 635) to give good results. The bulb A (Fig. 4) contains air under reduced pressure, and there is a vacuum over the mercury in the manometer M.

The mercurial thermometer.—For ordinary purposes the mercurial thermometer is the most convenient, for it may be made of any required size, is easily portable, and the bulb, if elongated, need not be wider or, indeed, so wide as the stem. The instrument consists of a spherical or cylindrical bulb fused to a capillary tube of suitable length. The bulb is filled with pure mercury, which must be boiled for some time to remove the film of gas or aqueous vapour which adheres obstinately to the surface of the glass.

If the thermometer is required for low temperatures only, there is usually a vacuum in the stem of the thermometer, but for high temperatures it is necessary, and for temperatures above 70° or 80° advisable, to fill the capillary

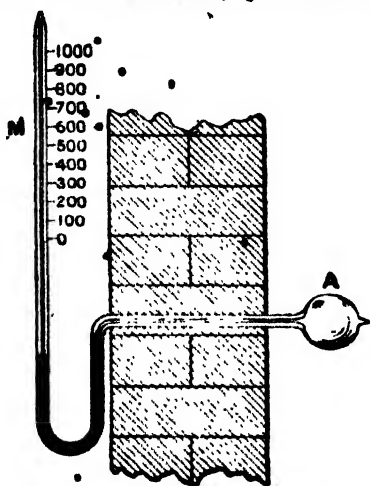


FIG. 4.

tube with nitrogen to prevent distillation of the mercury, a small bulb being blown at the upper end of the tube in order that when the mercury expands and compresses the nitrogen the pressure shall not rise too high.

An ordinary thermometer is graduated by placing it first in the steam from water boiling under known pressure and then in melting ice (v. Guillaume, *Traité pratique de la Thermométrie de Précision*, p. 112). The variation of the melting-point of ice with the pressure is so minute that this point may be taken as absolutely fixed, but the boiling-point of water varies considerably with the pressure, and therefore some standard pressure must be chosen. This is 760 mm. or 29.922 ins. of mercury measured at 0°C. and at the latitude of Paris for the Centigrade scale, and 29.925 ins. of mercury at 32°F. at the latitude of London for the Fahrenheit scale.

The position of the mercury in the stem is marked off at these two temperatures, and the space between these two fixed points is then usually divided into a certain number of equal parts—100 on the Centigrade scale, 180 on the Fahrenheit, and 80 on the Réaumur. On the Centigrade and Réaumur scales, the melting-point of ice is taken as the zero point, but on the Fahrenheit the zero of the scale is placed 32 divisions lower down, so that the melting-point of ice is 32°, and the boiling-point of water 212°.

A thermometer graduated in this manner does not, however, register true temperatures except at the two fixed points, for the following reasons:—1. It is impossible to obtain an absolutely cylindrical capillary tube, so that the volume corresponding to a scale division is not quite the same in all parts of the tube. Various methods have been devised for calibrating the stem (v. Brit. Assoc. Report, 1882, 145–204, also Guillaume, *l.c.* 43–99), but when this is done there remain other sources of error. 2. The position of the mercury in the stem at any

temperature depends on the expansion both of the mercury and of the glass, and in each case the rate of expansion increases with rise of temperature. Moreover, different kinds of glass have different rates of expansion, so that two thermometers made of different materials—even if the capillary tubes were perfectly cylindrical—would give different readings at the same temperature. The only really satisfactory method of correction of such a thermometer is to compare its readings either directly with an air thermometer, or with another mercurial thermometer which has previously been standardised by means of an air thermometer. Or a series of fixed points may be determined by immersing the thermometer in a number of freezing liquids (melting solids) or by heating it with the vapours of a series of pure liquids boiling under known pressures. The following table contains a list of suitable substances with their melting-points, transition-points, or boiling-points, and the variation of pressure corresponding to 1° at the boiling-points, temperatures outside the range of the mercurial thermometer being included for convenience:—

Temperature	Fixed point
–183.0°	b.p. of oxygen; $dp/dt=75.9$ mm. per degree.
–159.6	m.p. of isopentane.*
–126.3	m.p. of methyl cyclohexane.*
–116.3	m.p. of ethyl ether.*
–111.6	m.p. of carbon disulphide.*
–95.1	m.p. of toluene.*
–83.6	m.p. of ethyl acetate.*
–63.5	m.p. of chloroform.*
–45.2	m.p. of chlorobenzene.*
–38.87	m.p. of mercury.
–22.9	m.p. of carbon tetrachloride.*
0	m.p. of ice.
32.38	tr.p. of sodium sulphate.
46.2	b.p. of carbon disulphide; $dp/dt=24.8$.
50.67	tr.p. of sodium bromide.
78.3	b.p. of ethyl alcohol; $dp/dt=30.5$.
100.0	b.p. of water; $dp/dt=27.1$.
132.0	b.p. of chlorobenzene; $dp/dt=20.2$.
156.2	b.p. of bromobenzene; $dp/dt=19.4$.
184.1	b.p. of aniline; $dp/dt=19.6$.
218.0	b.p. of naphthalene; $dp/dt=15.2$.
231.8	m.p. of tin.
305.9	b.p. of benzophenone; $dp/dt=15.8$.
320.9	m.p. of cadmium.
356.7	b.p. of mercury; $dp/dt=13.3$.
419.4	m.p. of zinc.
444.55	b.p. of sulphur; $dp/dt=11.1$.
630.0	m.p. of antimony.
756.0	b.p. of cadmium; $dp/dt=8.1$ (calculated).
916.0	b.p. of zinc; $dp/dt=7.0$ (calculated).
960.5	m.p. of silver.
1063	m.p. of gold.

* Timmermans, Van der Horst and Kammerlingh-Onnes, Comm. No. 157, 1922. Samples of the liquids marked with an asterisk are supplied by the Bureau des Etalons physicochimiques, Université, Rue des Sols, Brussels. The m.p.s. are stated to be correct to 0.1° on the Leiden helium thermometer scale.

Temperature	Fixed point
1083 .	m.p. of copper.
1452±2 .	m.p. of nickel.
1549±2 .	m.p. of palladium.
1755±5 .	m.p. of platinum.
2910 .	m.p. (approx.) of tantalum.
3080 .	m.p. (approx.) of tungsten.

For additional fixed points between 0° and -160°, v. Timmermans, *Sci. Proc. Roy. Dubl. Soc.* 1912, and for a few very accurately determined temperatures, v. T. W. Richards, *J. Amer. Chem. Soc.* 33, 847; 36, 485, 1825; 40, 89. Steinmetz (*ibid.* 1918, 40, 96) gives the melting-points of a number of eutectic alloys. A table of melting-points of the elements has been published by the U.S. Bureau of Standards (v. *J. Soc. Chem. Ind.* 1919, 38, 67R). For the accurate calibration of short-range thermometers Richards and Shipley (*ibid.* 36, 1) recommend a floating-equilibrium method, hollow floats of glass or quartz being immersed in solutions of known concentration; Richards and Thorwaldson (*ibid.* 37, 81) have employed, with very satisfactory results, a method based on the heat of dilution of hydrochloric acid; and Richards and Tamaru (*ibid.* 42, 1374) describe a calorimetric method based on electric energy.

In this way a table or curve of corrections may be constructed showing the error at any scale reading of the thermometer. 'Normal' thermometers may now be purchased; they are compared with a standard thermometer before graduation, and nearly true temperatures are registered by them; or the thermometers may be sent to the National Physical Laboratory, the Reichsanstalt (v. Warburg, *Ann. Physik.* 1916, 48, 8, 1034), or the Bureau of Standards, and the necessary table of corrections obtained. The calibration of thermometers, as carried out at the Physik-Tech. Reichsanstalt, is described by Warburg (*Ann. d. Physik.* 1916, 48, 1034).

Tables of correction of readings of mercurial thermometers to true air-thermometer temperatures have been published by various observers; but as these tables must necessarily vary for different kinds of glass—the further correction for unevenness of bore being also required—they do not seem to possess much general value. It may be useful, however, to give references.—Rudberg, *Annalen*, 36, 121; Boescha, *Compt. rend.* 69, 875, 1185; Regnault, *ibid.* 69, 879, and *Mémoires*, 21, 239; Crafts, *ibid.* 95, 836; Recknagel, *Pogg. Ann.* 123; Guillaume, *Traité pratique de la Thermométrie de Précision*.

Even when the above corrections to true air-thermometer temperatures have been made, there remain some sources of error, the most important of which is the alteration of the capacity of the bulb, and doubtless also of the capillary tube after long-continued heating, and, indeed, after any considerable change of temperature. A vast amount of experimental work has been done on this subject, and the explanation of the observed changes has given rise to a great deal of discussion. The following references may be made to the literature of the subject:—Desspretz, *Compt. rend.* 4, 926; Person, *ibid.* 19, 1314; Legrand, *ibid.* 4, 173; Crafts, *ibid.* 91, 291, 370, 413; 94, 1298; Pernet, *ibid.* 91, 471; E. J. Mills, *T. Ed. 24, Part 2*, 587,

and Nature, 41, 100, 227, 538; Young, *ibid.* 41, 152, 271, 488; Tomlinson, *ibid.* 41, 198; Pernet, *Travaux et Mém. du Bureau Int. des Poids et Mesures*, i., B. 52, and I., 17; Guillaume, *Traité pratique*; Marchis, *Zeitsch. physikal. Chem.* 1899, 29, 1; 1091, 37, 553, 605; Ezer Griffiths, *l.c.* The most important facts regarding the alteration of zero point may be shortly described as follows:—

1. If a thermometer be graduated shortly after the bulb has been blown, the zero point will rise with comparative rapidity at first, then more and more slowly, and the elevation of the zero point may go on for many years. Joule (Scientific Papers, i. 558) took observations with one thermometer over a course of thirty-eight years, and the change, which then amounted to almost exactly 1°F., was still proceeding.

2. If a thermometer be maintained at a high temperature for a considerable time, the rise of the zero point takes place with much greater rapidity, and so far as is known the higher the temperature the more rapid is the rise, and apparently the higher is the final point reached. A total elevation of over 20° in the case of German soda glass has in several cases been observed, while larger glass bulbs, after continuous heating to 445°, or in one case 511°, have been found by Regnault, Crafts, and Callendar and Griffiths to suffer a contraction of from 0.25

0.34 per cent. In all cases the rise or contraction, which is rapid at first, becomes gradually slower, and it seems doubtful whether at any given temperature actual constancy of zero point or capacity has ever been attained. If, however, a thermometer has been heated for many hours to a given high temperature and then allowed to cool very slowly, subsequent heating to lower temperatures has very little effect on the zero point, and it is advisable to subject a thermometer to this process before determining the fixed points. According to Marchis (*l.c.*), a fluctuating high temperature is more effective than a steady one in raising the zero point. Hecker (*Zeitsch. f. Instrumentenkunde*, Beib. 1901, 5, 41) describes a method of electrical heating and slow cooling. Böttcher (*ibid.* Beib. 1903, 17, 154) states that the thermometer bulb should be heated for a short time to a temperature 100° above the initial softening temperature of the glass, and that slow cooling is unnecessary. The question is discussed by Dickinson (*Bureau of Standards*, 1906, 2, 189) and methods of treatment are recommended. Weibe (*Zeitsch. Instrumentenk. Beib.* 3, 21; 4, 33) states that Jena borosilicate glass 5914 thermometers should be kept at 500° for at least 10 days, and that slow cooling is of comparatively small importance.

3. Not only is the zero point liable to change, but the interval between the zero and 100° points may at the same time be increased, for the coefficient of expansion of glass suffers diminution after prolonged heating.

4. Internal or external gaseous pressure on the bulb appears to have little or no influence on the rise of zero point.

5. If a thermometer—even after its zero point has been rendered as permanent as possible—be heated and then cooled very rapidly, a fall of the zero point will be observed, but after a day or two the greater part of this

fall, will be recovered, and the remainder after a longer period. The alteration of the zero point depends greatly on the nature of the glass, and a special hard glass is used by Tonnelot of Paris, while Schott and Co. in Germany employ two kinds of glass, 'normal thermometer' glass, 16^{III}, and a boro-silicate glass, 59^{III}, for the best thermometers. The latter glass is now generally used; it has a very high melting-point and can be used up to 550°, the mercury being prevented from boiling by the introduction of carbon dioxide under pressure (*cf.* Murrie, *J. Soc. Chem. Ind.* 1885, 45, 189, 655). Glass suitable for thermometers is now being made in England, and information regarding composition and properties may be obtained from the Institute of Chemistry. It is stated by Ezer Griffiths that fused quartz is much superior to glass as regards changes of zero point.

Other possible sources of error are the following:—If the mercury in the stem of the thermometer—or a portion of it—is not heated to the same temperature as that in the bulb, a correction is required, *v.* DISTILLATION, *v.* also Dimmer, *Akad. Wiss. Wein. Ber.* 122, 2a, 1439. Wheeler (*J. Soc. Chem. Ind.* 1916, 35, 1198) gives a useful graph, based on Thorpe's formula, to facilitate this correction. In order to ascertain the mean temperature of the unheated column, Guillaume (*Compt. rend.* 1891, 112, 87) places a supplementary thermometer without a bulb at the side of the thermometer stem. Modifications of this method have been proposed by Mahlike, *Zeitsch. Instr.* 1893, 13, 58; 1894, 14, 73; and by Adam, *ibid.* 1907, 27, 101.

The bulb is slightly compressible, and considerable changes of external pressure affect the readings to some extent.

Mercury does not move very freely in a capillary tube, and in delicate thermometers, when the temperature changes, the movement of the mercury may take place in jerks instead of smoothly. This may be avoided by tapping the thermometer (Pickering, *Phil. Mag.* 1886, 21). Greater freedom of motion is attained (Duciaux and Hamelin, *J. Phys.* 1910, 9, 600) by placing dilute sulphuric acid over the mercury, and electro-capillary effects are prevented by means of a recess full of mercury at the upper end of the capillary, the mercury in recess and bulb being connected by a platinum wire. The increase in sensitiveness was found to be so great that variations in the melting-point of ice with moderate change of pressure were readily observed.

For temperatures below the freezing-point of mercury, -38.7°, various liquids have been suggested to take the place of that metal. Alcohol and toluene thermometers have been in use for many years, and, more recently, pentan has been found specially suitable for very low temperatures (Kohlrausch, *Wied. Ann.* 1897, 60, 463; Baudin, *Compt. rend.* 1901, 133, 1207; Rothe, *Zeitsch. Instr.* 1902, 22, 192; Hoffmann and Rothe, *ibid.* 1907, 27, 265). Baudin and Rothe recommend 'technical' in preference to pure pentane on account of its lower freezing-point. The b.p. is 25° to 33°, and the pentane thermometer can be used between 30° and -190°.

The molecular weight of a dissolved substance is very frequently calculated from the

depression of the freezing-point or the rise of the boiling-point of a solvent. Thermometers of small range but great sensitiveness have been devised for these determinations, by Beckmann, and a full description of various forms of the instrument is given by him (*Zeitsch. Chem.* 1905, 51, 329). The bulb is of large size and the same thermometer can be used for different temperature ranges by transferring part of the mercury from the bulb to a receptacle at the other end of the capillary. The value of a scale division is thereby slightly altered, and the necessary corrections are discussed and a table is given by Grützmacher (*Zeitsch. Instr.* 1896, 16, 171, 200).

Useful general information about mercurial thermometers is contained in the following papers: Chree (*Phil. Mag.* 1898, 45, 205, 299); Kohlrausch (*Zeitsch. Instr.* 1898, 18, 76); Scheel, (*ibid.* Beib. 1899, 9-13); Harper (*Bureau of Standards, Bull.* 8, 659); Coste (*J. Soc. Chem. Ind.* 1913, 32, 341; *v.* also Ezer Griffiths, *l.c.*

Other methods than those dependant on the use of the mercurial thermometer are in use for the determination of temperatures, but they are of varying degrees of accuracy. The method of determining the melting-points of minerals from the heating and cooling curves necessitates the use of a considerable amount of material, whilst the microscopic method lacks accuracy. Borgström (*Jahrb. Min.* 1816, 7, ref. 9-11) has made use of a method employed for organic substances, the substance being enclosed in a capillary tube of silica-glass and immersed in a transparent bath of fused salts (mixtures of sodium and potassium nitrates, sodium, potassium, and lithium chlorides, and sodium sulphate in various proportions according to the temperature required). A connection is traced between the melting-points and the geological occurrence of mineral substances, those with higher melting-points being found at greater depths in the earth's crust (*Chem. Soc. Abstr.* 1916, n. 191).

Platinum resistance thermometers.—The measurement of temperature by the alteration of the resistance to electricity of a platinum wire was suggested by Siemens (Bakeman Lecture, *Proc. Roy. Soc.* 1871), but in consequence of an adverse report to the British Association in 1874 this method was abandoned. Subsequently, however, the subject was investigated by Callendar (*Phil. Trans.* 1887, 178 A, 161; *Phil. Mag.* 1891, 32, 104; 1899, 47, 191); Griffiths (*Phil. Trans.* 182 A, 43), and both authors (*ibid.* 182 A, 119) with very satisfactory results. In order to insure accuracy the platinum wire must be pure in the first place; it must be prevented from alloying with silicon, carbon, tin, or other impurities, and it must not be subjected to strain—such as elongation. When these conditions were fulfilled, the resistance of a wire was always found to be constant at a given temperature. The form of thermometer recommended by Callendar and Griffiths is shown in Fig. 5. Two platinum wires are inter-wound in a double-screw thread, passing through holes in a thin mica plate *AB*. Each spiral is provided with a double and single electrode, symmetrically arranged. The six electrodes are insulated, and kept in place by passing through holes in thin mica wads

(one of which is shown at c) which are cut to fit the glass tube containing the thermometer. The electrodes are best made of platinum, the ends of the wires being fused to them by the oxy-hydrogen flame.

If R_0 and R_1 be the resistance at 0° and 100° , and R that at any other temperature, the corresponding value of the platinum temperature pt is deduced by the formula

$$pt = 100(R - R_0)/(R_1 - R_0).$$

To reduce the platinum resistance temperature to that of the air thermometer the following formula is employed

$$T - pt = \delta \left[\left(\frac{T}{100} \right)^2 - \frac{T}{100} \right]$$

the value of δ , generally 1.5, depending on the wire and being determined for each thermometer from observations at 0° , 100° , and 444.5° . The formula has been found to hold up to 1000° or 1100° . To avoid errors due to variation of the room temperature, compensating leads are used, and other improvements have been adopted from time to time. For further details, v. PYROMETRY; also, Mueller, Bureau of Standards, 1916, Bull. 13, 547; Sligh, J. Amer. Chem. Soc. 1921, 43, 470; Roebuck, J. Opt. Soc. Amer. 1922, 6, 865; and Ezer Griffiths, *l.c.*

For moderate temperatures, nickel is recommended in place of platinum by Marvin (Phys. Rev. 1910, 30, 522); Jaeger and v. Steinwehr (Ann. d. Physik, 43, 8, 1165; 45, 7, 1089) have studied mercury resistance thermometers. They are much less sensitive than platinum thermometers, but have the advantage that a preliminary

determination of resistance need only be made at a single normal temperature. Metallic oxide resistance thermometers have been constructed and investigated by Brown (Phys. Rev. 5, 126; 9, 205). Boron is recommended by Heraeus (D. R. P. 316416) (l. 4, 19) on account of its high temperature coefficient.

Dewar (Proc. Roy. Soc. 1904, 73, 244) states that platinum does not give good results at very low temperatures and recommends gold or silver. Meilink also (K. Akad. Wet. Amsterdam, 1904, 13, 212, 221) obtained better results with gold than with platinum. The resistance of gold, platinum, and other metals at low temperatures has been accurately determined by Kamerlingh Onnes and Clay, (Comm. 99c and 107c. Kamerlingh Onnes and Holst (Comm. 141d) found that platinum is unsuitable in the region of -200° , and that at the lowest temperatures manganin and constantan are more satisfactory than either platinum or gold; but Zernike (K. Akad. Amsterdam, Proc. 18, 6, 914) gives an interpolation formula for platinum which is claimed to be accurate to within 0.02° at all temperatures below -200° . The resistance of mercury, tin, cadmium, con-

stantan, and manganin down to the boiling-point of helium has been determined by K. Onnes and Holst (Comm. No. 142a), and of mercury with liquid helium (*ibid.* 142c); also of pure metals with liquid helium by K. Onnes and Tuya (*ibid.* 160a and b).

Comparisons of the platinum scale of temperature with the hydrogen, nitrogen, helium, or air scale have been carried out by Harker and Chappuis (Phil. Trans. 1900, 194, 37) at Sevres; Meilink (K. Akad. Wet. Amst. 1902, 10, 495); Holborn (Ann. Physik. 1901, [vi.] 2, 242); Harker (Proc. Roy. Soc. 1904, 73, 217); Travers and Gwyer (*ibid.* 1905, 74, 528); Kamerlingh Onnes and Clay (*l.c.*); Holborn and Henning (Ann. Physik. 1911, 35, 4, 761); Dickinson and Mueller (Washington Acad. Sci. 1912, 2, 176); Henning (Ann. Physik. 1913, 40, 4, 635); Kamerlingh Onnes and Holst (Comm. 141a); of the platinum, gold, and hydrogen thermometers by Kamerlingh Onnes and Clay (Comm. 95c, d, and e), and of platinum, gold, and helium thermometers between -218° and -246° by Cath, K. Onnes, and Burgess (Comm. 152c), completing the data from 0° to -258° ; v. also Timmermans (*l.c.*); Moeller, Hoffmann and Meissner (Zeitsch. Instr. 1912, 32, 217) give comparisons of mercury and platinum scales from 0° to 550° .

Thermo-electric thermometers.—The first attempt to employ a thermo-couple for the measurement of high temperatures was made by Becquerel in 1826, but he failed to obtain concordant results. In 1886, however, Le Chatelier devised an instrument which gave good results and came into practical use, and since then great improvements have been introduced.

The thermo-electric thermometer consists essentially of two fine wires of different metals or alloys, fused together at one end, and connected through a galvanometer at their other ends, the fused end being placed in the source of heat. An E.M.F. is developed, which is roughly proportional to the difference in temperature of the two ends of the couple. Le Chatelier employed wires of Pt and Pt-Rh (10 p.c. of Rh), and this couple may be used up to 1600° . The other couples which have been employed most frequently are Pt and Pt-Ir (10 p.c. Ir), and Cu and constantan (a Cu-Ni alloy with 40 p.c. Ni); the former may be used for temperatures as high as 1200° , the latter up to 500° . For full account of these thermometers v. PYROMETRY.

A great variety of couples have been tried for both high and low temperatures. For high temperatures the couples mentioned have been found to give the best results, but the Pt-Ir alloy has the disadvantage that the Ir volatilises, very slowly even at 900° , and much more rapidly at 1200° . Sosman (Amer. J. Sci. 1910, 30, 1) has investigated the Pt.—Pt.Rh (10 p.c. of Rh) thermo-element between 0° and the m.p. of Pt, $1755^\circ \pm 5^\circ$, and Adams and Johnston (*ibid.* 1912, 33, 534) the Cu-constantan thermo-element between 0° and 360° , and they give a standard scale of temperature between 200° and 1100° . Hevesy and Wolff (Phys. Zeitsch. 1910, 11, 473) find that the Ag—Ni thermo-element gives good results between -80° and 920° . Kowalko (Am. Electrochem. Soc. Trans.



FIG. 5.

1916, 29, 56) considers the Co—constantan element the best; cobalt withstands the action of hot gases better than nickel, remaining malleable and ductile. For low temperatures, Holborn and Wien (Wied. Ann. 1896, 59, 213) have recommended Fe—constantan; Pellat (Compt. rend. 1901, 133, 921), Fe—Zn; Dewar (Proc. Roy. Soc. 1905, 76, 316), Pt—German silver; whilst Kamerlingh Onnes and Clay (Comm. 1076) find that Ag—Au gives the best results. At about -256° this couple is about twice as sensitive as one of constantan—steel.

Comparisons of the thermo-electric scale of temperature with the air or hydrogen scale have been made by Holborn and Wien (Wied. Ann. 1895, 55, 95; 1896, 59, 213); Harker (Proc. Roy. Soc. 1904, 73, 217); and at low temperatures (-59° to -259°) by Kamerlingh Onnes and Crommelin, Comm. 95a; and with the platinum resistance scale by Waidner and Burgess, Bureau of Standards, Bull. 1909, 6, 149. White (Phys. Rev. 1910, 31, 135) discusses the utility of thermo-elements and the relative utility of thermo-elements and resistance thermometers.

The question of the calculation of the true temperature of the hot junction when the cold one is not at 0° has been fully discussed by Offenhaus and Fischer, Electrochem. Ind., New York, 6, 1908, 362.

Vapour pressure thermometer.—This form of instrument was recommended by Lord Kelvin (Pr. E. 1880, 432), and was introduced into practice under the name of the 'Thalpotassimeter' by Schaffer and Budenberg (Dittmar, J. Soc. Chem. Ind. 1885, 44). If the vapour pressures of a given liquid have been accurately determined through a certain range of temperature, any temperature within these limits may be afterwards determined by observing the pressure exerted by the vapour of the liquid.

The method possesses the great advantage that alteration of the capacity of the vessel containing the liquid and vapour is entirely without influence on the pressure, which is solely dependent on the temperature.

Probably the most serious objection to the method is the difficulty of filling the vessel or reservoir with the pure liquid *entirely free from air*, and if this difficulty be not overcome large errors may be introduced. For high temperatures, a mercury vapour pressure thermometer is sometimes serviceable (Ramsay and Young, Chem. Soc. Trans. 47, 651). The mercury must be well boiled to remove the film of air adhering to the glass, but this may be done without much difficulty. A liquid oxygen vapour pressure thermometer is recommended for temperatures between -183° and -200° by Stock and Nielson, Ber. 1906, 13, 39, 2066, and excellent results have been obtained with such an instrument by Kamerlingh Onnes and Braak, K. Akad. Wet. Amsterdam, 1908, 11, 333. Vapour pressure thermometers and pyrometers have been devised by Fournier, and an account of these instruments is given by Marieni (Electricità, Milan, 1908, 30, 82). H. v. Siemens (Ann. Physik. 1913, 43, 4, 871) describes a modification of Stock and Nielson's thermometer and gives the vapour pressures of CS_2 , CO_2 , O_2 , and N_2 , which he

determined by means of a Pt resistance thermometer. Stock, Henning and Küss (Ber. 1921, 54 [B], 1119) give vapour-pressure tables for measurement of temperature between 25° and -185° , and describe the apparatus they employ.

The following papers or memoirs on the subject of thermometry may be consulted: Sur les thermomètres à gaz, D. Berthelot, Paris, 1903; Kohlrausch, Zeitsch. Instr. 1898, 18, 16; Guillaume, Thermométrie de précision; Chrec, Phil. Mag. 1898, 45, 205, 299; Scheel, Zeitsch. Instr. 1899; Callendar, Nature, 1899, 59, 494, 519; Phil. Mag. 1899, 47, 191; Barus, Int. Phys. Congress, Paris, Rep. 1, 1900, 148; Burgess, Chem. News, 1913, 107, 169 and 182; Kamerlingh Onnes, Third Int. Congress of Refrigeration, 1913, section for Physics, Chemistry and Thermometry; Ezer Griffiths, Methods of Measuring Temperature, 1918; Scheel, Zeitsch. angew. Chem. 1919, 32, 347; Kayes, J. Amer. Chem. Soc. 1920, 42, 54; Het Natuurkundig Laboratorium der Rijks-universiteit te Leiden, Articles on Thermometry and Manometry, Keesom, p. 89, Crommelin, p. 211.

For the apparatus for the determination of the heat of evaporation of liquids of high boiling-points, see Awbery and Griffiths (The Phys. Soc. of London, 1924, 36, 303).

An inter comparison of high-temperature scales.

—An inter-comparison has been made by Forsythe (Astrophys. J. 1923, 58, 294) of the high-temperature standards used in certain research laboratories in the United States of America and abroad by the method of brightness temperatures as measured by the disappearing filament optical pyrometer. The 'brightness temperature' of a non-black body, as determined by measuring the brightness for a given wave-length λ with the pyrometer, is defined as the temperature to which a black body must be raised to give the same brightness for the same wave-length. Thus if the brightness temperature of a body is 1500°K. for $\lambda = 0.665\mu$, then for this wave-length the body has the same brightness as a black body for this same wave-length.

Several tungsten lamps which had been carefully aged in the Nela Research Laboratory were sent to the Bureau of Standards, the National Physical Laboratory of Great Britain, the University of Wisconsin, and the Research Laboratory of the General Electric Co., requesting that the temperatures of the lamps should be measured for specified currents. In each of the laboratories the temperatures were measured with a disappearing filament optical pyrometer, using a plate of red glass as the monochromatic screen. The results give not only a comparison of the brightness temperature of tungsten but also a valid comparison of the high-temperature scale. In each laboratory the high-temperature scale is based upon: (a) the melting-point of gold (1336°K.) or palladium (1828°K.), (b) extrapolation by means of Wien's equation using for C_2 the value 14350°K. Necessary reductions due to various factors such as a difference in the standard temperature, or a different value of the constant C_2 have been considered. A table is then given of the values obtained at the various

laboratories, the agreement being very good. Part of the table is given below :

Lamp		N.R.L. April, 1920	N.P.L. July, 1922	N.R.L. June, 1922	Bureau Jan., 1923	N.R.L. Jan., 1924
T-78-C.	15.4	1825	1825	1826	1824	1828
	20.4	2262	2265	2266	2265	2269
	27.4	2746	2757	2753	2755	2755

(Sci. Abstr. 1924, 27, 527).

The measurement of small sources of heat: The use of a compensated micro-calorimeter.—The instrument consists of a cell placed at the centre of a constant-temperature bath and separated from it by a thermal insulator. The evolution of the heat to be measured takes place in the cell. A thermopile, joined to a galvanometer, is connected by a series of junctions with the cell and by another series with the bath, and serves to measure the difference in temperature of the two media.

A second thermopile similarly placed is used to absorb, by the Peltier effect, the heat evolved. Compensation is effected by adjustment of the galvanometer deflection to zero. It is suggested that the method may be suitable for following the progress of chemical reactions where small changes in heat take place or for calorimetric observations in biology (A. Tian, *Compt. rend.* 1924, 178, 705; *Sci. Abstr.* 1924, 27, 527).

S. Y.

THERMONATRITE v. NATRON; TRONA.

THERMOSTATS. A thermostat may be defined to be an apparatus so arranged as to maintain the temperature of a space constant between certain definite limits. Previous to 1860, the forms of apparatus employed were comparatively few and simple, but during subsequent years refinement of physical and chemical experimental methods has led to the design of very numerous varieties of thermostats. Some few of these have been adapted to technical uses; in general these applications present little complexity and do not call for any detailed description. They have mainly been applied to the temperature regulation of steam and gas heating systems and more recently to the control of electrical heating. Among other purposes the temperature control of incubators heated by gas or electricity, of acetylene heated germinating stoves, and of pasteurising apparatus used in the sterilisation of milk are noteworthy. The automatic regulation of the temperature of fermenting vats, of dyevats, of evaporating pans and vacuum stills, has resulted in improvements in the sugar, spirit, and dyeing industries. Similarly, thermostats are extensively adapted to secure the more exact and economical working of lacquering, brazing, tempering, annealing, and roasting ovens and kilns. Numerous systems for the central heating of public buildings and houses by steam, hot water, gas, and hot air are now automatically regulated by thermostatic or electrical control apparatus. Similar thermostatic arrangements are also used in connection with steam-heating devices in railway carriages. In gas-testing stations, rooms are maintained at

a uniform temperature by thermostats controlling the gas-heating system. Automatic fire-alarm devices are usually supplied with thermometric or electrical thermostats arranged to give warning by telegraphic or mechanical signals.

The thermostats and thermo-regulators suggested may be classified as:—

I. Thermostats depending on a flow of heated liquid for the maintenance of a constant temperature.

II. Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body:

(a) Change of phase at freezing-point or cryohydric-point.

(b) Change of phase at boiling-point.

(c) Change of phase at inversion-point.

III. Other thermostats not automatically regulated through mechanical or electrical means.

IV. Self-regulating thermostats, including—

(a) Mercurial or other single-liquid thermometers:

1. Acting directly on the gas supply or other heat source;

2. Acting on the source of heat through electrical arrangements;

3. Acting on the source of heat through mechanical arrangements;

(b) Gas thermometers:

1. Acting on the gas supply by transmission of pressure through a liquid column;

2. Acting through electrical arrangements;

3. Acting through mechanical arrangements;

(c) Vapour-tension thermometers:

1. Air and vapour;

2. Vapour in contact with its own liquid only;

(d) Thermostats depending on the differential expansion of solid substances;

(e) Electrically heated thermostats with electrical control;

(f) Other mechanical regulators.

The limits of this article preclude the description of more than a few of the more typical examples of each of these classes; details of other forms and references may be obtained from: *Temperature Regulators*, J. T. Brown; *Laspeyres*, *Togg. Ann.* 152, 132; H. Hammerl, *Carl's Rep.* 18, 1882; K. Arndt, *Zeitsch. Chem. Apparatenkunde* 1, 255-263; Fr. Grützacher, *Zeitsch. Instrumentenkunde*, 22, 184, 193, 201; W. C. Geer, *J. Phys. Chem.* 6, 85-105, 1902, who gives a general discussion and a useful bibliography; M. Bodenstein, *Zeitsch. physikal. Chem.* 1899, 30, 113-139, who supplies a detailed account of thermostats used in gas-reaction researches, and H. W. Fischer and O. Bobertag, *Zeitsch. Elektrochem.* 1908, 14, 375. See also Cumming, *Trans. Faraday Soc.* 1912, 7, 253; Bousfield, *ibid.* 260.

I. *Thermostats depending on a flow of heated or cooled liquid for the maintenance of a constant temperature.*—The form of apparatus invented by C. Blaufus-Weiss may be adapted for use either as a pressure or temperature regulator (D. R. P. 43574, 1887). As used in the latter capacity, it consists essentially of a cylindrical

valve controlling the supply of hot or cold currents of either liquid or vapour to a worm arranged in the vat to be maintained at a uniform temperature. The valve is formed by an elliptical slit in a sheet cylinder, which passes half round the circumference of the cylinder, and, when the latter revolves, is brought more or less opposite to tubes opening into the sides of the drum, which serves as a valve-box. The space within the revolving cylinder is furnished with tubes passing through the head of the drum to serve as supply or exit pipes. The valve is worked by the rise and fall of a vertical piston, actuated by the expansion and contraction of a quantity of mercury, which is contained in a bell-shaped vessel of which the wider end is applied to a small chamber which forms a side continuation of the vat. The vertical movement of the piston is transformed into the circular motion of the valve in a horizontal plane by means of a pin working in a screw slot on a hollow cylinder.

A simple thermostat for use in connection with the refractometric examination of oils and fats, by T. E. Thorpe (Chem. Soc. Trans. 1904, 257), uses a constant current of liquid, under a defined pressure head, heated by passing through a coil in the vapour of a boiling liquid (*v. vol. v.*, 652).

W. Behrens (Zeitsch. Wiss. Mikrosk. 1895, 12, 1) describes a neat air-worked expansion valve for controlling a hot-water current supplied to the hot stage of a microscope.

Other forms using this principle are given by J. Ph. Grünig, D. R. P. 75882, 1893; J. C. Schalkwijk, Zeitsch. Inst. 1901, 21, 338; and T. M. Lowry, Trans. Faraday Soc. 1907, 3, 119.

A thermostat for low temperatures has been described by Walton and Judd, J. Phys. Chem. 1914, 18, 717.

II. *Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body.*—(a) References to types using the change of phase at the freezing-point and cryohydric point will be found in Geer's bibliography (*l.c.*). To these may be added Travers (Zeitsch. physikal. Chem. 1905, 52, 443), using alcohol and carbon dioxide snow for low temperatures.

(b) The change of phase at the boiling-point is more generally utilised. The vapour from a liquid boiling at the required temperature is caused to surround the oven or bath to be heated. Here the temperature will vary according to the pressure under which the liquid is boiled.

The liquids used for this purpose are:—Water, ether, methyl and ethyl alcohols, benzene, toluene, acetic acid, carbon disulphide, amyl alcohol, xylene, turpentine, aniline, naphthalene, glycerol, diphenylamine, the mono hydrate of sulphuric acid, mercury, paraffin, sulphur, zinc.

The temperatures so obtained lie between 22° and 1040°. At the ordinary atmospheric pressure one definite temperature is obtained for each substance used. Intermediate temperatures may be obtained in several ways:—

(1) The pressure under which the vapour is formed is varied; (2) mixtures of liquids in various proportions are used; (3) a solid is dissolved in a liquid, the boiling-point being

thus raised, and the vessel or bath is surrounded by the boiling liquid.

L. Meyer devised an apparatus for determining the boiling-point of a liquid at any pressure below that of one atmosphere. It may be used to control a constant-temperature bath (Annalen, 15, 303). The apparatus (see Fig. 1) is a pressure control valve. The mercury in AB cuts off the connection with the air-pump through H as soon as the pressure is reduced to the required point; CD is a mercury valve which admits air to the apparatus immediately the pressure falls below that fixed upon.

Brown has improved this apparatus, rendering it possible to use it for pressures higher, as well as lower, than one atmosphere. A mercury manometer is so constructed that, immediately the pressure falls below or rises above that determined upon, an electro-magnetic clutch, actuating a suitable stopcock, is placed in a battery circuit, and thus connection is made between the reservoir and the pump or outer air, as may be required for adjustment (Phil. Mag. 1879 [v.] 7, 411).

A. Fock has constructed a very serviceable bath, in which common petroleum is used as the mixture of liquids of different boiling-points. A double cylinder AB (Fig. 2), serving as a vapour-jacketed bath, is connected by means of the side tubes *a* and *b* with the reflux

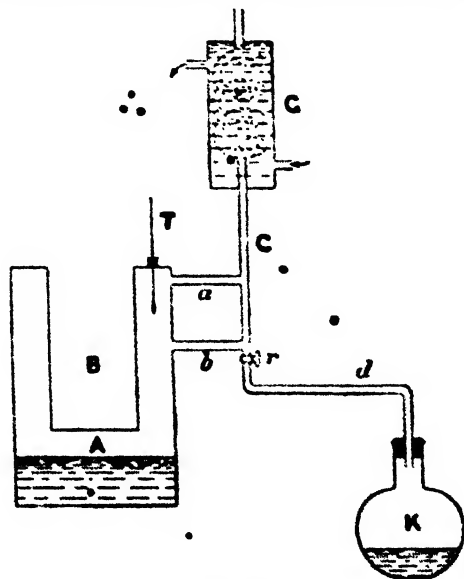
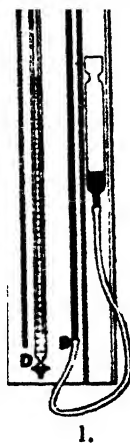


FIG. 2.

condenser *c*. The tube *c* connected with the condenser communicates, through the stopcock *r* and tube *d*, with the reservoir flask *K*. A mixture of liquids (e.g. common petroleum) is placed

in the bath and distilled, the distillate passing through the open stopcock *r* into the flask *K*. At the moment when the required temperature is attained, as indicated by the thermometer *T*, the stopcock *r* is closed; the distillate now returns through the tube *b* to the bath, hence the temperature of *B* will remain constant for any length of time (Ber. 1885, 18, 1124).

Ramsay has used a vapour-bath in which the temperature is controlled by regulating the pressure under which a selected pure liquid is boiled (Chem. Soc. Trans. 1885, 640).

J. Traube and L. Pincussohn (Zeitsch. Inst. Beib. 1897, 17, 49) have also devised a simple thermostat using a boiling liquid under a controlled pressure. For other forms see Geer (*l.c.*); F. H. Dupré and P. V. Dupré (Analyst, 1913, 38, 308); Field (J. Amer. Chem. Soc. 1914, 36, 72). Brame has described a constant temperature heating apparatus for explosives and experiments on the decomposition of nitro-celluloses (J. Soc. Chem. Ind. 1912, 31, 159).

An easily adjustable vapour thermostat has been contrived by Fletcher and Tyrer (Chem. Soc. Proc. 1911, 28, 189).

(c) Richards and Churchill (Zeitsch. physikal. Chem. 1898, 28, 313) have similarly used the change at inversion points.

III. *Other thermostats not automatically regulated.*—Instruments serving as indicators only have been devised by Hall (Q. J. Sci. 1818, 5, 52); Doyère (Ann. Chim. 1850, [iii.] 28,

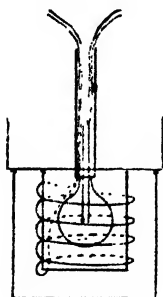


FIG. 3.

5); A. Fraser (Jour. Gas Lighting, 1881, 38, 798); J. Barnes (Chem. Soc. Trans. 1881, 39, 463); A. V. Harcourt (Proc. Roy. Soc. 1882, 34, 166); U. Kreusler (Chem. Zeit. 8, 1321); and C. Winkler (Ber. 1885, 18, 2533). Bunsen's thermostat (Annalen, 141, 273) is historically interesting. Exner's thermostat is of especial value, as it allows of constant temperatures being maintained between 0° and 10° (see Fig. 3). It consists of an inner flask, surrounded by two concentric glass vessels, with an air space between; the three vessels are fastened above to a zinc plate. A delicate thermometer and a thermoelement are placed in the centre of the flask; the stem and wires pass through a leaden pipe attached to the zinc plate. Between the two surrounding vessels is coiled a German-silver wire, the coils hanging freely without contact with either vessel; wires pass from the coil to a battery through the leaden tube. The whole is completely immersed in melting ice, contained in a fourth vessel; the leaden tube alone projects, and serves to keep the wires from contact with the ice. By passing an electric current through the German-silver coil, the temperature of the central vessel can be maintained at any desired point above 0° (Sitz. W. 1873, 6892).

The same principle is applied by H. Crew (Phil. Mag. [v.] 33, 89). The accompanying illustration (Fig. 4) shows the points in which this instrument differs from the preceding one.

Julien storage cells are used as the source of a constant current, which is regulated by alteration of the length of a resistance wire through which the current flows, by means of a slider and controlled by means of a Thomson balance. Other non-automatic instruments are described by Mahlke (Zeitsch. Inst. 1893, 13, 197),

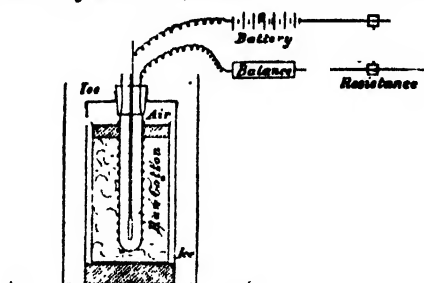


FIG. 4.

Pulfrich (Zeit. Inst. 1898, 18, 49), and Rotho (*ibid.* 143, 1899, 19).

IV. *Self-regulating thermostats:* (a) *Single-liquid thermometers* (1) *acting directly on the gas supply or other heat source.*—Thermostats of this and allied types have been frequently utilised in connection with technical processes and heating systems; references to a number of these are given at the end of this article.

Reichert's form of regulator is essentially that of a mercury thermometer, with a reservoir at the top of the column. The gas-supply tube is placed so that its contracted opening is vertically over and near to the surface of the top of the mercury column. The leading tube takes off gas at the side of the reservoir. A small side tube on the stem is supplied with a screw by means of which the mercury level may at any time be adjusted, and the temperature maintained thus altered at will (Fig. 5) (Zeitsch. anal. Chem. 11, 34; Pogg. Ann. 141, 467; cf. Fontaine, *Ann. Chim. Anal.* 1911, 16, 52; Fänder, *Chem. Zeit.* 1913, 37, 40).

Gerhardt's modification permits the instrument to be filled easily with mercury.

Regulators of the same type, but varying somewhat in form, have been constructed by Page (Chem. Soc. Trans. 1876, 24), Fletcher (*ibid.* 1876, 488), and Roulin (Dingl. poly. J. 227, 263);

Whitaker (Chem. News, 1913, 107, 242). The instrument devised by Roulin is made of iron and steel (cf. Fig. 6). The height of the mercury column is adjusted by means of a sliding tempered-steel rod, held in position by the set screw *f*. As this rod passes down the centre of the gas-supply tube, the gas can only reach the burner tube by passing through the ring-shaped aperture *d*, near the

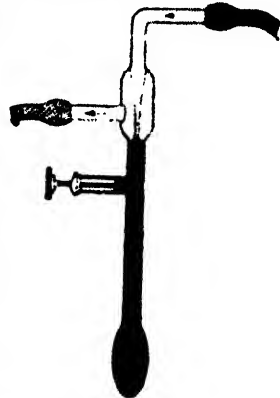


FIG. 5.

surface of the mercury. A small tap *g* maintains a sufficient supply of gas to the burner to avoid extinction of the flame by the complete interruption of the supply at *d*.

In the thermostat battery by Dibdin and Smith, in use at the metropolitan gas stations, large mercurial thermometers are employed. The tubes by which they communicate with the supply tube are provided with stopcocks, so that any one or more of them may be thrown out of action. They control the gas supply to the boiler connected with the hot-water pipes.

For more accurate work, the mercury has been replaced by 30 p.c. calcium chloride solution, alcohol, benzoline, petroleum, xylene, or toluene. The toluene regulator has gained general acceptance; a simple and easily constructed form, designed by H. Lunden and W. Tate (*Zeitsch. Chem. Appar. II.* 1, 13, 1907), is shown in the sketch (Fig. 7)

with dimensions in millimetres. The column of calcium chloride solution prevents contact of the toluene with the mercury and with the stopcock *R*, thus doing away with the slow

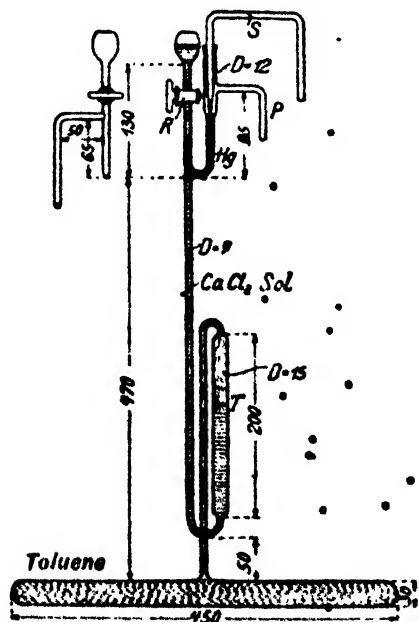


FIG. 7.

evaporation of the expanding liquid and allowing the use of ordinary lubricants with the stopcock provided to make temperature adjustments. This regulator, without the

aid of any form of pressure regulator (the gas pressure varying from 50 to 60 mm. of water), maintained the temperature of a water-bath of 150 litres capacity during 30 days constant in a room varying considerably in temperature. The greatest difference between the extreme temperatures (observed at regular and frequent intervals) was 0.02°. A small part of the heating gas only passed through the valve *D*, sufficient to heat the bath within a short interval of the required temperature was supplied direct from the main.

Another convenient form of toluene regulator is described by Lowry (*J. Soc. Chem. Ind.* 1905, 1033); there is a helical toluene reservoir tube coiled round a straight vertical stem containing mercury; it is provided with a wide bye-pass but has no provision for ready adjustment of the temperature, and the mercury and toluene are in contact near the lower end of the helix.

Slator has described (*J. Soc. Chem. Ind.* 1911, 30, 61) a modification of the ordinary toluene regulator by which it can be readily adjusted to any desired temperature.

Hannay (*Mon. Sci.* [iii.] 16, 1021) and F. W. Daffert (*Chem. Zeit.* 1886, 52, 789) have designed thermostats belonging to this class.

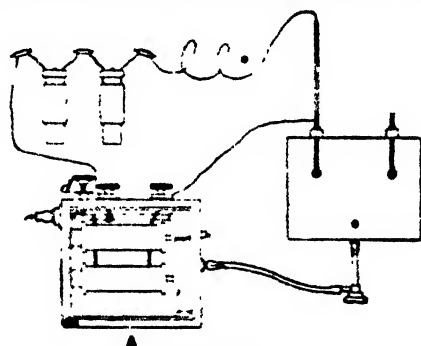


FIG. 8.

Further references are given by Geer (*J. Phys. Chem.* 1902, 6, 85); cf. Davis (*J. Amer. Chem. Soc.* 1915, 37, 1198). See also Starkey and Gordon (*J. Ind. Eng. Chem.* 1922, 14, 541).

(2) *Thermostats acting on the source of heat through electrical arrangements.*—The usual type of this class employs a mercury thermometer with one pole of a battery permanently connected with the mercury and a second adjustable pole which completes the circuit at the desired maximum temperature. An electro-magnetic arrangement in the circuit actuates a gas-cock, or works a gas valve either directly, or, by means of a plunger, indirectly controls a mercury valve of the usual type. This form of thermostat can be made very rapid in action and practically independent of variations in the gas pressure.

Scheibler has constructed an electro-thermostat, with the usual form of electric thermometer (Fig. 8). The electro-magnet is contained in the square box *A*; the upper end of the armature is provided with a leather pad, which works against the continuation of the gas-supply tube *b*, and with it forms a valve which cuts off the gas when the mercury comes into contact with the upper platinum wire. The extinction of the flame is avoided by having a small hole at *c* in the tube, more or less closed by means of the

screw *d*, through which a small stream of gas can escape into the box, and hence into the burner tube (Zeitsch. Anal. Chem. 1868, 88).

Kohlrausch adapted this principle to the regulation of the temperature of a hothouse (Dingl. poly. J. 389, 175). E. E. Reid (Amer. Chem. J. 1909, 41, 148-152) employs a mercury valve worked by a plunger controlled by an electro-magnet.

A high-temperature thermostat, capable of being kept constant to within 1° at 1000° , has been described by Haughton and Hanson (J. Inst. Metals, 1917, 18, 173).

A thermo-regulator for thermostats at temperatures close to ordinary room temperatures has been described by Powell (J. Soc. Chem. Ind. 1914, 33, 899).

An electrical contact vapour-pressure thermo-regulator has been contrived by Field (J. Amer. Chem. Soc. 1914, 36, 72). The regulator has proved sensitive to 0.1° - 0.005° .

Other forms are quoted by Geer (see iv. 1); to these we may add Clerget (Dingl. poly. J. 134, 23), Pfaundler (Carl's Rep. 18, 443), and Salet (Bull. Soc. chim. 1865); Morgan (J. Amer. Chem. Soc. 1911, 33, 344); Bunzel and Hasselring (J. Amer. Chem. Soc. 1914, 36, 949); Gouy (*ibid.* 1920, 42, 60).

The sensitiveness of a mercury thermo-regulator operated electrically is affected by the adherence of mercury to clean platinum. Mansfield Clark (J. Amer. Chem. Soc. 1913, 35, 1889) finds that by substituting a nickel or nichrome wire for platinum, the making and breaking of the circuit may be made to occur at temperatures much closer to one another.

For a description of a thermo-regulator with the characteristics of the Beckmann thermometer, see R. B. Harvey (J. Biol. Chem. 1920, 41, 9) in Abstract. Chem. Soc. Trans. 1920, ii. 161.

(3) *Thermostats acting on the source of heat through mechanical arrangements.*—Randall's apparatus (Dingl. poly. J. 224, 478) admits of direct technical applications, as it is adapted to the heating of large masses of water to a constant temperature by the use of steam. In Fig. 9 *b* is

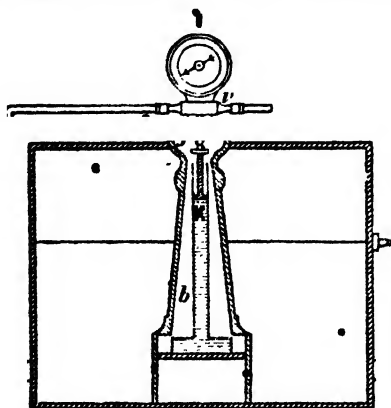


FIG. 9.

a thin-walled tubular vessel containing some expansible liquid, the movements of the surface of which are followed by the piston *x*. This piston works a valve *v*, which controls the

steam supply. The spring *f* insures the return of the piston, the movements of which are recorded by the indicator *i*, which thus acts as a thermometer.

D'Arsonval constructed a very delicate thermostat (Fig. 10) by surrounding his oven with a

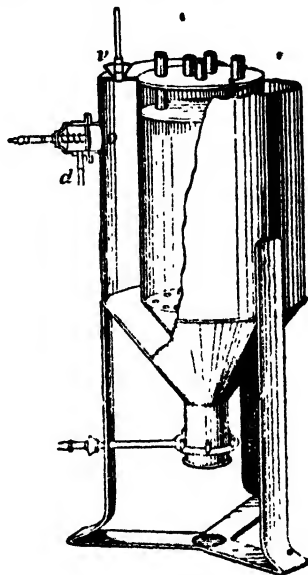


FIG. 10.

screw or by a cork through which a thermometer passes. Connected with this water chamber is the side tube *o*, closed by a caoutchouc membrane. Near to the centre of the surface of the chamber completely filled with water, which is introduced through an opening *v*, closed by a membrane the gas-supply tube terminates—in a small metallic valve-box, from which the gas is led off to the burner by the tube *d*. The expansion or contraction of the large volume of water in the outer chamber causes the caoutchouc membrane to lessen or increase the distance between the supply tube and its own surface, thus forming a very sensitive valve, which controls the supply of gas to the burner. This regulator is said to keep the temperature constant to $\pm 0.1^{\circ}$ (J. Pharm. Chim. [iv.] 26, 474).

To maintain constant higher temperatures than can be employed with water, D'Arsonval substitutes a brass tube (Fig. 11), containing petroleum or glycerol, for the surrounding water chamber. The membrane is replaced by a corrugated metallic plate such as would be used in an aneroid barometer; *b* is a leaden tube prolonging the brass tube; it is hermetically closed after charging the tube. The chamber at the back of the aneroid plate communicates with the main tube by two small tubes *m* and *n*.

Several other forms of this regulator, retaining the same kind of valve, have been constructed. The valve itself has been mounted separately on a stand, and provided with a funnel and stop-cock to adjust the amount of liquid in the connected reservoir and the lower part of the valve, and with a bye-pass to insure that the flame be never quite extinguished. The same type of valve has also been adapted to the

regulation of the flow of a cooling mixture, used for obtaining temperatures below that of the surrounding air.

G. Dorian (Bull. Soc. Ind. Mulhouse, 1900, 71, 249) described a combined heat and moisture regulator, in which the expansion of the liquid of a thermometer with a reservoir of spirally twisted tube controls a cock regulating the current of heating fluid and a hydrometer regulator works the moisture supply. T. S. Patterson (J. Soc. Chem. Ind. 1902, 21, 456),

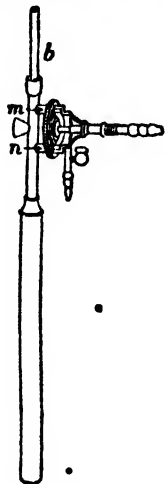


FIG. 11.

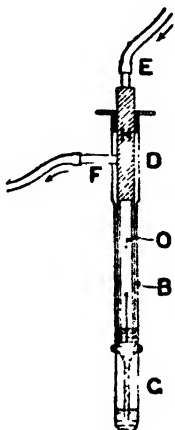


FIG. 12.

N. A. Randolph (Jour. Franklin Institute, 1883, 116, 465), V. H. Veley (Chem. Soc. Trans. 43, 370), and Nauman (Dingl. poly. J. 226, 276), give other forms, and various technical adaptations will be found in the list given at the end of this article.

(b) *Gas thermometer regulators.*

(1) *Acting on the gas supply through a liquid piston.*—A thermostat on this principle was devised by Kemp (Dingl. poly. J. 117, 352) and improved by Westly.

Bunsen's thermostat is a modification of Kemp's. The gas supply and exit tubes are arranged as shown in Fig. 12; the supply tube *E* passes through a brass cylinder *H*, which screws into the loose brass cap *D*. At its lower end is a slit, and it is provided with a minute orifice at *o*; the exit tube *F* is joined on to the side of the cylinder *H*, the latter being continued by the glass tube *B* to the same depth as the supply tube. The cap is fitted on a brass tube supplied with a slit in which the tube *F* can slide. A glass cylinder closed at the lower end continues this brass tube. In the lower part of this glass vessel is a glass air-chamber opening downwards and closed by the mercury contained in the cylinder; this air-chamber preferably takes the form shown at *C*. The expansion of air in the chamber causes the mercury to rise in the cylinder, and thus partially closes the slit; the position of the slit is regulated by the screw cap until the required temperature is attained. The minute orifice *o* insures that the gas supply should never be completely cut off (Dingl. poly. J. 143, 342).

Bunsen's low-temperature regulator has a larger air chamber, and is provided with a side tube and stopcock, by means of which the

amount of mercury present can be readily altered (Desaga's Catalogue). Pontallie divides the gas supply after passage through a Bunsen's regulator, using one part to heat the regulator only, the remainder heating the bath. As these quantities are in exact and determined proportion, the temperature of the bath is maintained constant when that of the regulator does not vary.

Schorer separates the air-thermometer reservoir from the valve to enable the instrument to be used for high temperatures (Zeitsch. anal. Chem. 9, 213).

D'Arsonval adapted his thermostat for use at temperatures between 150° and 1200° by substituting an air reservoir for the petroleum reservoir employed at lower temperatures. The reservoir was made of glass or porcelain. The aneroid valve was at the same time furnished with a lever-arm and weight *P*, by means of which the pressure on the lower surface of the aneroid plate could be more or less compensated, and the amount of gas supplied altered at will (Fig. 13) (J. Pharm. Chim. [iv.] 26, 474).

Although a number of varieties of this type have been used (see Geer's bibliography; J. Martenson, Chem. Zentr. 1872, 513; Clowes, Chem. Soc. Trans. 24, 639; L. Saarbach, J. Amer. Chem. Soc. 18, 511, 1901), and the principle has been technically applied in connection with furnaces of moderately high temperature for low temperature work the toluene thermometer forms are to be preferred for accurate long period temperature regulation; all gas and vapour thermostats suffer from the defect of needing regulation with the changes in pressure of the air.

(2) *Acting through electrical arrangements.*—These devices resemble the instruments in

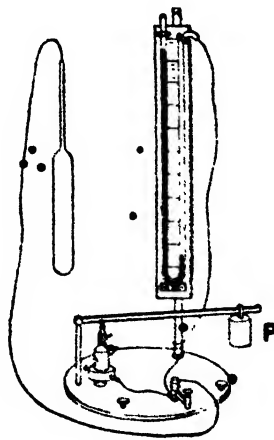


FIG. 13.

group iv. *a* (2). Pfaundler's apparatus (Carl's Rep. 18, 443) is similar to Scheibler's, the points of difference are sufficiently evident from the annexed figure (Fig. 14).

Solari (Bull. Soc. chim. 1923, [iv.] 33, 1000) has described an apparatus which consists essentially of a differential air thermometer with mercury as the moving liquid. One bulb is maintained at a constant temperature and the other is placed in a small auxiliary furnace of copper tube connected in series with the main furnace. The tube containing the mercury is

provided with three platinum contacts so arranged in connection with a resistance and a swinging commutator that automatic regulation of the current passing through the furnace is secured. If Q be the thermal capacity, R the radiating power, and C the conductivity of the tube carrying the heating coil of the main furnace, and q , r , and c the same constants for

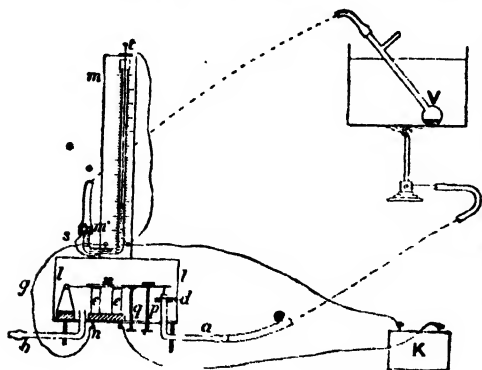


FIG. 14.

the small one, then temperature control to within $\pm 5^\circ$ may be obtained by making Q/q very large, R/r very small (but r must not be too great), and C/c very small (c may be very large).

(3) *Acting through mechanical arrangements.*—Jeannel's thermostat (Fig. 15) is an air-thermometer thermostat in which the air reservoir consists of a metallic vessel of 300-400 c.c. capacity. This is connected with one limb of a

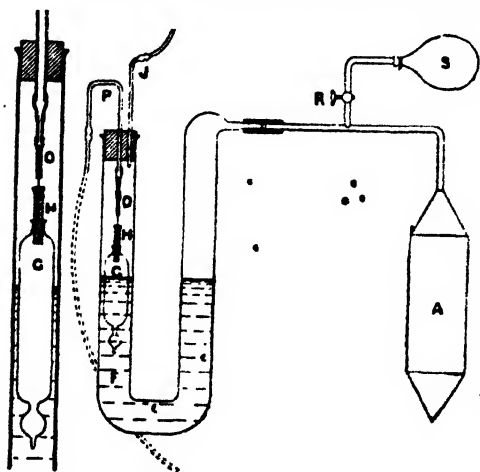


FIG. 15

U-tube containing glycerol. In the other limb a float G carries a steel needle working loosely in a fine caoutchouc tube O . By a rise of the liquid in r , the float, guided by the steel needle, brings the flat upper surface of the sealing wax H , in which the needle is mounted, near to the mouth of the tube O , thus forming a valve controlling the current of gas from the supply tube J to the exit tube P , of which O is a continuation. The pressure of the air in A is modified at pleasure by means of the caoutchouc pump S ,

with which connection is made through the tap R on a side tube (Ann. Chim. [iv.] 25, 386).

W. T. Richmond (Amer. Chem. J. 5, 287), Bendix and Lohse (D. R. P. 14242, 1880; Ber. 14, 2608), and Bechem (D. R. P. 18077, 1881; Ber. 15, 1226) have also devised self-acting thermo-regulators of this type.

(c) *Vapour-tension thermometers.*

(1) *Air and vapour.*—André's thermo-regulator is a Kemp thermostat in which the expansion of the air in the reservoir is increased by the addition of a small quantity of some readily volatile liquid. Such liquids as ether, alcohol, acetone, light petroleum and water may be employed for the purpose. Ether is particularly suitable, on account of the rapid increase of its vapour tension with increase of temperature. A thermostat of this form will maintain the temperature of a water-bath constant within $0.04-0.05^\circ$ (Wied. Ann. 4, 614).

Lothar Meyer has also made use of the same principle (Ber. 16, 1088).

The following mixtures of liquids of constant boiling-point, for use in constant temperature heating baths, have been suggested by A. Golodetz (Chem. Zeit. 1914, 38, 1253).

B.p.	Composition of liquid.
33°	Water and ether (heterogeneous).
36.5-37°	Alcohol (3) and ethyl bromide (97).
38°	Carbon disulphide (87) and methyl alcohol (13).
39-40°	Carbon disulphide (71) and methyl acetate (29).
42.5°	Carbon disulphide (91) and alcohol (9).
53.5°-54°	Methyl alcohol (12) and chloroform (88).
55.5°	Methyl alcohol (29.6) and carbon tetrachloride (70.4).
58°	Methyl alcohol (38.4) and benzene (61.6).
59°-59.5°	Alcohol (6) and chloroform (94).
62°	Methyl alcohol (47) and ethyl acetate (53).
64.8°	Benzene (74.1), alcohol (18.5), and water (7.4).
68°	Alcohol (32.4) and benzene (67.6).
71.5°	Alcohol (31) and ethyl acetate (69).
74.8°	Carbon tetrachloride (77.15) and alcohol (22.85).
79.5°	Benzene (90.5) and isobutyl alcohol (9.5).
84.5°	Water and toluene (heterogeneous).
87.7°	Water (26.3) and propyl alcohol (73.7).
91°-91.5°	Propyl alcohol (53) and toluene (47).
92.5°	Water (41) and pyridine (59).
91°-91.5°	Water and turpentine (heterogeneous).
95°	Water (7) and chloral (93).
98.5°	Water and ethylaniline (heterogeneous).
99°	Water and diethylaniline (heterogeneous).
104°	Toluene (70) and acetic acid (30).
113°-113.5°	Acetic acid (27) and xylene (73).
121°-122°	Amyl alcohol (30) and ethylene dibromide (70).
125°-126°	Amyl alcohol (52) and <i>m</i> -xylene (48).

Benott's thermo-regulator has the thermometer reservoir separated from the valve, connection being made by means of a caoutchouc tube containing mercury.

The reservoir consists of a thin tube, drawn out at one end for convenience in filling, which contains a small quantity of air, and a few drops of some volatile liquid; the remainder of the space in the tube is occupied by mercury in connection with the mercury in the valve by means of the caoutchouc tube. The valve differs somewhat from the ordinary form. It is provided with a side tube *A* (Fig. 16), by which a small amount of gas can directly pass from the supply tube *x* to the burner tube *y*. Mercury can be added by means of the side tube *B*, or withdrawn from the cock *c* to adjust the level within the valve. The whole is mounted upon a sliding board, fixed by the clamp-screw *m*, at any convenient height (Wied. Beibl. 4, 296; Guillaume's *Thermométrie*, 130).

(2) *Vapour in contact with its own liquid only.*
—The instrument devised in 1886 by G. W. A.

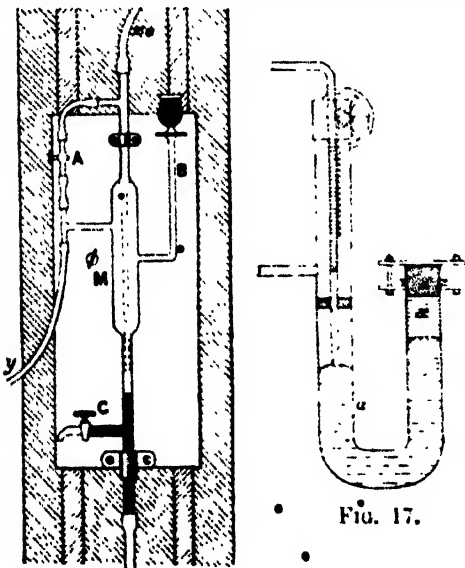


FIG. 16.

Kahlbaum belongs to this class. There is the usual mercury valve, the supply tube being bevelled off at the open end at an angle, and having a small hole opposite the exit tube to provide against total extinction of the flame. It may be adjusted according to the temperature required by the rack and pinion shown (Fig. 17). The other limb of the U-tube contains a liquid of boiling-point just below the temperature required in the bath or oven. For facility in changing the liquid, this end of the tube is closed by a tightly-fitting cork held in place by a clamp working against an india-rubber seat fixed on the collar of the glass tube.

The temperature rises just above the boiling-point of the liquid *x*, a portion of this volatilises, and mercury is forced up the limb *a*; the pressure on the liquid being now greater, its boiling-point is raised, and the temperature must increase for further volatilisation to occur. Owing to the rise of mercury in *a*, the gas supply is diminished, and hence the temperature falls.

Consequent on the fall of temperature, a portion of the vapour condenses, the valve is opened to a greater extent, and the temperature again rises. These actions soon reach a point of equilibrium, and a constant temperature is then maintained (Ber. 19, 2860).

(d) *Thermostats depending upon the differential expansion of solid bodies.*—Bonnemain (Dingl. poly. J. 16, 285) and Ure (*ibid.* 42, 173) devised regulators depending upon the expansion of simple or compound metallic bars.

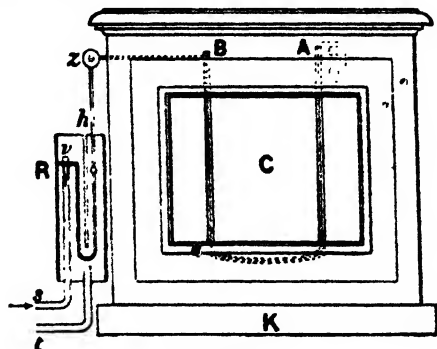


FIG. 18.

Hipp's thermostat is only available for temperatures between 30° and 40° (see Fig. 18). It consists of a copper vessel *K*, surmounted by a wooden box *C*, having glass front and back. A system of tubes on the walls of the oven communicate with the vessel *K*, and serve for the circulation of the water heated in that vessel. They are provided with openings for filling in water, and to serve as escape vents in case the

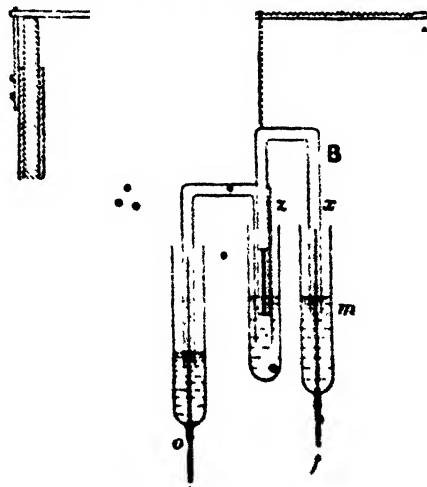


FIG. 19.

water may be accidentally boiled. The temperature is controlled by a regulator consisting of a bent compound metallic bar fixed upon the back wall of the oven at *a*; the free end *b* is connected by a copper wire with the lever *A* working a conical valve *c*; *z* is a regulating screw, by means of which any desired initial opening of the valve may be obtained; *s* is the gas-supply tube, and *t* draws off gas for the burner from the valve-box *a* (Dingl. poly. J. 191, 306).

Lothar Meyer in 1884 devised a sensitive temperature regulator on this principle (Fig. 19).

It consists of a long brass tube placed vertically in the bath, and closed at its lower extremity; in this tube a slightly longer glass rod is placed. The tube supports a rod carrying a movable lever-arm *A*, from which depends a floating valve *B*. The valve may be placed at varying distances along the lever-arm *A*, so that the difference between the expansions of the brass tube and glass rod may be magnified to a greater or less extent in the amount of movement imparted to the valve. The supply tube is a narrow-bore tube passing up the arm *x* of the valve working in the glycerol seal tube *m*. The supply tube and seal may be adjusted to any required height. A precisely similar arrangement allows of the drawing off through *o* of the gas for the burner. The valve *z* is essentially a Bunsen mercury-and-slit-tube valve. The mercury vessel is adjustable to any required height (Ber. 17, 478).

L. von. Babo arranged a gas regulator, in which the control valve depends for its action upon the unequal expansion of glass and copper. In Fig. 20, *A* is a copper tube, *B* a glass rod. The

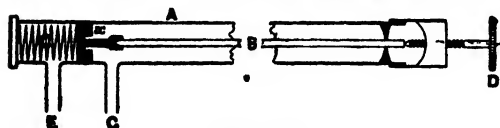


FIG. 20.

valve *z*, which regulates the flow of gas from the supply *g* to the burner tube *e*, is fixed in position by the glass rod *B*, against which it is pressed by a spiral spring *c*. The screw *d* serves to adjust the position of the glass rod, and renders it possible to obtain a greater or smaller supply of gas at will. As the temperature rises, the expansion of the copper tube being greater than that of the glass rod, the valve *z* is pressed by the spring *c* nearer to its seat, and so there is less gas supplied; the temperature then falls, and the valve partially re-opens, and so on (Ber. 13, 1221).

Kohlrausch employed a Breguet's metallic thermometer to make and break an electric current, which heated a fine platinum wire (Pogg. Ann. 125, 626).

E. Gumlich (Zeitsch. Inst. 1898, 18, 317) claims, by the use of a nickel and brass Breguet's spiral governing the gas supply through intermediary electrical arrangements, to have maintained a dry oven within 0.4° for long intervals.

Rieth's instrument consisted of a compound metallic bar working a cone valve, supplied with a regulator screw (Chem. Zentr. 1871, 615).

In Taliani's thermo-regulator (Ann. Chim. Applicata, 1914, 1, 405) two bimetallic zinc-steel vertical strips are fixed at their lower ends with the more expansive metals facing inwards. The free upper ends are connected by means of a very thin copper wire, on the middle point of which rests the valve regulating the flow of gas to the lamp of the thermostat. The valve is raised by the separation of the strips and lowered by their approach. By means of a slider operated from without the effective lengths of the strips, and consequently the constant temperature obtained, may be varied.

(e) *Electrically heated thermostats with electrical control.*—Thermostats of this type allow of more sensitive and rapid adjustment than

any other; they are particularly suitable for accurate scientific work but are not without technical applications.

Rothe (Zeitsch. Inst. 1899, 19, 143) gives a very complete account (with illustrations) of a thermostat designed for use in thermometer work at the Phys. Tech., Reichsanstalt. The same author (Zeitsch. Inst. 1902, 22, 14) adapts this principle to the construction of an instrument for use with very low temperatures. A Dewar vessel serves to prevent conduction of heat from without; the heating coil is of constantan wire wound on the ebonite ring of a stirrer, the stem of which is of glass tubing through which pass the leading wires for the current.

W. C. Geer (J. Phys. Chem. 1902, 6, 94) claims for his thermostat a variation of 0.002° only for a 9 hours' run with a 30-litre bath. A somewhat simpler form, which is essentially a modified Geer thermostat, is described by F. A. Osborn (*ibid.* 1905, 9, 297). The accompanying diagram (Fig. 21) shows its essential features. The heating of the 50-litre bath is accomplished by means of an iron wire *cc* carrying a current from the large storage battery *B*. The wire forms a layer of five turns against the sides of the bath, which latter is encased in a non-conducting layer of felt. *m* is a glass worm, 9.5 cm. diameter and 16 cm. long and holding 110 c.c. of mercury, serving as a reservoir of a regulating thermometer with a capillary stem. The bath is stirred by a

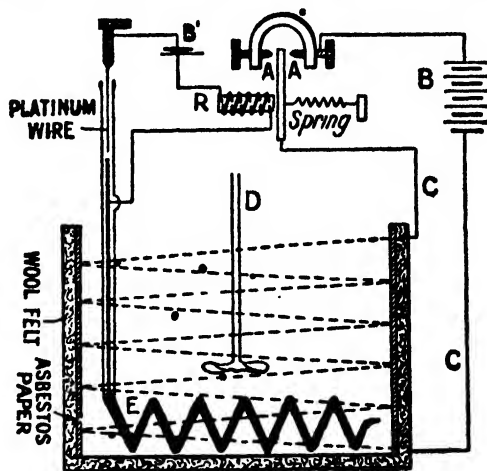


FIG. 21.

mechanically-driven stirrer represented by *D*. A platinum fused-in wire permanently connects an electro-magnet *R* with the mercury of the thermometer. *B* is connected through a storage cell *B'* with a second adjustable wire *p*. When the required temperature is reached, the mercury completes the circuit with *p* and the main current is broken at *AA* by the movement of the armature. The spring shown establishes the main circuit as soon as the mercury breaks contact with *p*.

This form can be brought to the required steady temperature in 15 minutes and shows no change of a hundredth of a degree in 8 hours.

Other forms are given by S. W. Young (J. Amer. Chem. Soc. 1901, 23, 327); C. Marie

and R. Marquis (Compt. rend. 1903, 136, 614), who use an acetone thermometer with mercury make and break and current through platinum wire; R. A. Macumber and C. G. L. Wolf (J. Path. Bact. 1904, 10, 105); H. Darwin (Phil. Mag. [vi.] 7, 408, 1904); J. P. Magnusson (J. Phys. Chem. 1907, 11, 25); Regaud and Fouilland (Ann. Chim. anal. 1909, 14, 141); L. Kolowrat (J. Phys. 1909, 8, 495), who describes the automatic regulation of an electric oven.

(f) *Other mechanical regulators* have been devised by J. W. Eichler and H. Hartig (D. R. P. 5492, 1878), and by Appold, whose instrument was a balance regulator (Proc. Roy. Soc. 1866, 15, 144).

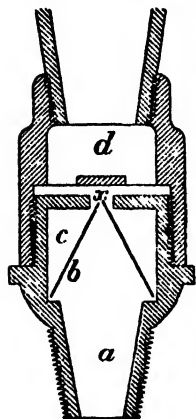


FIG. 22.

The invention of G. J. Meurlin (D. R. P. 4703, 1878) consists of a self-regulating cone valve to control the pressure of a gas supply, and hence the temperature of a space heated by the flame. The pressure of the gas in the chamber *a* raises the cone *b* (Fig. 22), partially closing the hole in the plate *x*, and thus restricting the current. The hole in the summit of the cone *b* prevents extinction of the flame.

• A. Schwabe (D. R. P. 93152, 1896) describes a device by which an areometer works a chain controlling the source of heat.

The choice of the type of thermostat most suitable will be governed by the requirements in each special case. Technical applications of these instruments are most frequently adequately met by the use of the simple mercury thermometer valve at moderate temperatures and the air-thermometer mercury-valve at higher temperatures, some form of differential expansion instrument being used when the liability to vibration or shock has to be provided for.

For accurate work, the reliability, sensitiveness, and independence of atmospheric changes are the most important considerations. Electrical thermostats with electrical control appear best able to fulfil the necessary conditions (see Geer, J. Phys. Chem. 1902, 6, 85); W. P. Bradley and A. W. Browne (*ibid.* 1902, 6, 118) claim to have constructed a thermostat sensitive to one thousandth of a degree. The toluene thermometer mercury-valve thermostat has found wide use; T. M. Lowry (J. Soc. Chem. Ind. 1905, 1030) discusses the conditions governing its sensitiveness and A. W. C. Menzies (Chem. News, 1902, 85, 68), in dealing with the same subject, shows that this type is able to keep a bath at 6° above room temperature constant within one hundredth of a degree.

The principal ways in which thermostats have been applied to technical purposes have been mentioned; recent instances of such applications are to be found in the following, not otherwise readily accessible, references.

Central heating and ventilating systems.—Consolidated Car-heating Co., Wheeling, U.S.A.,

D. R. P. 67775, 72164, 1892; Senff, Ges. Ing. 1901, 24, 393; Johnson thermostat control of steam heating, Eng. Rec. 47, 277, 1903; Walkor and Chambers, *ibid.* 47, 352, 1903; System Schultz, Ges. Ing. 27, 550, 1904; Narus-Gaye and Bloock, Met. Arb. 30, 99, 1904; Hainholzer Zugregulator, Tech. Zeit. 21, 485, 1904; Ohmes, Ges. Ing. 27, 545, 1904; Goebel, *ibid.* 28, 41, 1905; Webster, Eng. Rec. 53, 9; 54, 436, 1906; de Grahl, Ges. Ing. 29, 333, 1906; Mehl, Dingl. poly. J. 321, 698, 1906; Sc. Am. Supp. 64, 212, 1907; Pradel, El. Anz. 24, 1013, 1907; Gold Car Heating and Lighting Co., Railr. G. 2, 536, 1907; Fulton, Eng. Rec. 7, 56, 1907.

Incubators and germinating stoves.—Paul, Centralblatt Bakt. 1, 29, 129, 1901; El. Rev. N. Y., 1903, 43, 941; Schlösing, Gen. Civ. 1904, 44, 368; Joffin, Compt. rend. 1904, 138, 817; Rogers, Centralblatt Bakt. 2, 15, 236, 1905.

Distillation or evaporation.—Patterson, Chem. Ind. 21, 456, 1902; Bull. Sucr. 21, 619, 1903; Foth (fermenting worts), Z. Spiritusind. 27, 257, 1904.

A number of dyes, belonging generally to the triphenylmethane class, such as methyl violet, malachite green, and erythrosin, have the property of gradually and completely disappearing without residue when heated, the time taken for disappearance depending on the temperature, other conditions being the same. Such dyes can be used as heat indicators in a number of ways for the control of industrial operations, for instance, in cases where a certain amount of heat has to be applied during a certain interval of time, the disappearance of the dye indicating the completion of heating. Another use is to determine the heat distribution in a heated body. The method may be applied in the annealing of glass, the burning of cements, or to detect overheating of electrical equipment (P. A. Kober, Ind. Eng. Chem. 1923, 15, 837-838; J. Soc. Chem. Ind. 1923, 43, 913A).

Miscellaneous.—E. Clarenbach, D. R. P. 67146, 1892; Kramer, D. R. P. 67146, 1892; G. H. Stockbridge (Fire Alarm Telegraphs), Elect. London, 1896; E. Sartorius, D. R. P. 100294, 1897; R. Janz, D. R. P. 114457, 1899; O. Bohne, D. R. P. 133429, 1899; Fedeschi, Centralblatt Bakt. 1, 30, 969, 1901; P. Brouilh, D. R. P. 150962, 1903; Regaud and Fouilland (electric stoves), Zeit. Mikr. 20, 138, 1903; Casses (pasteurising apps.), Milch. Zeit. 33, 258, 1904; Keller and Co., Tech. Rundsch. 5, 1904; Voss, Zeit. Beleucht. 10, 216, 1904; Ginsberg, Zeit. Heiz. 9, 231, 1904; Sodeau, Chem. Ind. 23, 1134, 1904; ovens, kilns, &c., Eng. News, 51, 514, 1904; Système de Rougemont, Gén. Civ. 46, 213, 1905; damper regulator for boilers, Eng. Rec. 54, suppl. 12, 47, 1906; System Koefler, Ges. Ing. 29, 293, 1906; Zeit. Hirz. 12, 80, 1907; D. J. Beaver and J. J. Beaver, Ind. Eng. Chem. 1923, 15, 359. For a modified thermo-regulator, see Hume (J. Soc. Chem. Ind. 1924, 43, 250 T). W. T.

THESPASIA MACROPHYLLA (Blume) [T. Lampas (Dabz.).] This is a small bush common to the tropical jungles of India, Burma, and Ceylon. In Watts' Dictionary of the Economic Products of India, there is no mention of the use of this plant as a dyestuff, but, on the other hand, the capsules and flowers of the

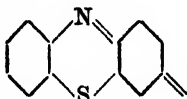
allied *T. populnea* (Soland.) are stated to give a yellow dye.

According to Perkin (Chem. Soc. Trans. 1909, 95, 1859) the flowers of the *T. macrophylla* yield quercetin and some quantity of *proto-catechuic acid*.

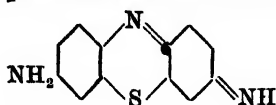
With mordanted woollen cloth* the flowers produce fairly good shades, but are in no way superior to the better-known Indian natural yellow dyestuffs. A. G. P.

THEVETIN *v.* **DIGITALIS**.

THIAZINE COLOURING MATTERS. The thiazines are colouring matters containing the group



The simplest member of this series is *thionine*

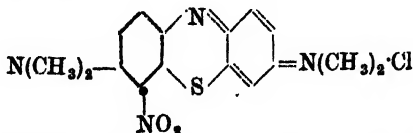


the hydrochloride of which constitutes Lauth's violet (see METHYLENE BLUE). The tetramethyl derivative is methylene blue (*q.v.*), which is by far the most important dyestuff of this class. The general method of preparation of these colouring matters has already been indicated (see METHYLENE BLUE).

Gentianine (Gy.), produced by oxidising *p*-phenylenediamine and dimethyl-*p*-phenylenediamine with ferric chloride in presence of sulphuretted hydrogen, is probably the zinc double chloride of a mixture of Lauth's violet and methylene blue; it dyes tannined cotton in bluish-violet shades.

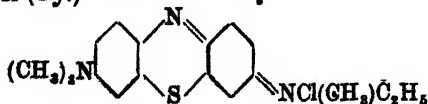
By the oxidation of methylene blue with acidified bichromate elimination of methyl groups occurs with the formation of **methylene azure**. This dye is the mixed chloride of di- and tri-methylated Lauth's violet; on cotton mordanted with tannin and tartar emetic it furnishes reddish-blue shades fast to washing.

Methylene green (S.C.I.), **Methylene green paste** (L.B.H.)



is obtained by treating methylene blue with sodium nitrite and nitric acid at 50°, the product being salted out and converted into double zinc chloride. It dyes in bluish-green shades on mordanted cotton, being the fastest green basic colouring matter used in silk dyeing and printing and in calico printing.

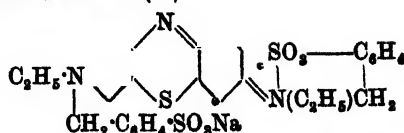
Thionine blue GO, O (M.); Thionine blue B, R (By.)



is prepared like methylene blue except that dimethyl-*p*-phenylenediaminethiosulphonic acid is oxidised together with methylethylaniline

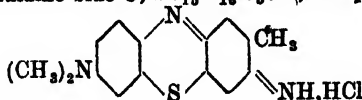
instead of dimethylaniline. It dyes tannin-mordanted cotton blue.

Thiocarmine R (C.)



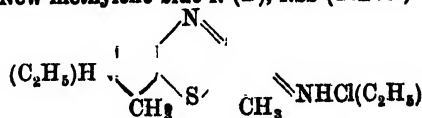
Benzylethyl-*p*-phenylenediaminethiosulphonic acid is oxidised in presence of sodium thiosulphate to sulphobenzylethyl-*p*-phenylenediaminethiosulphonic acid; the latter is oxidised together with benzylethylanilinesulphonic acid and the sulphoindaminethiosulphonate thus obtained is heated to boiling. The dyestuff is an indigo-blue powder giving a pure blue solution in water and dyeing wool and silk from an acid bath in blue shades (Cassella and Co., Eng. Pat. 4596, 1890; D. R. P. appl. C 3264; Amer. Pat. 434493; see also J. Soc. Chem. Ind. 1892, 11, 30; J. Pr. Chem. 1907, [ii.] 76, 498).

Toluidine blue O, $2C_{11}H_{10}N_2SO_2 \cdot ZnCl_2$;



Dimethyl-*p*-phenylenediaminethiosulphonic acid (*cf.* METHYLENE BLUE) is oxidised together with *o*-toluidine. The insoluble green indamine formed is boiled with a solution of zinc chloride and the resulting leuco compound is oxidised. The colouring matter is a dark green powder giving a bluish-violet aqueous solution and dyeing mordanted cotton blue (Badische Anilin und Soda Fabrik; Eng. Pat. 10314, 1888; D. R. P. 47374; U.S. Pat. 416055; Meister, Lucius und Brüning, D. R. P. 47345).

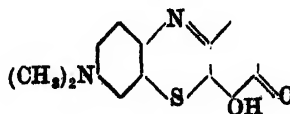
New methylene blue N (B), NSS (B.D.C)



Ethyl-*p*-tolylenediaminethiosulphonic acid, obtained by the oxidation of *p*-aminoethyl-*o*-toluidine in presence of sodium thiosulphate, is oxidised together with ethyl-*o*-toluidine and the green indamine obtained is heated. The solution of the dyestuff in water is violet-blue when cold and pure blue when hot. Tannin-mordanted cotton is dyed in redder and fuller shades than those produced by methylene blue (Cassella and Co., Eng. Pat. 8407, 1891; D. P. R. appl. C 3603; Amer. Pat. 469329). A satisfactory discharge is obtained with glucose and caustic soda.

Brilliant alizarin blue (Bayer); Indochromine T (Sandoz)

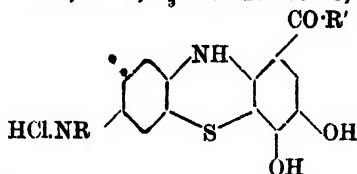
SO_2Na



1:2-Naphthaquinone 4:6-disulphonic acid is condensed with dimethyl-*p*-phenylenediaminethiosulphonic acid. The dyestuff gives fast blue

shades on chromed wool, cotton or silk, and is suitable for calico printing (F. Bayer and Co., Eng. Pat. 825, 1893; D. R. P. 83046, 86717; Fr. Pat. 227675).

Leucogallothionine (P.H.), a generic term, covering a group of leuco compounds of the following general formula (Eng. Pats. 5692, 1893; 20397, 1906; D. R. PP. 189479, 73556)



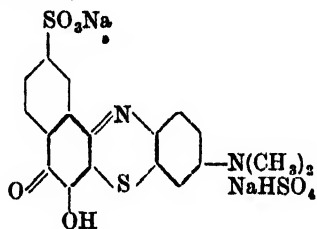
where R_1 are alkyl groups, R' is OH, NH_2 , or some other substituent in the carboxylic group of gallic acid. They are produced by condensing together *as*-dialkylated diaminoaryl-thiosulphonic acids such as



and gallic acid or a derivative such as gallamic acid. On chrome mordanted wool these acidic leuco-compounds dye with oxidation in violet to blue shades fast to light and washing.

The Gallothionines are obtained in bulk by oxidising a mixture of gallic acid (or a derivative) and a mercaptan of an *as*-dialkylated-*p*-phenylenediamine such as $N(CH_3)_2 \cdot C_6H_3(NH_2) \cdot SH$.

Indochromogen S (Eng. Pat. 3886, 1894; D. R. P. 109273)



resulting from the action of β -naphthaquinone 4 : 6-disulphonic acid on *as*-diethyl-*p*-phenylenediaminethiosulphonic acid in alkaline solution. Bright greenish-blue tints are produced on chrome mordanted fabrics, the colour being discharged with alkali chloride and ferrocyanide.

Uranis blue (W.D.C.), (Eng. Pat. 13118, 1896; D. R. P. 90275;) a bluish-violet acidic dye with bronzy lustre, obtained by oxidising with aqueous chromic acid a mixture of *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid and di- β -naphthyl-*m*-phenylenediaminedisulphonic acid. It dyes wool and silk from an acid bath in pure greenish-blue shades.

G. T. M.

THIAZOL DYESTUFFS v. PRIMULINE AND ITS DERIVATIVES.

THIET-SIE or **THITSI**. A resinous substance used as a varnish by the Burmese. It exudes from a tree in the form of a light-brown, very viscid liquid of the consistence of treacle, but on exposure to the air for a few minutes becomes quite black and hard on the surface. The same change takes place instantly in contact with potassium hydroxide. The resin spread in a thin layer on wood or other solid body quickly forms a hard deep-black coating of great brilliancy. On digesting the unaltered substance with alcohol of 80 p.c. at a gentle heat,

the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich-brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with potassium hydroxide, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves or the most part in ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This, then, is the portion of the original substance to which the property of blackening on exposure to the air is due.

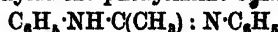
The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline acid which may be sublimed and which exhibits the characters of succinic acid. For reports of its uses and value as a lacquer, see Bull. Imp. Inst. 1917, 15, 42.

THIGAN. *Silver thiogenol.*

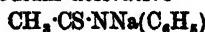
THIGENOL. Trade name for the sodium salt of ichthoform (condensation product of formaldehyde and ichthyol).

THIOACETAMIDE $CH_3 \cdot CS \cdot NH_2$, is prepared by the action of hydrogen sulphide on acetonitrile (Bernthsen, Annalen, 192, 46); or of phosphorus pentasulphide on acetamide in benzene solution (Hantzsch. *ibid.* 250, 264; cf. Hofmann, Ber. 1878, 11, 340). It crystallises in monosymmetric plates or prisms, m.p. 107.5°-108.5°, and is readily soluble in water or alcohol, less so in ether. Acids or bases decompose thioacetamide, yielding acetic acid, ammonia and hydrogen sulphide, whilst with silver nitrate solution, a precipitate of silver sulphide is obtained. It gives difficultly soluble compounds with mercuric chloride and with other metallic chlorides (Kurnakow, J. Russ. Phys. Chem. Soc. 1893, 25, 613).

THIOACETANILIDE $CH_3 \cdot C(SH) : N \cdot C_6H_5$ or $CH_3 \cdot CS \cdot NH(C_6H_5)$ is prepared by the interaction of acetanilide and phosphorus pentasulphide (Jacobson, Ber. 1886, 19, 1067; Hofmann, *ibid.* 1878, 11, 339), or of the chloride of acetanilide, $CH_3 \cdot CCl : N \cdot C_6H_5$ and hydrogen sulphide (Leo, *ibid.* 1877, 10, 2134). It crystallises from water in needles, m.p. 75°. On distillation it yields phenylamino-phenylimino-ethane



It is soluble in sodium hydroxide solution, from which it is precipitated by the addition of acids. The sodium derivative



is formed by the action of sodium ethoxide. Thioacetanilide yields two series of alkyl derivatives, viz. the normal alkyl thioacetanilides $CH_3 \cdot CS \cdot NR(C_6H_5)$ and the alkyl isothioacetanilides $CH_3 \cdot C(SR) : N \cdot C_6H_5$. The former are obtained by the action of phosphorus pentasulphide on alkylacetanilides, and the latter by the action of alkyl iodides on the sodium derivative of thioacetanilide.

THIOACETIC ACID $CH_3 \cdot COSH$ is best prepared by heating glacial acetic acid with phos-

phorus pentasulphide (Tarugi, Gazz. chim. ital. 1895, 25, i. 273; Schiff, Ber. 1895, 28, 1205; cf. Kekulé and Linnemann, Annalen, 123, 278; Kekulé, *ibid.* 90, 311). It may also be prepared by the interaction of acetyl chloride and potassium hydrosulphide (Jacquemin and Vosselmann, J. 1859, 354), or of lead acetate and anhydrous sodium thiosulphate (Froehde, Zeitsch. Chem. 1866, 543). It is an unpleasant smelling liquid, b.p. 93°, sp.gr. 1.074 at 10°, soluble in water and in alcohol: for electrical conductivity v. Ostwald, Zeitsch. physikal. Chem. 3, 182. By heating in a sealed tube with water at 180°–200° or by boiling with zinc and sodium hydroxide, the sulphur is removed (Schulze, Zeitsch. physiol. Chem. 1898, 25, 16). Strong sulphuric or nitric acid reacts explosively with thioacetic acid. Phosphorus pentachloride yields acetyl chloride, phosphorus trichloride and hydrogen chloride, whilst zinc chloride yields ethenyl trisulphide, $C_2H_4S_3$, acetic acid and hydrogen sulphide. Thioacetic acid condenses with aldehydes, ketones and ketonic acids in the presence of hydrogen chloride (Bongartz, Ber. 1886, 19, 1934). It has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, *ibid.* 1894, 27, 3437; Tarugi and Marchionneschi, Boll. Chim. Farm. 45, 629). For salts, v. Ulrich, Annalen, 109, 275; Tarugi, Gazz. chim. ital. 1895, 25, i. 341; 1897, 27, i. 316; ii. 153.

Ethyl ester.—Prepared by the interaction of acetyl chloride and ethyl hydrosulphide, but not from ethyl acetate and phosphorus pentasulphide (Michler, Annalen, 176, 182). Unpleasant-smelling liquid, b.p. 116.0°–116.2° at 749.3 mm. (Beckmann, J. pr. Chem. [ii.] 17, 461).

Dithioacetic acid, methylcarbothionic acid $CH_3CS\cdot SH$ is prepared by the action of carbon disulphide on magnesium methyl iodide in well-cooled ethereal solution. The product is decomposed with ice and hydrochloric acid. It is a reddish-yellow oil, b.p. 37°/15 mm., sp.gr. 1.24 at 20°, readily soluble in organic solvents. It displaces acetic and formic acids from their salts. It is readily oxidised to thioacetyl disulphide by water and produces black spots on the skin. The alkali, alkaline earth, silver and magnesium salts are soluble in water, giving coloured precipitates with the salts of the heavy metals (Houben and Pohl, Ber. 1907, 40, 1303).

Methyl ester.—Prepared as the acid, substituting ammonium chloride for hydrochloric acid. The product is shaken with methyl sulphate, and the red oil so formed distilled; b.p. 140°/760 mm., 80°–81°/95 mm., 71°/70 mm.; sp.gr. 1.096 at 21°/4° (Houben and Schultze, Ber. 1910, 43, 2481).

THIOANTIPYRINE or **THIOPYRINE**, $C_{10}H_{11}N_2S$. Prepared by treating the methochloride or methiodide of 1-phenyl-3-methyl-5-chloropyrazole with potassium hydrogen sulphide. Large soluble crystals, m.p. 166° (Michaelis and Bindewald, Ber. 1900, 2873).

THIOBENZYL DYE STUFFS v. PRIMULINE AND ITS DERIVATIVES.

THIOBENZOPHENONE v. KETONES.

THIOCHROMOGEN v. PRIMULINE AND ITS DERIVATIVES.

THIOCOLL v. SYNTHETIC DRUGS.

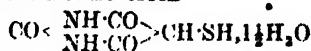
THIOCYANATES v. CYANIDES.

For the chlorides of thiocyanogen, see Kaufmann and Liepe (Ber. 1924, 57, [B] 923; Chem. Soc. Abstr. 1924, 126, 1, 839).

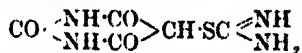
Addition of excess of a ferric salt to the solution of a commercial ferrocyanide, followed by filtration, results in a blood-red coloration in the filtrate if the ferrocyanide is contaminated with thiocyanate. The quantity of thiocyanate may be determined as follows: 10 grms. of ferrocyanide are dissolved in water to 100 c.c., the solution is filtered, and 10 c.c. of the filtrate are introduced into a 300 c.c. beaker, diluted with 50 c.c. of water, mixed with 25 c.c. of 5 p.c. ferric chloride solution, and filtered through a pleated paper into a 500 c.c. cylinder; the filter is washed with 0.5 p.c. potassium chloride solution until the latter passes through colourless, the total filtrate being then made up to 500 c.c. Into a similar 500 c.c. cylinder containing 10 c.c. of 5 p.c. ferric chloride solution, 1 p.c. ammonium thiocyanate is run from a burette until the two cylinders exhibit equal depths of colour. The method gives satisfactory results (F. Perciabosco, Annali Chim. Appl. 1923, 13, 346; J. Soc. Chem. Ind. 1924, 43, B, 252).

For the production of thiocyanogen by electrolysis of alkali thiocyanates, see Kerstein and R. Hoffmann (Ber. 1924, 57, [B] 491; Chem. Soc. Abstr. 1924, 126, i. 717).

THIODIALURIC ACID



obtained by hydrolysing with dilute potassium hydroxide thiopseudouric acid



(Noncki, Ber. 1871, 4, 772), or potassium thio-

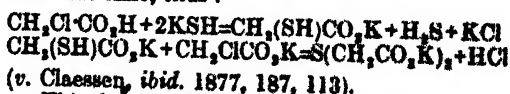
cyanobarbiturate $CO \begin{array}{c} \text{NH} \cdot CO \\ \text{NH} \cdot CO \end{array} > CH \cdot SCN$ (Trz-

cinski, *ibid.* 1883, 16, 1057); forms bright microscopic plates. The potassium salt is a yellow crystalline compound, sparingly soluble in water. Thiodialuric acid dissolves in nitric acid to form a pale red solution, and on warming a violent reaction takes place and dilituric acid is formed.

THIOFLAVINE T S v. PRIMULINE AND ITS DERIVATIVES.

THIOFORM and **THIOGENOL**, v. SYNTHETIC DRUGS.

THIOGLYCOLLIC ACID, α -thiolacetic acid, $SH \cdot CH_2 \cdot CO_2H$ was first prepared by Carius (Annalen, 1862, 124, 43) by heating 3 parts of monochloroacetic acid in concentrated aqueous solution with 5 parts of potassium hydrogen sulphide. Thiodiglycollic acid is formed at the same time, thus:



(v. Claassen, *ibid.* 1877, 187, 113).

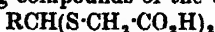
Thioglycollic acid is also formed by treating sulphochloroacetyl chloride, $SO_2Cl \cdot CHCl \cdot COCl$ with tin and hydrochloric acid (Siemons, Ber. 1873, 6, 659); by treating glyoxylic acid with sulphuretted hydrogen in presence of silver oxide, thiodiglycollic acid also being formed in this case (Böttinger, Annalen, 1879, 198, 215); by boiling

thiohydantoin⁶ or rhodanic acid with baryta (Andreasch, Ber. 1879, 12, 1385; Ginsburg and Bondzynski, *ibid.* 1886, 19, 117); or by treating salts of chloroacetic acid with alkali or alkaline earth polysulphides and subjecting the products, thus formed to the action of reducing agents (Kalle and Co., D. R. P. 180875).

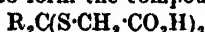
Thioglycollic acid is an uncrystallisable oil, soluble in water, alcohol, and ether. It has a faint smell, acts as a strong acid and forms a number of metallic salts (Claessen, *l.c.*; Ber. 1877, 10, 1354).

These are generally crystalline substances, readily soluble in water, but decomposing in aqueous solution especially in light, with production of a metallic sulphide (Myers, J. Lab. Clin. Med. 1921, 6, 359).

If a drop of ferric chloride is added to a slightly acidified thioglycollate, a transient indigo-blue colour appears, which changes to a deep violet-red on adding excess of ammonia and shaking in air. On standing the colour disappears, but it is reproduced by shaking the solution with air (Andreasch, Ber. 1879, 12, 1390). Thiodiglycollic acid does not give this reaction. Thioglycollic acid reacts with aldehydes yielding compounds of the type



with ketones to form the compounds



and also with ketonic acids (Bongartz, Ber. 1886, 19, 1931; *ibid.* 1888, 21, 478). It also unites with cyanamides forming hydantoins (Andreasch, Monatsh. 1881, 2, 735; Ber. 1880, 13, 1421).

Thioglycollamide $CH_2(SH)CONH_2$ forms thin white leaflets, m.p. 149° (Holmberg, J. pr. Chem. 1905, [ii.] 71, 264).

Ethyl thioglycollate $CH_2(SH)CO_2C_2H_5$ is formed by boiling the acid with absolute alcohol in the presence of a few drops of sulphuric acid (Claessen). It is an offensive smelling heavy oil, b.p. above 155° (decomp.), insoluble in water and in alcohol. For some of its derivatives, see Wislizenus, Annalen, 1868, 146, 145; Heintz, *ibid.* 1865, 136, 223; Letts and Collie, J. 1878, 685.

Ethylthioglycollic acid $CH_2(C_2H_5S)CO_2H$ is formed by the interaction of ethyl chloracetate and sodium mercaptide, the ethyl ester thus formed being hydrolysed with baryta water (Claessen, Bull. Soc. chim. [ii.] 23, 444). It is an oil soluble in water, alcohol, and ether, and yields metallic salts and esters. Its amide



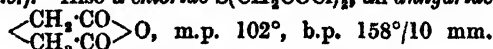
has m.p. 440°.

Nitrosothioglycollic acid $(SH)CH(NO)CO_2H$ is obtained, together with cyanamide and dicyanamide, by boiling nitrosothiohydantoin with baryta water. A number of its metallic salts have been prepared (Andreasch, Ber. 1880, 13, 601).

Dithioglycollic acid $(SCH_2-CO_2H)_2$, forms leaflets or prisms, m.p. 100°, gives metallic salts, an ethyl ester, b.p. 280° (decomp.), and is reduced by zinc and hydrochloric acid to thioglycollic acid (Claessen, Ber. 1881, 14, 410; Ginsburg and Bondzynski, *l.c.*).

Thiodiglycollic acid $S(CH_2-CO_2H)_2$ may be prepared by treating calcium chloracetate with calcium hydrogen sulphide in presence of hydro-sulphide (Schreiber, J. pr. Chem. [ii.] 13,

472); or by mixing a concentrated aqueous solution of sodium chloracetate with an equivalent amount of sodium sulphide dissolved in the smallest quantity of water. The mixture is acidified with sulphuric acid and the thiodiglycollic acid is shaken out with ether (Lövén, Ber. 1884, 17, 2818; *ibid.* 1894, 27, 3059). It forms rhombic tablets, m.p. 192°; gives metallic salts; a dimethyl ester, b.p. 135°/11 mm. (Anschütz and Biernaux, Annalen, 1893, 273, 69), and a diethyl ester, b.p. 267°-268° (corr.) (Wislizenus, *l.c.*). Also a chloride $S(CH_2COCl)_2$, an anhydride



(Anschütz and Biernaux, *l.c.*), and amides.

THIOINDIGO DYESTUFFS v. INDIGO, ARTIFICIAL, AND INDIGOID DYESTUFFS; VAT DYES.

THIOINDOXYL. Thioindoxyl carboxylic acid v. 2-HYDROXYTHIONAPHTHEN-1-CARBOXYLIC ACID.

THIOKETONES v. KETONES.

THIOL v. SYNTHETIC DRUGS.

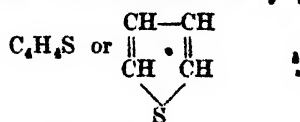
o-THIOBENZOIC ACID. Thiosalicylic acid.

THIOLINE v. ABIETENE.

THIONINE v. METHYLENE BLUE and THIAZINE COLOURING MATTERS.

THIONURIC ACID v. PYRIMIDINES.

THIOPHEN. THIOPHENE. Thiofurfuran



Discovered by Victor Meyer in coal-tar benzene, which contains about 0.5 p.c. of thiophen (Ber. 1883, 16, 1465; see also Bull. Soc. chim. 1900, 23, 384; *ibid.* 24, 357; Heusler, Ber. 1895, 28, 488; Witzcek, Chem. Zentr. 1903, i. 1053). In order to extract the thiophen, a large quantity of the best commercial benzene was shaken for some hours with one-tenth of its volume of concentrated sulphuric acid, the black acid layer separated, diluted with water, and converted into the lead salt of the sulphonic acid thus obtained. This lead thiophen-sulphonate, which was contaminated with lead benzeno-sulphonate, was dried, mixed with one-fourth of its weight of ammonium chloride, and distilled. The sulphonic acid was thus hydrolysed, and an oil passed over which was purified by shaking with caustic alkali to remove mercaptans, dried over calcium chloride and rectified.

K. E. Schulze (Ber. 1885, 18, 497) recommends that the thiophen sulphonic acid, after diluting the crude acid with water, should be hydrolysed by steam-distillation. Thiophen may also be completely removed from commercial benzene by treating the latter with form- or acet-aldehyde or with phthalic anhydride (D. R. P. 211239; *Frdl.* 1908-1910, 9, 96).

According to Steinkopf (Chem. Zeit. 1911, 35, 1098), thiophen may be very readily prepared by passing acetylene over pyrites or marcasite heated to 300°, the thiophen separated from the other products by fractional distillation. Among the products occurs a substance $C_4H_4S_2$, b.p. 36°-38° of garlic-like smell which, when treated with alkalis, loses some sulphur and also its unpleasant smell. Thiophen has been artificially prepared by numerous methods: amongst others by passing

74, 1347, Marousson, *ibid.* 1893, 26, 2457; Töhl and Schultz, *ibid.* 1894, 27, 2834; *ibid.* 1895, 28, 2217; Eberhard, *ibid.* 2385).

Thiophen diiodide $C_4H_2I_2S$ forms crystalline plates, m.p. 40.8° , and is sometimes used as a substitute for iodoform in surgical cases.

In the presence of anhydrous ether, magnesium dissolves in 2-iodothiophen giving magnesium thiophen iodide which reacts with ketones forming tertiary alcohols, some of which products are described by Thomas (Compt. rend. 1908, 146, 642; see also Tschelintzeff, Chem. Zentr. 1905, i. 146).

Tetra-iodothiophen C_4I_4S is an odourless, tasteless, pale yellow, crystalline powder, m.p. 198° (Paolini and Silbermann, Atti R. Accad. Lincei, 1915, [v.] 24, ii. 206).

Sodium thiophen sulphonate $C_4H_2S \cdot NaSO_3$ is a white crystalline powder which has been employed in prurigo, being non-toxic and non-irritant: it has proved more effective than β -naphthol. Nitrothiophen (Stadler, Ber. 1885, 18, 530), like nitrobenzene, yields, with reducing agents, the corresponding amino compound (Stadler, *ibid.* 1490; 2316; Goldschmidt and Schulthess, *ibid.* 1887, 20, 1701).

Homologues of thiophen are present in coal-tar benzene and may be separated by methods similar to those used for separating thiophen (Messinger, Ber. 1885, 18, 563, 1636; Keiser, *ibid.* 1896, 29, 2560). Many of these α - and β -homologues are known and may be obtained by a variety of synthetic methods. By treating a mixture of 2-iodo-thiophen and methyl iodide with sodium, 2-methylthiophen (thiolen) can be obtained (Kues and Paal, Ber. 1886, 19, 555; Meyer and Kreis, *ibid.* 1884, 17, 1558). 2-Ethylthiophen may be obtained similarly. For various homologues and their halogen and other derivatives, see Grünwald (Ber. 1887, 20, 2585); Zelinsky (*ibid.* 2017; *ibid.* 1888, 21, 1835); Thiele (Annalen, 1892, 267, 133); Opolski (Chem. Zentr. 1905, i. 1255; *ibid.* ii. 1796) amongst others.

2-Phenylthiophen is obtained by distilling β -benzoylpropionic acid or benzoylsuccinic acid with phosphorus tri- or penta-sulphide (Kues and Paal, *ibid.* 1886, 19, 3142). It crystallises in small plates, m.p. $40-44^\circ$.

3-Phenylthiophen is obtained by the interaction of thiophen and nitroacetanilide. The compound obtained by Möhlau and Berger (*ibid.* 1893, 26, 2001) from diazobenzene chloride and thiophen in the presence of aluminium chloride is a mixture of 2- and 3-phenylthiophens (Bamberger, *ibid.* 1897, 30, 36). 3-Phenylthiophen crystallises in plates, m.p. $90-90.5^\circ$, b.p. $254-260^\circ$. Renard (Compt. rend. 1889, 109, 699) describes another phenylthiophen, n.p. 330° , which was obtained by passing a mixture of the vapours of toluene and sulphur through an iron tube heated to redness.

Di-, tri-, di-, and other diarylthiophens may be obtained by heating mixed aliphatic aromatic ketones in the presence of water and monium sulphide at 215° under pressure (Willgerodt and Scholtz, Chem. Zentr. 1910, 1909). For another method of obtaining the phenylthiophens, v. Baumann and Fromm (1895, 28, 2001).

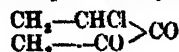
Dianisylthiophen $C_{12}H_{10}S$, and **benzothiophen**, have been isolated from the pro-

duct obtained from the interaction of the vapours of sulphur and naphthalene at a red heat. The former crystallises in pearly yellow scales, melts at 250.5° (corr.), and boils above 440° . It yields a hexabromo derivative $C_{10}H_6Br_6S$, m.p. 260° , and a tetranitro derivative $C_{10}H_6(NO_2)_4S$, m.p. 210° (corr.). Oxidation with chromic acid gives phthalic acid. The latter crystallises in ruby red leaflets, melts at 118.5° (corr.), and boils at 345° . It gives the thiophen reaction with sulphuric acid and isatin. From it a tetrabromo derivative $C_{10}H_6Br_4S_2$, m.p. $247-248^\circ$, and a tetranitro derivative $C_{10}H_6(NO_2)_4S_2$, decomposing at 300° , have been obtained (Lanfray, Compt. rend. 1911, 152, 92, 1254). Other naphthalene thiophens have been described by Dziewonski (Bull. Soc. chim. 1904, [iii.] 31, 925).

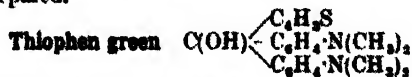
Dithienyl (C_4H_2S) $_2$, m.p. 83° , is formed when the vapour of thiophen is passed through a red-hot tube, just as diphenyl (C_6H_5) $_2$ is formed under these conditions from benzene (Nahnsen, Ber. 1884, 17, 789). Töhl (*ibid.* 1894, 27, 665) obtained another dithienyl, m.p. 33° , by the action of anhydrous feebly fuming sulphuric acid on ice cold thiophen. A third dithienyl, m.p. 132° , was obtained by Auwers and Predt (*ibid.* 1741) by heating butane tetracarboxylic acid with phosphorus sulphide.

Thiophen carboxylic acids may be obtained by oxidising the corresponding alkyl thiophens and also by various other methods (Nahnsen, Ber. 1884, 17, 2197; Peter, Ber. 1885, 18, 542; Messinger, *ibid.* 563; Nahnsen, *ibid.* 2304; Schlechter, *ibid.* 3015; Damsky, *ibid.* 1886, 19, 3282; Levi, *ibid.* 656; Curtius, Chem. Zentr. 1902, i. 457; Holleman and Voerman, Proc. K. Akad. Wetensch. Amsterdam, 1907, 9, 514; Rec. trav. chim. 1907, 26, 293; Schorigin, Ber. 1910, 43, 1938). Thiophen 2-carboxylic acid, m.p. $126-127^\circ$; thiophen 3-carboxylic acid, m.p. 136° ; and three dicarboxylic acids are known.

Thiophen aldehyde $C_4H_2S \cdot CHO$, a pale yellow oil, b.p. 198° , having a pleasant smell, is obtained by the distillation of α -thienylglyoxylic acid $C_4H_2S \cdot CO \cdot CO_2H$ (Biedermann, Ber. 1886, 19, 1853) or by the action of sulphuretted hydrogen on chlorodiketopentamethylene



(Hantzsch, *ibid.* 1889, 22, 2838; Hantzsch and Witz, *ibid.* 1901, 34, 841). On oxidation it yields the α -acid. Many of its derivatives are known. Thiophen ketones and a large number of other derivatives of thiophen have been prepared.



This compound, which was discovered by L. E. Levi (Ber. 1887, 20, 513), is an analogue of malachite green. The leuco base



is first prepared by heating a mixture of one part of thiophenaldehyde, 2 parts of dimethylaniline with a little alcohol, and 3 to 4 parts of zinc chloride for 6 hours, adding the zinc chloride gradually, and, if the mass becomes thick, diluting slightly with water. The product

is made alkaline with caustic soda, steam-distilled, extracted with ether, and the crystalline residue which is left on evaporating the ether recrystallised from alcohol. This crystalline leuco base is then oxidised with manganese dioxide and dilute sulphuric acid, when it yields thiophen green. The colouring matter is extracted with hot water, filtered from manganese dioxide, precipitated with ammonium chloride and ammonia, and extracted with ether. It is, as represented by the formula, the carbinol corresponding with the leuco base. Like malachite green, it forms a double salt with zinc chloride. It dyes silk and wool a shade very much like that of malachite green, but somewhat yellower.

W. Krause (Internat. Monatschr. Anat. u. Physiol. 4, 2; J. Soc. Chem. Ind. 1887, 507) recommends the use of the zinc double salt of thiophen green for staining sections, especially as a complementary colour to carmine. It dissolves readily in water, alcohol, and chloroform, but is insoluble in benzene.

THIOSACCHARIN $C_6H_4 < \begin{smallmatrix} CS \\ SO_2 \end{smallmatrix} > NH$, obtained by heating an intimate mixture in equimolecular proportions of saccharin and phosphorus pentasulphide to 220° and extracting with boiling benzene. Crystallises in yellow needles, m.p. 180° . Has a bitter taste. Hydrolysed by water, alkali hydroxides and carbonates with production of saccharin and hydrogen sulphide. Soluble in ammonia solution from which it is precipitated unchanged by acids. Heated with dilute hydrochloric acid forms ammonium o-sulphobenzoate (Mannessier, Gazz. chim. ital. 1915, 45, i. 540).

THIOSALICYLIC ACID (o-Thiolbenzoic acid)

$CO_2H \text{---} \text{C}_6H_4 \text{---} SH$. (1) Formed by heating sodium o-chlorobenzoate with sodium hydrogen sulphide and copper powder to $150^\circ\text{--}250^\circ$, dissolving the product in water and precipitating by acid (Cassella & Co., D. R. P. 189200). (2) A mixture of anthranilic acid and strong hydrochloric acid is diazotised, and the solution is mixed with a cooled aqueous alkaline solution of sodium sulphide containing sulphur in suspension. After nitrogen ceases to be evolved, the solution is acidified with hydrochloric acid, filtered, the residue dissolved in sodium carbonate solution, filtered from sulphur, and heated with finely divided iron or zinc dust until no hydrogen sulphide is evolved after acidification. The product is then treated with hot sodium hydroxide solution, filtered, and the thiosalicylic acid precipitated by hydrochloric acid (Kalle & Co., D. R. P. 205450). Colourless or pale yellow crystals, m.p. $164^\circ\text{--}165^\circ$.

THIOSEMICARBAZIDE v. HYDRAZINES.

THIOSINAMINE, allyl-thiourea



Formed by the action of ammonia on allyl-mustard oil



A white crystalline substance, sparingly soluble in water. Used in the treatment of lupus, and in relaxing scar-tissue. With ethyl iodide forms iodine, which is readily soluble in water.

THIOSTANNIC ACID v. TIN SALTS AND OXIDES.

THOLAFORM. Trade name for a mixture of menthol and trioxymethylene.

THOMAS SLAG v. FERTILISERS.

THOMSONITE. A zeolitic mineral with the composition $(Na, Ca)O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ crystallised in the orthorhombic system. Sp.gr. 2.3–2.4; H. 5–5½. A massive variety known as *lintonite*, with a radially fibrous structure and concentric bands of green, red, and white, is occasionally used as a gem-stone. This occurs in amygdaloidal basalt at Grand Marais in Minnesota, and is collected as water-worn pebbles on the shores of Lake Superior.

L. J. S.

THORIANITE. A heavy, black mineral consisting of thoria (51–80 p.c.) with uranium oxides (11–32.7 p.c.), &c. It is isomorphous with pitchblende (q.v.) and very similar to the crystallised varieties of this in most of its characters. The principal difference between the two minerals is in the relative amounts of the thorium and uranium oxides, thorianite being essentially $(Th, U)O_2$ and pitchblende $(U, Th)O_2$. Thorianite is derived principally from Ceylon, where it is found in the stream-beds and in the gem-bearing alluvial gravels at several spots in the Central, Sabaragamuwa, and Southern provinces. The heavy minerals occurring with it, and separated by the gemmers from the alluvia by a simple process of washing, are zircon, ilmenite, thorite, gold, &c. The largest amounts have been obtained from the Kuda Pandi-oya, a small stream in the Bambarabotuwa district, about 20 miles from Balangoda in the Sabaragamuwa province; but the deposits are of limited extent, and soon become exhausted. The occurrence of the mineral *in situ* has also been noted at one or two places (Gampola and Maddegama) in Central province, a few crystals having been found in pegmatite-veins. Prospecting for the original sources is, however, difficult, owing to the thick growths of jungle.

Two isolated crystals from an unknown locality in province Betroka in the south of Madagascar have been described by A. Lacroix (1914). This material is richer in thoria than the Ceylon thorianite; analysis gave: ThO_2 , 93.02; UO_2 , 4.73; Fe_2O_3 , 0.29; PbO , 1.80 = 99.84; sp.gr. 9.33. The mineral has also been found as water-worn grains in the gold-sands of the Boshogocha river, Transbaikial, Siberia. Analysis of this material gave: ThO_2 , 74.2; UO_2 , 14.1; Ce_2O_3 , etc., 6.3; Fe_2O_3 , 3.1; SiO_2 , 0.8 = 98.5 (S. D. Kuznetsov, Bull. Acad. St. Pétersbourg, 1912, 6, 361). It is recorded from Travancore, a preliminary analysis showing ThO_2 , 32.27; U_2O_5 , 39.86 p.c. (Rec. Geol. Survey, India, 1917, 48, 9).

Thorianite is found as small, simple cubes, usually only a few mm. across, and only exceptionally reaching 2 or 3 cm. Interpenetration twins, like those of fluor-spar, are occasionally met with. The colour is jet-black, and, when the surface is not water-worn and dulled, the lustre is bright and pitchy. The streak is brown with a tinge of green; thin sections are translucent and optically isotropic. The high sp.gr. of about 9.5 is a striking feature; hardness nearly 7. The mineral is soluble in nitric acid.

and in sulphuric acid, but is scarcely attacked by hydrochloric acid. It is the richest known source of helium, 8.2-9.5 c.c. per gram being given off when the mineral is heated or dissolved in acid. Its radioactivity is less than that of pitchblende, there being less radium but more radiothorium. Nipponium and some other possibly new elements have been extracted from thorianite (M. Ogawa, 1908; C. de B. Evans, 1908).

Analysis I of thorianite from near Balangoda (W. R. Dunstan and B. M. Jones, Proc. Roy. Soc. 1906, A, 77, 546). II, same locality (Dunstan and G. S. Blake, *ibid.* 1905, A, 76, 253). III, ditto (Dunstan, Nature, 1904, 69, 510). IV, ditto (E. H. Büchner, Proc. Roy. Soc. 1906, A, 76, 385). V, and VI, from Galle, Southern province (Dunstan and Jones, *l.c.*).

	I	II ¹	III ²	IV ³	V	VI
ThO ₂	78.98	78.86	72.24	70.96	62.16	58.84
UO ₂		6.03			10.32	
UO ₂	13.40	9.07	11.19	13.12	18.88	32.74
Ce ₂ O ₃		1.02	6.39			
(La,Di) ₂ O ₃	1.47	—	0.51	1.96	1.84	0.85
PbO	2.54	2.03	2.25	2.42	2.29	2.56
Fe ₂ O ₃	0.87	0.46	1.92	2.05	1.11	1.31
CaO	0.91	1.13		0.13	0.59	0.19
H ₂ O	1.28			3.20	1.05	1.26
Insol.	0.47	0.20	0.41		0.77	0.45

¹ Also Hc, 0.39.

² Also ZrO₂, 8.68 (due to enclosed zircon); SiO₂, 1.84; sp.gr. 8.98.

³ Also ZrO₂, 0.23; SnO₂, 0.65; Sb₂O₃, 0.11; Al₂O₃, 0.15; etc.

Thorianite contains a higher percentage of thorium than any other known mineral, and it has been employed as a source of thorium for use in incandescent gas mantles. The amount exported from Ceylon in 1905 was about 9 tons, which sold for £1600 to £1700 per ton; since then, however, the price of thorium has fallen considerably.

For local details of occurrence, &c., see Administration Reports, Ceylon, Colombo 1903-6, &c.; Colonial Reports, Miscell. Ser. Ceylon Mineral Survey, London, 1904-14, &c. Bull. Imp. Inst. London, 1916, 14, 321.

L. J. S.

THORITE. A mineral consisting essentially of thorium silicate, ThSiO₄, crystallising in the tetragonal system and isomorphous with zircon. Analyses show: SiO₂, 12-19; ThO₂, 48-74 (the formula requires 81.5); U₂O₃, 1-10; Ce₂O₃, 0-3; H₂O, 6-10 p.c. The presence of water appears to be due to secondary alteration; and the fact that the mineral is frequently optically isotropic and amorphous indicates that it is not fresh. The colour is yellow to dark brown, and in the orangite variety (*q.v.*) a bright orange-yellow; the lustre is resinous; sp.gr. 4.4-5.4. The mineral occurs as small masses and indistinct crystals in the augite-syenite on the Langesundfjord and near Arendal, and a few other places in the south of Norway. It is also found, together with thorianite, in the gem-gravels of Ceylon. Small amounts are collected for the preparation of thorium compounds and used principally for the mantles of incandescent gas-lights.

L. J. S.

THORIUM. Sym. Th. At.wt. 232.2 This element, which has the highest atomic weight of

the metals of the rare earth series, was identified by Berzelius in 1829 as occurring in the form of silicate in the mineral thorite, obtained from the island of Löv-ön (near Brevig, Norway).

For position in the Periodic system, see Vogel (Zeitsch. anorg. Chem. 1918, 102, 177-200).

Occurrence.—Thorium occurs as a constituent of most rocks of volcanic origin to the extent of 3×10^{-3} in acid, and 0.22×10^{-3} in basic deposits. It is present as the main constituent in thorite, orangite, and their alteration products, mackinoshite, auerlite, calcliothorite, and freyalite, and in thorianite (Dunstan and Jones, Proc. Roy. Soc. 1905, 76 A, 253; 1906, 77 A, 546; Szilárd, Compt. rend. 1907, 135, 463). It occurs also in tthocrasite (Amer. J. Sci. 1906, [iv.] 22, 515). The only source of commercial importance, however, is monazite sand, which contains from 2 to 10 p.c. ThO₂.

Extraction and Purification.

1. *Separation from thorite, orangite, and thorianite.*—These minerals are easily decomposed by the strong mineral acids when silicic acid separates, and the solution containing the metallic constituents is freed from lead, bismuth, &c., by hydrogen sulphide. Thorium is then separated in the form of its octahydrated sulphate Th(SO₄)₂.8H₂O, which separates from aqueous solutions below 47°, by stirring into the cold chloride or nitrate solution (about 20 p.c.) a moderate excess of cold 50 p.c. sulphuric acid. This salt is re-dissolved in water, and oxalic acid added to precipitate thorium oxalate, which is then ignited to thorium and the cycle of operations repeated. For this purpose the thorium must be attacked by concentrated sulphuric acid; the product is dissolved in ice and water, and the solution warmed to 20° or 30° to separate the hydrated thorium sulphate (Krüss and Nilson, Ber. 1887, 20, 1665).

Thorium salts may be separated from those of the cerite metals by solution in excess of alkali carbonate or oxalate. But this process brings into solution also small amounts of the cerium and yttrium earths, which, however, do not occur in thorium minerals except monazite to any large extent; moreover, the extraction of the thorium is never complete. Solutions of thorium salts readily undergo hydrolytic change when boiled with sodium thiosulphate, a basic thorium thiosulphate being precipitated mixed with sulphur; this operation separates thorium from all rare earth metals excepting scandium and zirconium, but the separation is not perfect if more than 2 to 3 p.c. of other earths are present (Bunsen, Pogg. Ann. 1875, 155, 379; Moissan and Étard, Compt. rend. 1896, 122, 573; Urbain, Bull. Soc. chim. 1896, [iii.] 15, 338; Brauner, Chem. Soc. Trans. 1898, 73, 951).

2. *Separation from monazite sand.*—Monazite, an orthophosphate of the cerite metals which contains varying proportions of thorium, is very widely diffused in the earth's crust, occurring primarily as an accessory constituent of certain plutonic rocks (granites, diorites, gneisses, &c.). It is, however, chiefly in its secondary form of monazite sand that the mineral is exploited for the gas-mantle industry. The erosive action of rivers and tides on the original monazite

containing rocks gives rise to enormous accumulations of monazite sands found in littoral and fluviatile deposits.

Up to 1909 the deposits on the coast of Brazil (6 to 7 p.c. ThO_2), and since then the richer sand discovered on the coast of Travancore (9 to 10 p.c. ThO_2) have been exploited to the extent of 1600 to 2000 tons annually. Attempts have also been made to work commercially the sand of Ceylon (Bull. Imp. Inst. 1916, 14, 321-369). Monazite is also found in Australia, North and South Carolina, and the Malay Archipelago.

For an account of the Travancore workings, see E. White (Pharm. J. 1922, 440).

In addition to the yellow grains of monazite, the sand contains fragments of magnetite, chromite, titanite, quartz, felspar, hornblende, rutile, brookite, zircon, and small quantities of rare-earth minerals (e.g. samarskite, aschynite). The sand is concentrated by washing, followed by electromagnetic concentrations, until it contains 90 to 96 p.c. of actual monazite.

The monazite sand is decomposed by heating with a minimum of concentrated sulphuric acid, and the product dissolved in cold water, the residue containing the unattacked constituents of the sand, quartz, zircon, titanite, &c. Another way of effecting the initial breakdown of the monazite by fusing in an electric furnace with carbon, lime, and calcium fluoride, slaking the product with water and washing off the lime from the residual heavy rare earth carbides, is recommended by Baskerville (U.S. Pat. 1087099, 1914), but does not appear to be used. The acid solution is partially neutralised with magnesia, sodium hydroxide or ammonia, or suitably diluted with water, until precipitation of the phosphates of the rare-earth metals occurs, when thorium phosphate, being the least soluble of this series, is concentrated in the first fractions. The use under varying conditions of acidity and dilution of pyrophosphoric acid (J. Amer. Chem. Soc. 1914, 36, 1134-11439; D. R. P. 286087, 1914; U.S. Pat. 1182880, 1916; Eng. Pat. 112380, 1917) and of sodium hypophosphate (Koss, Chem. Zeit. 1912, 30, 686; Fr. Pat. 444798, 1912; Wirth, Chem. Zeit. 1913, 37, 773-774) have been proposed for the separation of thorium at this stage. The phosphate is dissolved in hydrochloric or sulphuric acid and the thorium precipitated by oxalic acid. The greater part of the phosphoric acid is thus removed. The sparing solubility of thorium oxalate in solutions containing excess of mineral acid serves also to separate thorium from the commoner metals (iron, manganese, calcium, &c.). Sometimes the separation with oxalic acid is replaced by precipitation with hydrofluoric acid.

The crude, well-washed thorium oxalate when warmed with excess of aqueous sodium carbonate yields a solution containing the greater part of the thorium, together with small quantities of the cerium and yttrium earths.

The thorium in the filtered carbonate solution is precipitated either as oxalate by adding acid or as hydroxide by adding caustic soda. Alternatively, the oxalate may be converted into sulphate previous to solution in sodium carbonate. Final purification is effected by converting the nearly pure oxalate or hydroxide into sulphate and crystallising repeatedly the

octahydrated salt until it is free from didymium and phosphate (Koppel and Holtkamp, Zeitsch. anorg. Chem. 1910, 67, 266).

Pure thorium sulphate obtained by the foregoing or by a slightly modified process is converted almost exclusively, via the hydroxide, into thorium nitrate. For this purpose it may be dissolved in slight excess of ammonium carbonate, the diluted solution freed from iron and heavy metals with hydrogen sulphide and boiled until ammonia ceases to be evolved. The precipitated thorium is washed and dissolved in nitric acid.

It is customary to adjust the solution so that the finished nitrate will contain sulphate equivalent to 1 or 2 p.c. H_2SO_4 , since in this form it is most generally suitable for use in the gas mantle industry. It is then concentrated until it contains 48 p.c. ThO_2 , and vigorously stirred as it cools, when the granular thorium nitrate of commerce is obtained.

Few commercial chemicals attain such a high degree of purity as thorium nitrate, since an extremely pure product is essential for the manufacture of gas mantles. Didymium and other rare earths must be entirely absent, phosphoric acid must not exceed 0.004 p.c. P_2O_5 , and lead, iron, lime, silica and soda are not permissible except in the merest traces.

Many processes for the separation of thorium from the other rare earths have been described, most of which have no commercial value. Hydrated thorium peroxide is precipitated by hydrogen peroxide from very slightly acid (preferably nitric) solutions of thorium salts, but in presence of cerite metals a certain amount of cerium is co-precipitated. The operation must be repeated several times to effect a complete separation (Wyrouboff and Verneuil, Bull. Soc. chim. 1898, [iii.] 19, 219; Compt. rend. 1898, 127, 412).

A separation of thorium and zirconium from the cerium and yttrium elements is brought about by stirring thoroughly into a dilute solution of the nitrates (containing trivalent cerium) an excess of freshly-prepared lead carbonate. After 12 hours the hydrates of thoria, zirconia, and ferric oxide are completely precipitated, the hydroxides of aluminium, chromium, and uranium are partially deposited, whilst cerium, yttrium, and other rare earth metals remain in solution. The precipitate is re-dissolved and the thoria present is further purified (Giles, Chem. News, 1905, 92, 130). The sparingly soluble basic acetate (Böhm, Die Darstellung der seltenen Erden, vol. i. 40, 1290) and the chromate (Ber. 1900, 33, 2028) have been recommended for separating thorium from the cerite metals, and the acetate method has been used commercially. The acetylacetone may be employed in purifying small quantities of thoria; the well-dried salt is extracted with chloroform, in which thorium acetylacetone alone dissolves (Urbain, Bull. Soc. chim. 1896, [iii.] 15, 338, 347; Ann. Chim. 1900, [vii.] 19, 184). Repeated precipitation of thorium by potassium azide is recommended as a mode of separation and purification (Dennis and Kortright, Amer. Chem. J. 1894, 16, 79; J. Amer. Chem. Soc. 1896, 18, 947).

Thorium is precipitated quantitatively as iodate from even very dilute solutions by iodine

acid or potassium iodate in the presence of excess of nitric acid; hydrochloric acid should be absent (Meyer, Zeit. anorg. Chem. 1911, 71, 65-69).

Thorium in neutral solution is precipitated quantitatively by sebacic acid at the boiling-point (D. R. P. 266459, 1912), by phenoxycetic and pyrotartaric acids (Smith and James, Chem. News, 1912, 105-109), and by the ammonium salt of nitrosophenylhydroxylamine (Thornton, Chem. News, 1916, 114, 13-14). Thorium can be determined volumetrically as molybdate (J. Ind. Eng. Chem. 1912, 4, 493-495).

m-Nitrobenzoic acid precipitates thorium quantitatively as thorium *m*-nitrobenzoate from neutral solutions of the rare-earth nitrates derived from monazite, and a repetition of the process affords a complete separation from cerium, lanthanum, neodymium, and praseodymium, but the first of these elements must be in the tervalent condition, otherwise the sparingly soluble yellow ceric *m*-nitrobenzoate is deposited (J. Amer. Chem. Soc. 1904, 26, 780; Zeitsch. angew. Chem. 1905, 18, 92). This method avoids the use of alcohol, which is required in the separation of these metals with fumaric acid.

Certain organic bases have a selective action in the precipitation of the hydroxides of the rare earths; *p*-toluidine separates thorium and zirconium from lanthanum, neodymium, and praseodymium, whilst hexamethylenetetramine and the chloranilines serve to separate thorium from zirconium (Hartwell, J. Amer. Chem. Soc. 1903, 25, 1128).

The separation of thorium from rare earth mixtures by the electrolysis of solutions with a mercury cathode (Dennis and Ray, J. Amer. Chem. Soc. 1918, 40, 174-181; U.S. Pat. 1115513, 1914), and from tungsten by fusion with sodium carbonate are described (Ann. Chem. Analyst, 1913, 18, 257-260).

For the estimation of thorium in monazite sand by an emanation method, see Helmick, J. Amer. Chem. Soc. 1921, 43, 2003; J. Soc. Chem. Ind. 1922, 96 A.

Metallie thorium. The isolation of the metal in a pure state is a matter of considerable difficulty owing to its infusibility, and to its power of combining with nitrogen, hydrogen, carbon, silicon, and the metals. The reduction of thoria with magnesium is not complete (Ber. 1891, 24, 873); the action of silicon and aluminium on thoria or on potassium thorium fluoride leads respectively to the formation of a silicide ThSi_2 , and an alloy ThAl_3 (Compt. rend. 1906, 142, 157, 280). Thorium can also be obtained by passing the vapour of the iodide over a heated tungsten filament (van Arkel and de Boer, Zeitsch. anorg. Chem. 1925, 148, 345; Chem. Soc. Abstr. 1925, ii. 1193). The pure metal is said to be obtained by the action of metallic calcium on the oxide (Fr. Pat. 419043, 1909; U.S. Pat. 1085098, 1914), and by the treatment at 500°C. of the anhydrous chloride with sodium in a steel bomb exhausted of air (Zeit. anorg. Chem. 1914, 87, 209-228). So prepared the metal is leaden grey in colour, ductile and in the coarse form unattacked by water. A rolled specimen of the metal obtained by reduction melted at 1450° and had sp.gr. 12.14 (Ber. 1883, 16, 163; Compt.

rend. 1883, 96, 346; Ann. Chim. 1906, [viii.] 8, 182; Zeitsch. Elektrochem. 1908, 14, 768). Electrolysis of thorium chloride dissolved in a fused mixture of sodium and potassium chlorides contained in a graphite crucible affords a product melting at 1700° (*ibid.* 1909, 15, 866). Alloys of thorium are obtained by reducing, with sodium or with carbon and sodium hydroxide, mixtures of thorium salts with those of more fusible metals (Sn, Pb, Sb, Al, or Cu), and thorium fluoride heated with tin or lead gives thorium alloys of these metals (D. R. P. 146503). The alloys of thorium with tungsten are of commercial importance (Grotthus Metall. u. Erz. 1913, 10, 844; D. R. P. 2939532, 1913).

Reduction of thoria by amorphous boron leads to the formation of two thorium borides, ThB_4 , prismatic crystals, sp.gr. 7.5 at 15°, and ThB_3 , reddish-violet mass, sp.gr. 6.4 at 15°; the former is soluble and the latter insoluble in concentrated hydrochloric acid (Compt. rend. 1905, 141, 191).

Thoria is reduced to thorium by heating with tungsten, the tungsten oxide combining with unchanged thoria to form a thorium-tungsten bronze.

Colloidal thorium is prepared by rubbing 95-96 p.c. thorium with cold dilute hydrochloric acid and washing the mass on a filter until a grey opalescent solution passes through; this liquid is stable to acids, but not to alkalis. On electrification the thorium particles are found to carry a positive charge (Zeitsch. Chem. Ind. Kolloide, 1909, 5, 191).

Thorium hydride ThH_4 is stated to be produced by direct combination of the metal and hydrogen at red heat, or by absorption of the gas by a heated mixture of thoria and magnesium. It is not decomposed by water, but evolves hydrogen on treatment with hydrochloric acid (Ber. 1891, 24, 873; Compt. rend. 1900, 131, 891; 1901, 132, 36; Ann. Chim. 1907, [viii.] 10, 130). Its existence has also been observed by Klauber and von Mellenheim (Zeitsch. anorg. Chem. 1920, 113, 306), who formed it by the action of water or dilute acids upon an alloy of thorium and magnesium. It was said to be decomposed by heat yielding metallic thorium. Its existence is denied by Schwarz and Konrad (Ber. 1921, 54, [B] 2122).

Thorium carbide ThC_2 , yellow microscopic crystals, sp.gr. 8.96 at 18°, prepared by heating an intimate mixture of thoria and carbon in the electric furnace (900 amperes, 50 volts), is decomposed by cold water evolving acetylene, methane, ethylene, and hydrogen (Compt. rend. 1893, 116, 1227; 1896, 122, 573; Ann. Chim. 1897, [vii.] 12, 427; Bull. Soc. chim. 1914, 15, 367-370).

Thorium silicide ThSi_2 , quadratic plates, sp.gr. 7.96/16°, produced by heating to 1200° a mixture of potassium silico- and thorofluorides and aluminium (Chem. Zeit. 1906, 29, 1031; Compt. rend. 1906, 142, 157).

Thorium nitride Th_3N_4 , brown powder, obtained by direct union of its components at high temperatures, rapid cooling of the product is said to cause decomposition; by heating a mixture of thorium and ammonium chlorides in hydrogen chloride, or by passing ammonia over heated thorium carbide; it is decomposed by water with evolution of ammonia (Compt. rend. 1896, 122,

573; 1900, 131, 837; 1901, 132, 36; Ann. Chim. 1897, [vii.] 12, 427; 1907, [viii.] 10, 130).

Thorium sulphide ThS_2 , dark-brown lamellae, sp.gr. 6.7 at 0°, and **thorium oxysulphide** ThOS , yellow crystalline powder, sp.gr. 8.42 at 0°, are produced by passing hydrogen sulphide over a mixture of thorium chloride and excess of sodium or potassium chloride at red heat (Compt. rend. 1908, 146, 815; cf. Zeitsch. anorg. Chem. 1907, 53, 74), or at a temperature below that at which the chloride sublimes (U.S. Pat. 941071, 1909).

Thorium fluoride ThF_4 , white amorphous powder, resulting from the interaction of hydrogen fluoride and thorium chloride or bromide at 354°–400° (Compt. rend. 1908, 146, 973). The *hydrate* $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$, a gelatinous precipitate, obtained on adding hydrofluoric acid to solutions of thorium salts, changes to a heavy white powder, the insolubility of which in excess of the precipitant serves as a separation of thorium from zirconium (Bull. Soc. chim. 1897, [iii.] 20, 69); *double fluorides* have been prepared approximating to the composition $\text{KTh}_2\text{F}_9 \cdot 6\text{H}_2\text{O}$ and $\text{KThF}_5 \cdot \text{H}_2\text{O}$, and not to the typical fourth-group formula $\text{K}_2\text{R}^{\text{IV}}\text{F}_6$ (Zeitsch. anorg. Chem. 1903, 35, 424).

Thorium chloride ThCl_4 can be prepared by the following methods, but unless oxygen and moisture are carefully excluded, the product is always contaminated with oxychloride: (i.) heating metallic thorium in hydrogen chloride (Ber. 1887, 20, 1665; Zeitsch. physikal. Chem. 1887, 1, 301); (ii.) heating thoria in carbon tetrachloride vapour or in a mixture of carbon monoxide and chlorine (Compt. rend. 1901, 132, 36, 1908; 147, 1046; Ann. Chim. 1907, [viii.] 10, 130); (iii.) heating thoria in the vapour of sulphur chloride (Bourion, Ann. Chim. 1910, [viii.] 20, 547; 21, 49; cf. Compt. rend. 1904, 138, 631; Ber. 1905, 38, 817; Zeitsch. anorg. Chem. 1914, 87, 209–228); (iv.) decomposing the heated carbide with chlorine (Compt. rend. 1905, 140, 1510). When purified by sublimation *in vacuo* (720°–750°) the chloride is obtained in colourless needles or prisms, sp.gr. 4.59, m.p. 820°.

Thorium oxychloride ThOCl_2 is an intermediate product obtained in the foregoing operation (No. ii.); it crystallises from alcohol and absorbs $6\text{H}_2\text{O}$ from moist air. The *hydrate* $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ is readily soluble in water or alcohol, and the soluble *hydroxy-chlorides* $\text{Th}(\text{OH})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Th}(\text{OH})_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ have been isolated.

Thorium chloride combines with ammonia to form several additive compounds, of which $\text{ThCl}_4 \cdot 4\text{NH}_3$ alone is stable above 120° (Compt. rend. 1910, 151, 387). Additive compounds are also formed with organic bases and with alcohols, aldehydes, and ketones (Zeitsch. anorg. Chem. 1903, 35, 424; Ber. 1904, 37, 3662; Jantsch and Urbach, Helv. Chim. Acta, 1919, 2, 490).

Thorium bromide ThBr_4 , transparent colourless needles, sp.gr. 5.62, unstable in the light, evolving bromine, boils at 725° and sublimes *in vacuo* at 600°–620° (Compt. rend. 1905, 140, 1510; 1907, 145, 243).

Thorium platino-cyanide $\text{Th}[\text{Pt}(\text{CN})_4]_2 \cdot 16\text{H}_2\text{O}$, yellow rhombic prisms from thorium sulphate and barium platino-cyanide.

Thorium hydroxide $\text{Th}(\text{OH})_4$, heavy white

powder, readily soluble in mineral acids or in aqueous alkali carbonates. It dissolves readily in less than its equivalent of hydrochloric or nitric acid, forming solutions which are colloidal, but which readily revert to the normal salts on boiling with a slight excess of acid. The hydrosol form of this hydroxide is produced by dialysing solutions of thorium nitrate or by adding thorium nitrate solution gradually to the well-washed hydrosol and boiling the mixture until an opalescent solution is obtained. Thorium hydroxide hydrogel is also converted into the hydrosol form by diluted (N/20) hydrochloric acid, or by solutions of aluminium or ferric chloride (Biltz, Ber. 1902, 35, 4436; 1904, 37, 1100; Müller, *ibid.* 39, 2857; Zeitsch. anorg. Chem. 1908, 57, 314; J. Chim. Phys. 1907, 5, 488, 495; Zeitsch. Electrochem. 1916, 22, 145–161; J. Soc. Chem. Ind. 1916, 688; Lemoine, Compt. rend. 1916, 162, 702–708).

The electrometric precipitation of thorium hydroxide has been studied by Britton (Chem. Soc. Trans. 1925, 127, 2110).

The so-called *thorium meta-oxide* is a soluble modification of thoria, produced by igniting the oxalate or hydroxide at comparatively low temperatures and evaporating the residue with hydrochloric or nitric acid until a syrup is left, which dissolves in water to a milky solution, appearing yellow by transmitted light (Cleve, Jahrb. Min. 1874, 161; Stevens, Zeitsch. anorg. Chem. 1901, 27, 41; Wyruboff and Verneuil, *ibid.* 28, 90; Compt. rend. 1898, 127, 863). It corresponds with the colloidal hydroxide described by D. R. P. 228263, 1909.

Thorium dioxide (*thoria*) ThO_2 , white powder, sp.gr. 10.220 at 17°, is obtained by heating the hydroxide or the thorium salts of volatile acids.

It is ordinarily very resistant to the action of even concentrated hydrochloric and nitric acids, but particles reduced to sizes less than 1μ are soluble in hydrochloric acid (J. Chem. Soc. 1917, 112, [ii.] 300). It melts and volatilises at 2000°C. in the cathode ray furnace (Zeitsch. anorg. Chem. 1914, 87, 129–168). Advantage is taken of the refractory nature of the oxide for the making of cupels, &c. (U.S. Pats. 1121988; 1121890, 1914).

The resolution of thoria into three chlorides differing in volatility and containing respectively three elements with different atomic weights has not been confirmed (Baskerville, *ibid.* 1904, 26, 922; Ber. 1905, 38, 1444; cf. R. J. Meyer and Gumpertz, *ibid.* 1905, 38, 817; Eberhard, *ibid.* 38, 826).

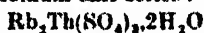
Thorium peroxide is a gelatinous white precipitate, retaining acid and of somewhat uncertain composition, formed by adding hydrogen peroxide to solutions of thorium salts; its peroxide character is manifested by the liberation of iodine from potassium iodide (Compt. rend. 1898, 126, 340; Bull. Soc. chim. 1898, [iii.] 19, 219; Ann. Chim. 1906, [viii.] 6, 441; Zeitsch. anorg. Chem. 1900, 25, 378; 1902, 31, 359; R. Accad. Sci. Torino, 1911, 46, 195; Gazz. chim. ital. 1912, 42, ii. 21–28).

Thorium sulphate $\text{Th}(\text{SO}_4)_2$, obtained in the anhydrous condition by treating thoria with concentrated sulphuric acid, dissolves in ice-cold water to a 25 p.c. solution, which is super-saturated at all temperatures from 0° to 100° and yields between 0° and 43° either spon-

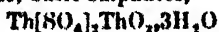
taneously or after seeding, monoclinic prisms of the *nonahydrate* $\text{Th}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, and above the latter temperature needles of the *tetrahydrate* $\text{Th}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$; these hydrates are isomorphous with the corresponding uranous compounds $\text{U}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{U}(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ (Zeitsch. Krist. 1900, 32, 250; 1901, 34, 307).

The *octohydrate* $\text{Th}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, prismatic crystals, separates under conditions similar to those which favour the formation of the more stable nonahydrate, and is the hydrate usually obtained in practice. It owes its production to the existence of a metastable phase having a very low velocity of transformation (Bull. Soc. chim. 1901, [iii.] 25, 105; Bull. Soc. Min. 1901, 24, 105; Ber. 1887, 20, 1665; 1905, 38, 817). The octo- and nonahydrates are very sparingly soluble in cold water and (in presence of excess of sulphuric acid) in mineral acids. For the solubility of the sulphate, see Wirth (Zeitsch. anorg. Chem. 1912, 76, 174-200; Bull. Soc. chim. 1912, 11, 645-648).

The *acid sulphate* $\text{ThSO}_4(\text{HSO}_4)_2$, needles, is obtained by drying *in vacuo* at 130° , the product of the action of concentrated sulphuric acid on a saturated solution of the anhydrous normal sulphate (Zeitsch. anorg. Chem. 1904, 38, 322); a *hydrated acid sulphate* $2\text{Th}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Gazz. chim. ital. 1903, 32, ii. 523); and a *basic sulphate* $\text{ThOSO}_4 \cdot 2\text{H}_2\text{O}$ (Compt. rend. 1883, 96, 1860; 1910, 151, 70; Ber. 1910, 43, 2776) have been described. The following *double sulphates* have been isolated: $\text{K}_2\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, sparingly soluble; $\text{K}_2\text{Th}(\text{SO}_4)_6 \cdot 2\text{H}_2\text{O}$; the corresponding ammonium salt series:



$\text{Cs}_2\text{Th}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$; $\text{Na}_2\text{Th}(\text{SO}_4)_3 \cdot 4$ and $12\text{H}_2\text{O}$ (Bull. Soc. Min. 1901, 24, 105; Zeitsch. anorg. Chem. 1903, 35, 424; Gazz. chim. ital. 1903, 32, ii. 523). On heating the sulphate to 55°C . with excess of water, basic sulphates,



and $6\text{H}_2\text{O}$ are formed (Barré, Compt. rend. 1910, 151, 70-72).

Thorium ethylsulphate has been described as intermediate in the production of pure thorium nitrate (Fr. Pat. 414463, 1910).

Thorium nitrate $\text{Th}(\text{NO}_3)_4$, with 5, 6, and $12\text{H}_2\text{O}$, the dodecahydrate separating in hygroscopic plates (Cleve, l.c.; cf. Zeitsch. anorg. Chem. 1897, 115; Chem. Soc. Trans. 1898, 73, 951). The commercial product, which is not a definite hydrate, but approximates to $\text{Th}(\text{NO}_3)_4$ with $4\text{H}_2\text{O}$, contains sulphate equivalent to 1 to 2 p.c. H_2SO_4 , and swells considerably on heating, leaving a finely divided residue of snow-white thorium. Commercial thorium nitrate should contain a minimum of 48 p.c. of ThO_2 .

Thorium nitrate unites with the nitrates of univalent and divalent metals, forming complex nitrates, having respectively the general formulae $\text{R}_2\text{Th}(\text{NO}_3)_6$ and $\text{R}'\text{Th}(\text{NO}_3)_8 \cdot 8\text{H}_2\text{O}$, which correspond with the double nitrates containing quadrivalent cerium. Similar double nitrates (and sulphates) are formed with organic bases (Zeitsch. anorg. Chem. 1901, 27, 359; 1908, 60, 123).

Complex thorium carbonates. Normal thorium carbonate is not known, but complex carbonates are prepared by adding soluble carbonates to thorium solutions until the pre-

cipitate first formed redissolves or by dissolving thorium hydroxide in aqueous alkali bicarbonate, saturated with carbon dioxide, and precipitating with alcohol or by the interaction of thorium and carbon dioxide under pressure (Compt. rend. 911, 153, 66-68). *Sodium thorium carbonate* $\text{Na}_2\text{Th}(\text{CO}_3)_2 \cdot 12\text{H}_2\text{O}$ separates in prismatic crystals; the thallous salt $\text{Tl}_2\text{Th}(\text{CO}_3)_2$ is precipitated as a crystalline powder on adding a soluble thallous salt to a solution of ammonium thorium carbonate (Cleve, l.c.; cf. Zeitsch. anorg. Chem. 1903, 35, 424). For the thorium chromates, see H. T. S. Britton, Chem. Soc. Trans. 1923, 123, 1429.

Thorium molybdate $\text{Th}(\text{MoO}_4)_2$, obtained by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate, forms tetragonal crystals, $a : c = 1 : 0.73565$, $d^{75} 4.92$, which exhibit mutual miscibility in the solid state with cerous molybdate (Ferruccio Zambonini, Atti R. Accad. Lincei, 1923, [v.] 32, i. 518-524; cf. A. 1916, ii. 249).

Thorium formate $\text{Th}(\text{HCO}_2)_4 \cdot 3\text{H}_2\text{O}$ and **thorium acetate** $\text{Th}(\text{CH}_3\text{CO}_2)_4$, crystallising respectively in leaflets and needles, are produced by dissolving thorium in the corresponding acids; interaction between thorium salts and soluble formates and acetates leads to basic salts $\text{Th}(\text{OH})_2(\text{HCO}_2)_2$ and $\text{Th}(\text{OH})_2(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ (Haber, Monatsh. 1897, 18, 687).

Thorium oxalate $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ is precipitated completely by adding oxalic acid to thorium solutions even in the presence of considerable proportions of mineral acid (Brauner, Chem. Soc. Trans. 1898, 73, 951). Complex oxalates such as $\text{K}_4\text{Th}(\text{C}_2\text{O}_4)_6 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_4\text{Th}(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$ are produced by dissolving thorium oxalate in concentrated solutions of alkali oxalates (Cleve, l.c.; and Brauner, l.c.). The existence of double oxalates with ammonium oxalate $2\text{Th}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$ is established by solubility curves (James, J. Amer. Chem. Soc. 1914, 36, 1853-1856).

Complex chloro-oxalates, e.g.



have been described (Compt. rend. 1913, 156, 1075-1076; *ibid.* 1913, 156, 1907-1909).

Thorium acetylacetonate $\text{Th}(\text{CH}(\text{CO}\cdot\text{CH}_3)_2)_4$, m.p. 171° , soluble in alcohol or chloroform, is prepared by adding acetylacetonate dissolved in aqueous ammonia to 13 p.c. thorium nitrate solution. This salt can be distilled *in vacuo* (Urbain, Bull. Soc. chim. 1896, [iii.] 15, 1338; Biltz, Annalen, 1904, 331, 334; Zeitsch. anorg. Chem. 1904, 40, 218).

Thorium tartrates and complex tartrates, v. Cleve, l.c.; Haber, l.c.; Rosenheim, Zeitsch. anorg. Chem. 1903, 35, 424.

Thorium salts of other organic acids, v. Morgan, Pharm. J. 1904, [iv.] 19, 472; and Karl, Ber. 1910, 43, 2068.

Thorium olate has been employed therapeutically in ointment form for carbuncles and other skin troubles (Martindale, Extra Pharmacopoeia).

Pharmacological action of thorium, v. Solimann and Brown, Amer. J. Physiol. 1907, 18, 426.

Thorium compounds are used to render the internal organs opaque to Röntgen rays (D. R. P. 223375, 1909).

Biological action of thorium.—Elemental thorium inhibits the growth of certain micro-organisms and algae without endangering the life of higher organisms (*Amphioxus*, *Zeitsch. Elektrochem.* 1911, 17, 816; *Arch. Sci. Phys. Nat.* 1911, [iv.] 32, 347); the salts inhibit the growth of cholera vibrio (*Compt. rend.* 1914, 159, 410-413).

Industrial application of Thoria v. Gas Mantles. Gas mantles are generally woven in cotton or preferably ramie fibre, but artificial silk has also been employed, and formerly the thorium-cerium solution was added to the dissolved cellulose before it was spun into thread. The present practice, however, with viscose artificial silk is to impregnate the woven stocking just as in the case of ramie or cotton fibre. The rare earth nitrates may be replaced by the corresponding acetates or formates and, with artificial silk, the impregnated stocking is treated with ammonia or some volatile alkali such as hydrazine or tetraethyl-ammonium hydroxide in order to produce within the fibres the hydroxides of thorium and cerium. Hydrogen peroxide may also be employed as the precipitant. In either case, the stockings are washed free from soluble salts (ammonium nitrate, &c.) or acid; the head is hardened with a solution of magnesium, aluminium, zirconium, glucinum or chromium salt, and the mantle 'burnt off' and 'seasoned' as in the case of the ramie fibre.

From a kilogram of thorium nitrate 600 to 800 mantles can be made; hence each mantle contains about 0.5 gram of thoria.

Although in most instances the optimum effect is attained by mixing the thorium and cerium salts in such proportions that the mixed oxides of the mantle consist of 98.8 p.c. of thoria and 1.2 p.c. of ceria, yet owing to the yellow colour of the light produced by this amount of ceria in inverted mantles, it is customary in this form of illumination to reduce the proportion of ceria to from 0.5 to 0.7 p.c.

According to R. L. Swan (*J. Chem. Soc.* 1924, 125, 780) the catalytic activity of mixtures of ceria and thoria on the combination of hydrogen and oxygen at 450° reaches a maximum when the mixtures contains 1 p.c. of ceria (Welsbach mixture). The activity of pure thoria is the same as that of a mixture containing 9 p.c. ceria. The light-giving powers of these are also equal. The author considers that the Welsbach mixture represents the best illuminant obtainable from the two oxides in question. The ceria may act as a carrier of oxygen (*cf. A.* 1907, ii. 557) or as a promoter of the electronic emission from the thoria (*Chem. Soc. Abstr.* 1924, 126, ii. 400).

A pure thoria mantle gives no emission in the visible region of the spectrum and only a slight radiation of infra-red rays of short wave-length. A cerium dioxide mantle gives a maximum radiation at the extreme red end of the visible spectrum, the intensity at first diminishes in the infra-red region and then increases again for heat rays of longer wave-length. In this mantle there is, on the whole, a relatively considerable loss of heat by radiation, the temperature remains comparatively low and consequently the emission of light rays is only feeble.

In the Welsbach mantle containing 0.5 p.c.

to 1.5 p.c. cerium dioxide, the emission of light is selective and attains its maximum in the blue region of the spectrum. On the other hand, the heat radiation is remarkably small, except for rays of comparatively long wave-length. Consequently the temperature attained by the mantle is comparable with that of the flame itself. The cerium dioxide colours the transparent ground mass of thoria so that an intense selective absorption is developed in the visible region of the spectrum and, providing that the amount of colouring oxide is small, this result is attained without any appreciable increase in the loss of heat by radiation and consequently without diminution in the intensity of illumination.

One hundred parts of thoria can hold in solid solution 6.7 parts of cerium dioxide, and as the mantle contains only about 1 p.c. of the latter oxide, it is entirely in the dissolved condition. Owing to this intimate mingling of the two oxides, a very small addition of cerium dioxide suffices to bring about the intense emission of light waves whilst the increase in heat radiation is too slight to act injuriously. If, however, the proportion of cerium is raised, the greater loss of heat by radiation leads to lowering of the mantle temperature and consequent diminution in luminosity. Cerium dioxide itself is stable in the Bunsen flame, but nevertheless the ignited mixed oxides, when treated with hydrochloric acid and potassium iodide solution liberate an amount of iodine corresponding with only a portion of the dioxide originally introduced into the mixture. This result suggests the possibility of some chemical combination between the cerium and thorium oxides which may be the chemical cause of the characteristic physical properties of the Welsbach gas-mantle (*cf. White and Traver, J. Soc. Chem. Ind.* 1902, 21, 1012; *Lewes, Chem. News.* 1905, 28, 62; *Journ. Gas Beleuchtung*, 1903, 46, 787, 974; *R. J. Meyer and Anschütz, Ber.* 1907, 40, 2639). For the testing of incandescent mantles, *see Coste and Powney, J. Soc. Chem. Ind.* 1911, 30, 65.

RADIOACTIVITY OF THORIUM.

Thorium preparations, in general, exhibit radio-activity, yielding α -rays of similar intensity but greater penetrative power than those of uranium. The long range of these α -particles was discovered by Rutherford and Wood (*Phil. Mag.* 1916, vi. 31, 379-386), who state that they have greater velocity than any α -particles previously known. The β -rays from thorium are about one-tenth as intense as those from uranium, and have less penetrating power. The γ -rays are relatively feeble but very penetrating. It has been stated that the radio-activity of thorium from monazite is due to the uranium present in this mineral, and that minerals free from uranium yield inactive thorium (*Baskerville, J. Amer. Chem. Soc.* 1904, 26, 1642; *Zerban, Ber.* 1903, 36, 3911; 1905, 38, 557). On the other hand, minerals free from radium have been found to give helium and thorium emanation (*Strutt, Proc. Roy. Soc.* 1905A, 76, 88, 312; 1907A, 80, 56; *Hahn, Ber.* 1905, 38, 2371). After allowing for uranium, a constant ratio between the radio-activity and amount of thorium was found for thorium minerals in which, probably,

thorium and radio-thorium are in equilibrium. In thorium salts, where the radio-thorium is largely removed, this constancy does not exist. Boltwood has not succeeded in obtaining inactive thorium (Amer. J. Sci. 1906, 21, 415, and 433).

Thorium hydroxide precipitated by ammonia from a solution of a thorium salt has no emanating power and only a greatly diminished α -radiation. The filtrate retains the whole of the emanating power; and the minute residue obtained on evaporation and ignition possesses the radio-activity which the precipitate has lost. The emanating power and radio-activity of this product, thorium X, disappear in the course of a month, decaying to half their original value in four days. The precipitated thorium hydroxide recovers the properties just as fast as they

disappear from thorium X, and a second treatment of its acid solution by ammonia after one month leads to the separation of another quantity of thorium X having the same activity as the first fraction. Thorium X, a short-lived radio-active product of thorium, produces gaseous thorium emanation, and this in turn gives thorium 'active deposit,' which imparts radio-activity ('induced activity') to solid objects brought into contact with this disintegration product (Rutherford and Soddy, Chem. Soc. Trans. 1902, 81, 321, 837; Phil. Mag. 1902, 4, 370, 569).

Owing to the complicated nature of the disintegration changes the radio-activity of a thorium preparation is a complex function of its age. The sequence of these changes is indicated in the annexed diagram. All thorium emanations

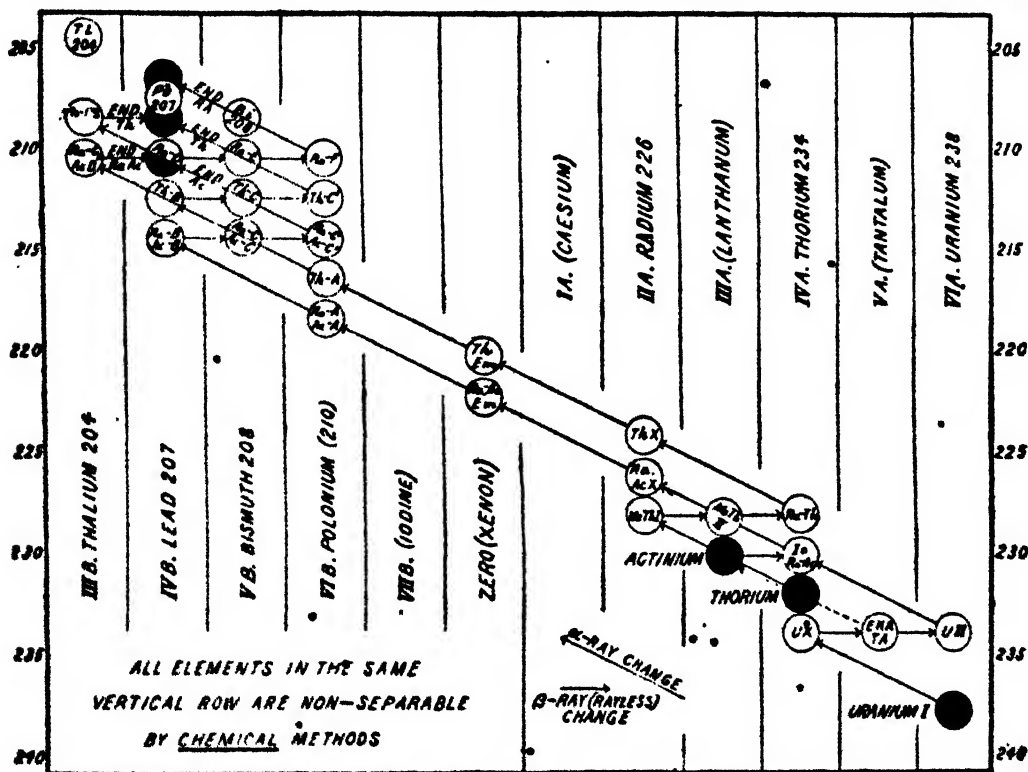


FIG. 1

are condensed at 5°C. (Fleck, Phil. Mag. 1915, 20, 337-362).

Mesothorium 1 is separated from thorianite by adding 26 grms. of barium nitrate to 1.5 litres of a slightly acid solution of 600 grms. of the mineral in nitric acid and by shaking the solution for an hour with excess of sulphuric acid when the sulphate of mesothorium 1 is co-precipitated with barium sulphate. The radioactive precipitate is reduced to sulphide by heating with carbon in a quartz crucible. Various methods are described for the reduction of this radio-active sulphate. Hahn (Ber. 1907, 40, 1462, 3304) recommends reduction with sugar carbon in a quartz crucible; Ebler (Eng. Pat. 1173, 1914), ignition with calcium carbide; and firing of a mixture of the dry sulphates and calcium hydride is suggested (Zeitsch. anorg.

Chem. 1913, 82, 149-158). The product is dissolved in hydrochloric acid. The lead is precipitated from this solution by hydrogen sulphide and traces of iron and thorium by ammonia. The radio-active chloride in the filtrate is crystallised out fractionally when mesothorium 1 is concentrated in the least soluble portions (Hahn, Ber. 1907, 40, 1462, 3304).

From monazite sand, mesothorium 1 is isolated by adding 0.1 p.c. of barium carbonate and heating the sand (400 grms.) with 800 grms. of concentrated sulphuric acid. The product is thoroughly mixed with cold water when the sediment contains practically the whole of the mesothorium 1 and radium. These two active components are concentrated from the barium sulphate precipitate by converting this product

successively into sulphide and chloride, and fractionating the latter from water when the mesothorium 1 accumulates in the least soluble crystals (Soddy, Eng. Pat. 25504, 1910; Chem. Soc. Trans. 1911, 99, 75).

In practice, the radioactive residues from monazite sand consist mainly of lead sulphate, silica, and rare earth phosphates. They may be boiled with a large excess of a mixture of caustic soda and sodium carbonate (10:1), the residue well washed, and the treatment with the preceding mixture repeated once or twice, when the silica and lead are almost completely removed and the barium, mesothorium, and rare earths left as carbonates. The residue is extracted with hydrochloric acid and the clear liquor precipitated with sulphuric acid. The crude radioactive barium sulphate may then be transformed into carbonate by boiling with excess of concentrated sodium carbonate solution several times in succession, with intervening washings (see Strong, J. Amer. Chem. Soc. 1921, 43, 440).

Another method for the separation of the radio-active constituents from monazite without the addition of barium salts is by the precipitation of these along with a small proportion of the thorium from phosphate solutions by dilution and boiling (U.S. Pat. 1084734, 1914; see also U.S. Pat. 1100743, 1914; D. R. P. 274874, 1913).

Mesothorium cannot be separated from radium by fractionation of the double barium salts, but in the fractional crystallisation of the picrates, bromates, and ferrocyanides from alcohol or acetic acid mesothorium separates before radium (Kunheim, D. R. P. 264901, 1912).

On account of this complete similarity of chemical properties all radium compounds separated from uranium minerals containing thorium contain mesothorium 1, and all mesothorium preparations include the radium present in the thorium minerals. In fact, technical mesothorium, produced from monazite sand, contains about 99 parts by weight of radium to one of mesothorium, but nearly 90 p.c. of the radiation it emits is due to the active products of mesothorium 1 (Hahn, Chem. Zeit. 1911, 35, 845).

Mesothorium 1 is rayless, and it disintegrates into mesothorium 2; its period of average life is 7-9 years, the period of half-change being 6-7 years (Phys. Zeitsch. 1918, 19, 257-263; J. Chem. Soc. Abs. 1918, ii. 347). It behaves like a metal of the alkali earths.

Mesothorium 2 reacts like a metal of the rare-earth series, and accordingly ammonia serves to precipitate it from solutions of mesothorium 1, a trace of zirconium salt being generally added to serve as a nucleus for precipitation (Hahn, Zeitsch. physikal. Chem. 1908, 9, 246; Russell and Soddy, Phil. Mag. 1911, [vi.] 21, 130). Two other disintegration products, radio-thorium and thorium X, are co-precipitated, but if the precipitation is repeated on the solution after one or two days the second precipitate will contain mesothorium 2, relatively free from radio-thorium. Mesothorium 2 has an average life period of 8.9 hours, the half-change period being 6.2 hours; it gives β - and γ -rays; the former are heterogeneous, the absorption coefficient

increasing as absorption proceeds; the γ -rays resemble those of uranium X.

Radio-thorium. Period of average life 1063 days (?), period of half-change, accurate to 1 p.c., 696 days. It is chemically identical with thorium, and is only distinguished from the latter by preparing it through mesothorium 1 and 2. Mesothorium 1 is readily separated from thorium, and when left to itself produces radio-thorium, which is separated by precipitating a solution of the two disintegration products with ammonia in the presence of a trace of zirconium salt. When first precipitated in this way the radio-thorium will contain mesothorium 2, but this decays completely in the course of 3 days, while the formation of the next disintegration product, thorium X, causes an increase in the radio-activity of the preparation over a period of 3-4 weeks. The emanating power increases with the growth of thorium X, but after a month the total activity and emanating power decay to zero.

Radio-thorium can be prepared by evaporating to dryness the nitric acid solution of the washed ammonia precipitate from solutions of thorium X, freed from barium, calcium, iron, and lead salts and phosphates. The residue is washed free from ammonium salts by a solution of sodium chloride free from carbon dioxide.

Radio-thorium preparations, especially when kept moist, are very suitable for demonstrating the properties of the thorium emanation. When the air in the tube containing a radio-thorium compound is blown between two darkened zinc sulphide screens with films turned inward, a brilliant luminescence is observed, and the decay and reproduction of the emanation can be thus illustrated (cf. Hahn, Ber. 1905, 38, 3371; Zeitsch. physikal. Chem. 1905, 51, 717; Phil. Mag. 1906, [vi.] 11, 793; Elster and Geitel, Chem. Zentr. 1906, ii. 302).

Radio-thorium emits α -rays which have a range of 3.9 cm. of air (Leslie, Le Radium, 1911, 8, 356).

Thorium X. Period of average life 5.35 days, period of half-change 3.7 days. Resembles radium, mesothorium 1, and the metals of the alkaline earths and remains in solution when thorium is precipitated with ammonia. The residue left on evaporating the filtrate gives on ignition a small amount of an intensely radioactive product, this activity being due to thorium X. If, however, thorium is precipitated by a carbonate or phosphate, thorium X is also rendered insoluble; the precipitate retains the initial radio-activity of the thorium compound, and when dissolved it exhibits the initial emanating power. The emanating power of a thorium solution is a measure of the amount of thorium X present (Zeitsch. anorg. Chem. 1909, 61, 338; 63, 197).

When fumaric or *m*-nitrobenzoic acid or pyridine is used to precipitate thorium both thorium X and thorium R are left in solution. In this way thorium hydroxide is freed from thorium X and its disintegration products. Four precipitations with *m*-nitrobenzoic acid give thorium hydroxide, having neither β -activity nor emanating power and a minimum of α -activity; the activity of this preparation then increases regularly without the initial decay characteristic of the precipitate obtained by

hydroxides and acids, are difficultly soluble in boiling water and in organic solvents, but more soluble in potassium iodide solution (Phil. Mag. 1913, 25, 330-332).

Thorium C is removed from a solution of thorium active deposit by absorption with animal charcoal when thorium B remains dissolved. Thorium C is also deposited alone when the solution is electrolysed or shaken up with metallic nickel. Zinc, however, deposits both thorium B and C, but not thorium X.

Thorium C gives two sets of α -rays having different ranges, these being attributed to the presence in this active product of the two constituents thorium C_1 and thorium C_2 ; these products have not, however, been separated, and the two sets of rays are due to concurrent changes (Hahn, Phil. Mag. 1906, [vi.] 11, 793; Ber. D. physikal. Ges. 1909, 11, 55).

Thorium C_2 . When the thorium active deposit coating a plate or wire is kept in a vacuum at the ordinary temperature, the powerful α -ray disintegrations of thorium C and C_1 , one of which is the strongest known, cause a considerable proportion of thorium C_2 to 'recoil,' i.e. to become projected from the plate or wire on to surrounding surfaces of the vacuum space, these receiving surfaces being kept negatively charged.

According to von Lerch's rule the disintegration of radio-active elements is accompanied by a regular increase in the electro-negative character of the successive products. But to this rule thorium C_2 is an exception, as it dissolves more readily in acids than the other products, and is moreover more volatile than its generators, being completely volatilised at 700°C. from an active wire placed for 30 seconds in a Bunsen flame (Sitzungsber. Akad. Wiss. Wien. 1907, 116, [11a], 1443; 1909, 118 [11a], 1575; Zeitsch. physikal. Chem. 1911, 12, 273, 378). It can be separated by volatilisation from thorium C, which sublimes at 780°C. (Wood, L.C.).

Thorium C_2 is probably non-separable by chemical methods from thallium, and like this element is co-precipitated with potassium platichloride (Chem. News, 1913, 107, 97). Barratt has found that thorium C undergoes dual disintegration into thorium C_1 and thorium C_2 (Proc. Physical Soc. 1912, 24, 112).

Thorium C_2 , which emits only β - and γ -rays is the last active member of the series; its decay is regular and complete, and the ultimate product (thorium D) is regarded as an element indistinguishable chemically from ordinary lead.

Thorium-lead, which is the stable end product from thorium C_1 (α -ray change) or from thorium C_2 (β -ray change), has the atomic weight 208, and is an isotope of ordinary lead and of the lead (206) derived from radium.

The relationship existing between radio-active elements and the ordinary elements of the periodic classification is illustrated by the diagram on p. 41, in which can be seen the connection between the degradation products of thorium and the elements non-separable from these products by ordinary processes (Soddy, L.C.).

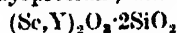
Bibliography.—Koppel, Die Chemie des Thoriums; Aegg, Handbuch der anorganischen Chemie, vol. iii. part 2; Böhm, Die Darstellung der seltenen Erden; Wyruboff and

Verneuil, La Chimie des Terres rares; Truchat, Les Terres rares; Rutherford, Radioactivity; Soddy, The Chemistry of the Radio-elements, 1911; Main Smith, Chemistry and Atomic Structure, 1924.

THORN APPLE v. DATURA.

THORON. A term given to the emanation of thorium. This gas is an isotope of radon and actinon, the emanations of radium and actinium respectively. A number of springs in the Pyrenees and in the Central Plateau of France have been examined to ascertain their content of radium and thorium emanations. The former occurs in various proportions in all the waters, but thorium emanation is found in traces only in those of the Central Plateau. Even in those cases in which thorium emanation is not detectable, it is probable that the water comes into contact with this emanation, but that the time elapsing between the termination of this contact and the appearance of the water at the outlet of the spring exceeds 10 minutes, which is the duration of the life of thorium emanation (A. Lepape, Compt. rend. 1924, 178, 931; Chem. Soc. Abstr. 1924, 126, ii. 295).

THORTVEITITE. A silicate of scandium with yttrium, dysprosium, and erbium



forming monoclinic prisms, reaching a length of 35 cm., of a greyish-green colour and somewhat resembling epidote in appearance. Useful as a source of scandia. It occurs in some quantity in pegmatite at Iveland and Evje in Sætersdalen, Norway, and is remarkable in being the only mineral containing scandium (analysis I.) as an essential constituent (J. Schetelig, Centr. Min. 1911, 721; Norsk Geol. Tidsskr., 1922, 6, 233; Vid.-Selsk. Skrifter, Kristiania, 1922, No. 1, 49. In the last paper is given a history of the element scandium).

A very similar mineral, as prismatic crystals 10 cm. long and 3 cm. across, was discovered in 1920, also in pegmatite, at Befanambo, Madagascar; this gave analysis II. (Boulanger and Urbain, Compt. rend. 1922, 174, 1442) with traces of Cl , Mn , Sn , Sb , and Pb . The figure for scandia includes about 0.5 p.c. of yttrium, neoytterbium, and lutecium. The mineral is only slightly attacked by hydrofluoric acid, or by fused bisulphates, but is decomposed by repeated fusion with sodium carbonate.

The Madagascar mineral being rather richer in scandia and with zirconia in place of yttrium-earths, it is regarded by A. Lacroix (Minéralogie de Madagascar, 1923, 3, 311) as representing an end-member of the thortveitite group, and for it the name *befanamite* is proposed.

	SiO_2	Sc_2O_3	O_2	ZrO_2	Al_2O_3	Fe_2O_3	FeO	Ign.
I.	42.9	37.6	17.7	—	—	2.1	0.8	0.4
II.	44.1	42.4	—	8.4	3.3	2.0	—	—

L. J. S.

THROMBOPLASTIN. An extract from the brain of cattle, dissolved in common salt solution. Used as an hæmostatic.

THSING-HOA-LIAO. A Chinese name for a cobaltiferous aluminium silicate used in the manufacture of porcelain; also applied to a cobaltiferous manganese ore used for producing a blue colour on porcelain.

THUJONE v. **KETONES.**

Probable presence of thujone in the essential oil of *artemisia herba alba*. This oil, d_{40}^{20} 0.9257, n_D^{20} +3.88°, n_D^{20} 1.4553, contains 14.4 p.c. of free, and 7.39 p.c. of combined alcohols, calculated as $C_{10}H_{18}O$. The presence of camphor has been demonstrated, and that of thujone is probable (cf. Grimal, Chem. Soc. Abstr., 1904, ii. 605; E. Alinari, Annali Chim. Appl. 1924, 14, 109; Chem. Soc. Abstr. 1924, 126, i. 754).

THULITE v. **ZOISITE.**

THULIUM. Sym. Tm. At.wt. 169.4 (James and Stewart, J. Amer. Chem. Soc. 1920, 42, 2022). The erbium sub-group of the yttrium metals contains the three elements, erbium, dysprosium, and thulium; the compounds of the last of which have been hitherto studied only by few workers owing to difficulties of isolation.

Occurrence.—Thulium is a very rare element, the best sources being euxenite, sipylite (a columbite from Northern Norway), ytterspar (Norwegian xenotime) and samarskite. It occurs in small quantities in the yttrium earths from other rare minerals.

Separation. Cleve first indicated the existence of the rare earth, *thulia* (Compt. rend. 1879, 89, 478, 521, 708; Thalén, *ibid.* 1880, 91, 376), and Lecoq de Boisbaudran, by decomposing fractionally the nitrates of the yttrium group, discovered thulium fractions between those of erbium and ytterbium (Compt. rend. 1879, 89, 516). A separation of erbium and thulium has been effected by fractional crystallisation of the ethyl-sulphates (Urbain, Ann. Chim. 1900, [vii.] 19, 184).

According to Auer von Welsbach, spectroscopic examination indicates that thulium consists essentially of three elements. Of these three thulium I. and thulium III. cannot be isolated by the present methods of purification. The salts of the former absorb rays in the extreme red down to $\lambda 700$, and show characteristic lines between 2700 and 3270 (spark spectrum). Thulium III. exhibits a characteristic spark spectrum between 2800 and 3260. Thulium II. forms an almost white sesquioxide. Its salts are pale yellowish-green in daylight and emerald-green in artificial light, and exhibit the absorption spectrum hitherto ascribed to thulium. The oxides of those fractions which are richest in thulium II. and neo-ytterbium exhibit a characteristic phenomenon in the flame; before becoming actually incandescent the oxides give out a purple light for a short time. The spark spectrum shows many strong lines between 3400 and 3800 (Monastch. 1911, 32, 373). According to Eder (Sitzungsber. K. Akad. Wiss. Vienna, IIa, 124) thulium I. contains a new element, *dansbium*; thulium II. has substantially the same spectrum as the original complex material, and *neo-thulium* is suggested as the name for the chief element present; thulium III. gave an arc spectrum containing a set of lines which are attributed to a new element, "*dubbium*" (cf. Paulson, Physikal. Zeitsch. 1915, 16, 352).

The minerals containing thulium are decomposed by hydrochloric or sulphuric acid; the rare earth oxalates precipitated, ignited, and the resulting oxides converted successively into

oxalates and sulphates. The latter salts are heated with barium bromate in aqueous solution from which the rare earth bromates are fractionally crystallised. After 15,000 operations the absorption spectrum underwent no change.

Thulium bromate $Tm(BrO_3)_3 \cdot 9H_2O$, hexagonal prism, which has been obtained in considerable amount by repeated crystallisation of the more soluble portions of the rare earth bromates, is more soluble than erbium bromate, but less soluble than ytterbium bromate. Fractional crystallisation of the bromates of the yttrium earths gives a fairly rapid separation of thulium from its associates (C. James, Chem. News, 1908, 97, 61; 1911, 104, 73; J. Amer. Chem. Soc. 1910, 32, 517; 1911, 33, 1332).

Thulium salts are pale bluish-green, but their colour is readily masked by small quantities of erbium, the hue changing to yellowish-green, yellow, white, and finally pink as the amount of this impurity increases.

Thulium oxide (*thulia*), Tm_2O_3 , a dense white powder with a greenish tinge, is prepared by igniting the oxalate; it is the least basic of the oxides of the erbium sub-group and dissolves slowly in strong acids. It exhibits a reddish incandescence on heating.

Thulium hydroxide is a white precipitate filtering readily even in the cold.

Thulium chloride $TmCl_3 \cdot 7H_2O$, deliquescent crystals very soluble in alcohol or water.

Thulium sulphate $Tm_2(SO_4)_3 \cdot 8H_2O$ is precipitated by alcohol from an aqueous solution of thulium chloride and sulphuric acid.

Thulium nitrate $Tm(NO_3)_3 \cdot 4H_2O$, deliquescent crystals obtained from solution in strong nitric acid.

Thulium oxalate $Tm_2(C_2O_4)_3 \cdot 6H_2O$, a greenish-white precipitate, soluble in aqueous alkali oxalates to form double oxalates.

Thulium acetylacetonate

crystallises from an alcoholic solution of thulium hydroxide in acetylacetone; the absorption spectrum of this compound differs appreciably from that of the inorganic salts, nitrates, chlorides, &c. Other organic salts of thulium have been described by James and his co-workers.

Absorption spectrum, v. Cleve, *l.c.*, and Forsling, Bit. Sv. Vet. Akad. Handl. 1899, 24, 1, No. 7). G. T. M.

THUNDERITE. An explosive consisting of a mixture of ammonium nitrate, trinitrotoluene, and flour.

THURINGITE. A member of the chlorite group of minerals of some importance as an ore of iron. The best crystallised members of this group and those containing the least iron have the composition $H_2Mg_4Al_2Si_2O_{12}$, as in clinocllore and penninite. The magnesium is, however, isomorphously replaceable by ferrous iron and the aluminium by ferric iron; when this replacement is complete the formula would be $H_2Fe''_4Fe'''_2Si_2O_{12}$ with Fe 50.7 p.c. Depending on differences in composition and in physical characters, a large number of species and varieties have been distinguished by special names. Those forming distinct crystals or plates are grouped as *orthochlorites*, whilst those forming compact masses composed of minute scales or fibres are

called *leptochlorites*. Like the micas, the chlorites crystallising in the monoclinic system often with pseudo-rhombohedral forms; and they have a perfect micaceous cleavage parallel to the basal plane. The characteristic colour is dark green to blackish-green, hence the name, from *χλωπῖτις*, a green stone. They are quite soft (H. 2-3) and often greasy to the touch; sp.gr. 2.6-3.5, depending on the amount of iron; decomposed by hydrochloric acid with separation of silica. They are of abundant occurrence as alteration products of silicate minerals of almost all kinds; and are found in igneous rocks, metamorphic rocks (e.g. chlorite-schist), and as beds in sedimentary rocks. In the last case they frequently present an oolitic structure (compare glauconite and greenalite). The following are the leptochlorites, all closely allied to thuringite, that have been worked as ores of iron.

Thuringite $H_2Fe''(Al,Fe''')_2Si_2O_{11}$ is compact with a fine scaly or granular structure and an olive-green to blackish-green colour; sp.gr. 3.15-3.19. It occurs as beds in clay-slates of Lower Silurian age near Schmiedefeld in eastern Thuringia (anal. I). The main ore-bed is 15-20 metres in thickness, and the ore, consisting of thuringite with chalybite and oolitic chamosite, yields 32-40 p.c. of metallic iron. Thuringite occurs abundantly amongst the iron ores of the diabase and schalstein zone between Sternberg in Moravia (anal. Ia) and Bennisch in Silesia. It is also met with in the Lake Superior iron mining district, and in the French Creek mines in Pennsylvania.

Chamosite or **Chamosite** (anal. II) is compact or oolitic with a greenish-grey or greenish-blue colour; sp.gr. 3-3.4; Fe 28-37 p.c. It forms thick beds in strata of Jurassic age at Chamoson in Canton Valais, and also at the Windgällen in Canton Uri in Switzerland. A chamosite ore is also extensively mined in Silurian rocks at Nučič in Bohemia. Identical with chamosite is the so-called *berthierine* (anal. III, by P. Berthier, 1827), which occurs with chalybite in Jurassic strata at Hayanges in Dept. Meurthe-et-Moselle and in Lorraine, and which by its alteration gives rise to the important *minette* (q.v.) ores of this district. Another similar oolitic ore is the *bavilite* in the Lower Silurian rocks of Brittany and Normandy.

	I.	Ia. ¹	II.	III.	IV. ²	V. ³
SiO ₂	22.35	24.50	25.23	12.4	33.30	17.34
Al ₂ O ₃	18.39	18.45	19.97	7.8	4.37	—
Fe ₂ O ₃	14.86	11.23	—	—	44.33	43.05
FeO	34.34	31.20	37.51	74.7	—	30.27
MgO	1.25	2.86	4.39	—	1.73	—
H ₂ O	9.81	9.93	12.90	5.1	14.10	9.18
	101.00	99.59	100.00	100.0	99.76	100.0

¹ Also MnO, 0.07; CaO, 0.93; P₂O₅, 0.44.

² Also MnO, 0.34; CaO, 1.22; P₂O₅, 0.37.

³ Also MnO, 0.16.

Stilpnomelane $H_2(Fe,Mg)_2(Fe,Al)_2Si_2O_{11}$ is present in the ores of the diabase and schalstein zone between Sternberg in Moravia and Bennisch in Silesia. From this district several other closely allied minerals have been described by F. Kretschmer (1905, 1906, 1918), including *moravite* $H_2(Fe,Mg)_2(Al,Fe)_2Si_2O_{11}$, and *stilpnokhlorane* $H_2(Ca,Mg)(Al,Fe)_2Si_2O_{11}$ (anal. IV). The latter forms shining yellow scales and results from the alteration of thuringite; it is found in the iron mines at Gebitzgau near

Sternberg. **Viridite** $H_2Fe_2''Si_2O_{11}$; and *mücken-sile* $H_2Fe'''_2Si_2O_{11}$, he regards as end-members of the thuringite series.

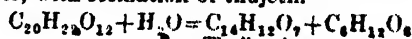
Cronstedtite $H_2Fe''_2Fe'''Si_2O_{11}$ (anal. V) is found in some quantity in mineral-veins at Kuttenberg and Příbram in Bohemia, and in Cornwall. L. J. S.

THUS AMERICANUM v. RESINS.

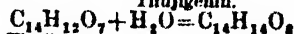
THUYA OCCIDENTALIS. *Thuya occidentalis* (Linn.).—In 1858 Rochleder and Kawaler (Wien. akad. Ber. 29, 10) isolated from the green portions of the *Thuya* (*Thuja*) *occidentalis* a glucoside *thujin*, which, when hydrolysed, gave a yellow colouring matter *thujetin*.

Thujin $C_{20}H_{22}O_{12}$. The plant is extracted with alcohol, the extract when cold filtered from wax, and evaporated to a small bulk. The residue is diluted with water, a few drops of lead acetate solution added, the precipitated impurities removed, and the clear brown filtrate treated with lead acetate. The yellow lead compound is collected, extracted with dilute acetic acid, and basic lead acetate now added to the solution. The bright yellow precipitate is suspended in water, decomposed with sulphuretted hydrogen, the lead sulphide removed, the filtrate treated with carbon dioxide in order to free it from sulphuretted hydrogen and evaporated *in vacuo* over sulphuric acid. Crystals gradually separate, and these are crystallised repeatedly from dilute alcohol until when treated with ammonia a green coloration is no longer produced.

Thujin is described by these authors as citron yellow microscopic prisms sparingly soluble in cold water. The alcoholic solution becomes yellow on treatment with alkalis, whereas with ferric chloride a dark green coloration is produced. When thujin is digested in alcoholic solution with dilute hydrochloric or sulphuric acid it is hydrolysed with formation of glucose and *thujigenin*, apparently an intermediate product, which readily takes up a molecule of water, with formation of *thujetin*—



Thujigenin.



Thujetin.

Thujetin $C_{14}H_{14}O_8$, forms yellow crystals, and is characterised by the fact that its alcoholic solution is coloured blue-green with ammonia, and green coloured by potassium hydroxide solution.

With lead acetate it gives a deep red precipitate. When thujetin is digested with boiling baryta water it is converted into *thujetic acid* $C_{14}H_{22}O_{13}$, which consists of yellow microscopic needles, sparingly soluble in water, readily soluble in alcohol.

Thujigenin $C_{14}H_{12}O_8$, crystallises in fine yellow needles, soluble in alcoholic ammonia, with a blue-green coloration.

The quantity of thujin which is present in the plant is very small; thus, from 240 lbs. Rochleder and Kawaler were successful in isolating a few grams only.

Perkin (Chem. Soc. Trans. 1914, 105, 1408), who re-examined this subject and employed methods almost identical with those of Rochleder and Kawaler, found that the glucoside corresponding to *thujin* possessed the formula $C_{21}H_{22}O_{11}$, melted and when

hydrolysed gave rhamnose and quercetin and was identical with the *quercitrin* of quercitron bark. The plant also contained a small amount of quercetin, and this also, prepared by the hydrolysis of the glucoside which, evidently corresponds to the thujetin of Rochleder and Kavalier, dissolved in alkaline solutions with a pale green tint, but failed to give the blue-green coloration with ammonia described by these authors. During a preliminary investigation of this plant (Chem. Soc. Trans. 1899, 75, 829), the sample then examined gave a trace of yellow colouring matter soluble in alkalis with a strong green coloration, the acetyl compound of which after frequent recrystallisation melted at 205°-206°. It thus seems probable that the thujin of Rochleder and Kavalier consisted of quercitrin contaminated with a second glucoside, possibly that of myricetin. The quantity of this latter present in the plant may possibly vary according to its environment or with the season of the year.

THYMACEOL. Condensation product of acetone and o-thymic acid.

THYMATOL. Trade name for thymol carbonate.

THYME CAMPHOR *v.* CAMPHOR.

THYMEGOL. Trade name for the mercury potassium salt of thymol-p-sulphonate.

THYME OIL *v.* OILS, ESSENTIAL.

THYMINES *v.* PYRIMIDINES.

THYMOL *v.* CAMPHORS; also PHENOL AND ITS HOMOLOGUES.

According to Howards & Sons, Ltd., and John William Blagden (Eng. Pat. 200151) *m*-cresol is condensed with isopropyl alcohol in the presence of phosphoric acid at a temperature of 70°-80°. If the reaction temperature is higher (e.g. 150°), a condensation product melting at 114° and possessing antiseptic properties is obtained (J. Chem. Soc. 1923, 123, 124, i. 1006).

p-Cymene isolated from the crude oil obtained from the sulphite spruce pulp mill, after purification, is nitrated and the nitro-cymene reduced to cymidine by means of iron powder and hydrochloric acid. Sulphonation of cymidine gives a mixture of *o*- and *p*-cymidine sulphononic acids, which, by diazotisation and subsequent treatment with ethyl alcohol and copper powder, are successively converted into the corresponding diazocymenesulphonic acids and the same cymene 3-sulphonic acid, the sodium salt of which yields thymol on fusion with sodium hydroxide (Max Phillips and H. D. Gibbs, J. Ind. Eng. Chem. 1920, 12, 733-734; see also J. Amer. Chem. Soc. 1923, 45, 1489-1493).

Thymol in oil of thyme may be determined by extracting the phenols by repeated shaking with sodium hydroxide solution. On adding strong hydrochloric acid to an aliquot part of the extract the phenols separate. The thymol is obtained by crystallisation and weighed after collection and drying (Mastbaum, Anal. Fia. Quim. 1922, 20, 501; J. Soc. Chem. Ind. 1923, 244 A).

THYMOLIN. Trade name for a mixture of naphthalene, camphor, and thymol.

THYMOLOPHORE *v.* SYNTHETIC DRUGS.

THYMUS CAPITATUS OIL. The flowers and leaves of *Thymus capitatus*, grown in Sicily, yield on distillation about 1.5 p.c. of an oil,

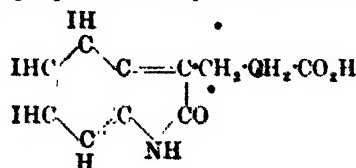
d_{20}^{15} 0.9582, n_D^{20} = 1.5106, α_D^{22} = -0.70°, which contains 73-84 p.c. by volume of phenols (carvacrol) and shows a corresponding high solubility in dilute alcohol. These results agree moderately well with those given by Pellini (Z. 1923, 858 A), and show that the figures given by Schimmel und Co. (Bericht, 1889, ii. 36) refer to an oil other than that of *Thymus capitatus* (F. C. Palazzo and C. Lutri, Annali Chim. Appl. 1924, 14, 103; J. Soc. Chem. Ind. 1924, 43 B. 537).

THYRESOL. Syn. for santalol methyl ether.

THYROGLOBULIN, THYROIDIN, THYROXIN *v.* THYROID GLAND.

THYROID GLAND. *Glande thyroïde*, Fr.; *Schilddrüse*, Ger. In 1891 Murray introduced the oral administration of thyroid gland in diseases where the natural secretion is defective (myxœdema, cretinism), and the subsequent success of the remedy has been one of the greatest triumphs of organotherapy. Baumann (Zeitschr. physiol. Chem. 1895, 21, 381) discovered the iodine content of the gland and obtained, by boiling with dilute sulphuric acid, an impure amorphous substance, iodothyron (thyroidin), containing 9-10 p.c. of iodine, and Oswald (*ibid.* 1899, 27, 15) separated a protein (thyroglobulin), also containing iodine.

The active constituent has been isolated by E. C. Kendall (J. Biol. Chem. 1915, 20, 501; Proc. Amer. Soc. Biol. Chem., J. Biol. Chem. 1917, 29, 29; Endocrinology, 1917, 1, 153; 1918, 2, 81; Proc. Amer. Physiol. Soc., Am. J. Physiol. 1918, 45, 540; J. Amer. Med. Assoc. 1918, 71, 871). It is obtained by hydrolysis of the gland with alcoholic sodium hydroxide and fractional solution in various organic solvents. It represents that half of the iodine containing substances of the gland which is insoluble in acids; the other half, soluble in acid, is also organic, but physiologically inert. Kendall has named the hormone thyroxin (from thyroxindol) and assigned to it the formula $C_{11}H_{10}(O)_2NI_2$ and the subjoined constitution:



Thyroxin forms crystals, m.p. 220°, soluble in alcohol, ether, water, acids and sodium carbonate, readily soluble in dilute sodium and ammonium hydroxides, with opening of the lactam ring. It is perhaps closely related to the important amino acid tryptophan and is extraordinarily active. On cretinism and myxœdema it has the full action of the entire gland, in daily doses of a fraction of a milligram. A dose of 10 mg. per day increases the basal metabolism of an adult by 30 p.c., and the total quantity present in the human body is estimated at 23 to 50 mg. The iodine content of the thyroid has generally been regarded as some measure of its activity. Hunt (Amer. J. Physiol. 1923, 23, 257) has recently found a close parallelism between iodine content and activity as tested by his acetonitrile method (see below), but on the other hand, Romeis (Arch. f. Entwicklungsgemech. d. Organ. 1922, 50, 410)

prepared from thyroid a crystalline iodine-free substance, which accelerates the development of tadpoles. The estimation may be carried out by Baumann's process (fusion with sodium hydroxide and colorimetric comparison in chloroform solution; cf. Riggs, J. Amer. Chem. Soc. 1909, 31, 710; 1910, 32, 692; Seidell, *ibid.* 1909, 31, 1326). Hunter's method (J. Biol. Chem. 1910, 7, 321; Seidell, *ibid.* 1911, 10, 95) appears to be preferable and has been adopted by the United States Pharmacopœia. One gram of the dried gland (corresponding to about 5 grms. of the fresh organ) is mixed in a nickel crucible of 125 c.c. capacity with 15 grms. of a mixture of anhydrous sodium and potassium carbonates and potassium nitrate in the molecular proportion of 1 : 1 : $\frac{1}{2}$ respectively. Five grms. of the salt mixture is spread on top; the mass is fused, dissolved in 150 c.c. water in a half-litre conical flask and mixed with 50 c.c. of sodium hypochlorite solution containing 2.4 p.c. Cl by weight. Syrupy phosphoric acid, diluted with an equal volume of water, is added until the yellow colour of free chlorine appears. Then 10 c.c. of the phosphoric acid solution is added in excess, the solution is diluted with an equal volume of water and boiled down to 150 c.c. or for half an hour, to expel the excess of free chlorine. After cooling 10 c.c. of 1 p.c. potassium iodide solution is added, and the liberated iodine (corresponding to 6 times that originally present, which was converted into iodic acid) is titrated with N/200 thiosulphate, of which 1 c.c. = 0.01058 mg. iodine present in the gland. *Thyroideum siccum*, U.S. P., should contain 0.17-0.23 p.c. iodine. (= about 0.034-0.046 p.c. in the fresh gland) and should contain not more than 6 p.c. of moisture. It is also official in the B. P. Seidell and Fenger (J. Biol. Chem. 1913, 13, 517) state that the glands of the sheep, ox, and pig contain from June to November about three times as much iodine as in the rest of the year. Aldrich (Amer. J. Physiol. 1912, 31, 152) finds the ratio for these three animals as 5 : 7 : 9 respectively. The amounts found by Seidell and Fenger were for sheep, ox, and pig respectively 0.08-0.24, 0.03-0.33, and 0.16-0.44 p.c. of dry weight. They remark that a standard of 0.2 p.c. could only be obtained with sheep's thyroids in the United States during a small part of the year. In English sheep the amount apparently does not fall so much in winter.

The physiological estimation of the hormone is more satisfactory but complicated. Quantitative experiments on the rate of metabolism are best, but very laborious. In a simplified form they may be carried out on tadpoles, which, in a solution containing very little of the hormone, have their normal growth retarded and their metamorphosis (loss of tail and development of hind limbs) greatly accelerated (Gudernatsch. Arch. f. Entwicklungsmech. d. Organ. 1912-13, 35, 457; cf. e.g. Rogoff and Marjé, J. Pharm. exp. Therap. 1916, 9, 57).

This method has been proposed for the commercial standardisation of thyroid preparations. Reid Hunt (J. Amer. Med. Assoc. 1907 [ii.] 240; J. Biol. Chem. 1905, 1, 33) finds that as little as 0.1 mg. of the gland may double the resistance of mice to poisoning by acetonitrile. On account of its effect on metabolism thyroid may be useful in reducing the weight of the constitu-

tionally corpulent, who are incapable of sufficiently oxidising fat. G. B.

THYROXIN. See **THYROID GLAND.**

TIEMANNITE. Mercury selenide, HgSe, crystallised in the cubic system with tetrahedral hemihedrisms, and isomorphous with metacinnabarite (HgS). Compact granular material is more usual than crystals. Greyish-black colour with metallic lustre; sp.gr. 8.19-8.47; H. 2 $\frac{1}{2}$. It occurs in some quantity with barytes, calcite, and manganese oxide in a vein in limestone near Marysville in Utah; and large masses have been found in the mercury districts in Lake, Orange, and Santa Clara counties, in California. Other localities are near Clausthal in the Harz, and the Sierra de Umango in Argentina.

L. J. S.

TIERS ARGENT v. **ALUMINIUM.**

TIGER-EYE v. **CROCIDOLITE** AND **QUARTZ.**

TIGLIC ACID v. **OILS, FIXED, AND FATS.**

TIGLIC ALDEHYDE, TIGLIC ANHYDRIDE v. *Guvaiacum*, art. **RESINS.**

TIKITIKI. A preparation of rice-polishing extract used in the treatment of beriberi. It contains a high percentage of antineuritic vitamin, and is a cure for infantile beriberi. For a method of preparing it, see A. H. Wells, Philippine J. Sci. 1921, 19, 67 (in abstract J. Soc. Chem. Ind. 1922, 41, 77 A).

TIL or **TEEL OIL** v. **SESAME OIL.**

TILE ORE v. **CUPRITE.**

TILIACORA ACUMINATA (Miers). The dried powdered bark by exhaustive treatment with alcohol yields quercitol, fumaric acid, an alkaloid, *tiliacorum* (C₂₂H₃₂N₂O₅, m.p. 260°-261° (decomp.), $\alpha_D^{20} = +105.3^\circ$, a phytosterol, a solid fatty acid, m.p. 47°, a mixture of unsaturated acids containing oleic and linolenic acids, with some linolic acid, a resin, and dextrose. Tiliacorum contains two methoxyl groups, but no methyl imide, or methylene oxide group; no acetyl or methyl derivative could be obtained. A solution of the alkaloid in sulphuric acid becomes first blue, and then green on treatment with oxidising agents (Van Itallie and Steenhauer Pharm. Weekblad. 1922, 59, 1381; J. Soc. Chem. Ind. 1923, 159 A).

TIMA. A medicinal preparation imported from Tampico as a remedy for phthisis. Is prepared as a syrup by boiling the fruit of *Parmentaria edulis* (DC.) with sugar, and mixing the product with almond oil (Arch. Pharm. [iii.] 107, 375).

TIMBER AND DRY ROT. E. H. Ellis (Chem. News, 1923, 127, 402) describes the fungus *Merulius lacrymans*, to which this disease is due, its method of growth and action upon timber, and the means adopted for its extermination. This fungus is rarely, if ever, found upon living trees, but is common upon worked timber, the term 'dry rot' referring to the condition of the wood upon which it grows and not to the infecting organism. Infection of the wood often occurs in the timber yard, but is rarely caused by the spores, which, although remaining alive for several years, appear to develop upon sound timber with difficulty. During dry weather the protoplasm of the fungal spawn (*mycelium*) breaks up into small bodies (*oidia*), which are easily scattered and readily germinate, thus leading to re-infection. Development of the fungus proceeds by the growth of a fine

network (*mycelium*) within the wood, followed by the well-known growth upon the surface, the form of which depends upon conditions such as moisture, temperature, &c. Various enzymes are produced by the *mycelium*, which cause the breakdown of certain constituents of the wood to water and carbon dioxide, whilst the lignin, tannin, and calcium oxalate remain as a spongy skeleton of the original timber.

Under favourable conditions the fungus is capable of penetrating mortar, thus spreading infection to distant wood. Various human diseases have been attributed to the growth of this fungus, but the impossibility of this is shown by the fact that 'dry rot' is killed at blood heat (98°F.). Infection of timber may be prevented by avoiding contact with infected material, the selection of well-seasoned timber, and storage of the wood both before and after use in dry and well-ventilated situations. In dealing with existing infection, timber may be impregnated with various antiseptics, among which the best are sodium fluoride, boric acid, magnesium silico-fluoride, creosote and tar, but the process is costly. Treatment with potassium or sodium dinitrophenates or dinitro-cresylates is effective, and kiln-drying of the wood is also recommended. In cases of serious infection all damaged timber should be removed, the exposed surfaces treated with formalin, followed by coating with an antiseptic, and precautions should be taken to avoid future access of damp (J. 1923, 29, 344; J. Inst. Brewing Abstr. 1924, 30, 123).

TIMBER FIRE-PROOFING. In the fire-proofing of wood the methods of impregnation are closely similar to those used in applying wood preservatives (see Chem. Trade Journal and Chem. Engineer, Oct. 5th, 1923, 39). The pressures applied will depend on the structure of the wood, as an excessive pressure will tend to crush the cells. Too high a temperature during drying may lead to brittleness. In order to assist penetration, an initial vacuum may be applied, followed by injection under about 170 lb. pressure. In the application of water-glass and its subsequent precipitation with hydrochloric acid, salt is left in the wood. To obviate this, it has been proposed to utilise pure silicic acid, prepared and impregnated by electro-osmotic methods (Eng. Pat. 101205 of 1917). Many fibres, such as kapok, have cuticles which are penetrated with difficulty by soluble salts. To facilitate penetration in such cases the material may be treated with alcohol or other volatile solvent or with a dilute solution of hydrofluoric acid (2 parts of the commercial acid in 100 parts of water). Coating with metal by electro-deposition is suggested as a method of fire-proofing aircraft linen without loss of tensile strength (Eng. Pat. 149745 of 1919).

For most practical purposes, the direct method of testing the efficacy of a fire-proofing treatment—that is, by applying a flame—should be sufficient. In certain cases, notably for aircraft fire-proofing, some method of testing the comparative protective action is necessary. Very little information is available, however, with regard to the inflammability of fire-proofed fabrics, although some results of comparative tests with unproofed materials have been made public (Aeronautical Advisory Committee

Report, No. 573 of 1918; Pharm. J. 1924, 112, 692).

Magnesium ammonium phosphate, which decomposes on heating into magnesium pyrophosphate and ammonia, has been patented by the Du Pont Company of America for reducing the inflammability of cellulose-ester and oil-varnish films. In the latter case the boiled linseed oil is incorporated with about one-third its weight of the phosphate (U.S. Pat. 1316881 of 1919).

For fire-proofing and preserving wood, the material may be impregnated with a solution of the double ammonium magnesium sulphate or with cuprammonium sulphate. In order to lower the melting-point of the magnesium sulphate, sodium or potassium sulphates may be added, preferably in quantity to form the eutectic mixture—that is, the mixture with the lowest melting-point (D. R. P. 306600 of 1914). Calcium sulphate or barium carbonate may be deposited in the body of the wood, the former by impregnation with ferrous sulphate followed by treatment with calcium chloride, the latter by treatment with a solution of barium sulphide and subsequent injection of gaseous carbon dioxide (U.S. Pat. 1346287 of 1920; Pharm. J. 1924, 112, 691).

TIMBO. The name of a narcotic medicine, the root rind of a variety of *Conchocarpus*. The rind appears in the form of tubes or rolls, is bright reddish-brown on the outside* and yellowish on the inside. The outer and middle rind break off short, but the inner rind has a long fibrous fracture and the interior colour is whitish. It possesses a weak aromatic taste somewhat like cascarilla bark, but has no special odour. A cross-section shows an interrupted yellow zone near the outer side, whilst the inner rind is faintly streaked in radiating lines. Some of the cells contain crystals of calcium oxalate (Chem. Zeit. 11, 315; J. Soc. Chem. Ind. 6, 560).

TIN. Sym. Sn. At.wt. 118.71. Atomic number 50. According to Aston, ordinary tin is a mixture of isotopes—eight in number, and of atomic masses 120, 118, 116, 124, 119, 117, 122, 121. The average atomic weight, in proportion to the intensities of the lines of the positive rays, agrees well with the accepted value (Nature, 1922, 109, 813). The molecular weight of tin at different temperatures has been studied by Jouniaux (Bull. Soc. chim. 1925, [iv] 37, 67; Chem. Soc. Abstr. 1925, ii. 489). *Tin was known and prized in the earliest historic ages, for it is mentioned without comment as one of the common metals in the days of Moses (Numbers xxxi. 22), and was an important commodity in the fair at Tyre; numerous bronze instruments of very early date have also been discovered in Assyria, and, particularly by Layard, in the ruins of Nineveh. Many of these bronzes are now preserved in the British Museum. The tin so employed was obtained by the Phœnicians from Cornwall and the Scilly Isles in this country, and from the mountains of Spain, and there is no evidence of the occurrence of tin in those countries in which, in ancient times, the metal was most largely used. Pliny appears to have been familiar with tin, and states that it occurs in grains, in alluvial soil, from which it is obtained by washing. These grains, the further

states, are black, and their metallic character can only be recognised by their great weight. Though tin was regarded by the ancients as one of the baser metals, its cost was greater in the days of Homer and Pliny than at present, for in the days of the latter of these writers an avoirdupois pound of tin cost 8s. 7½d. sterling, or about four times its present value. The uses of tin among the Romans were similar in many respects to those of the present day. It was chiefly employed in the form of an alloy with copper, on account of the hardness imparted to the alloy by a comparatively small proportion of tin, and some of the very earliest known bronzes agree closely in composition with those used for similar purposes at the present day. Tin was also used with lead by the Romans for the production of solder, and for tinning the inside of copper and brass vessels, in which art the Roman workmen appear to have attained considerable skill. Alloys containing more tin, corresponding somewhat to the modern *speculum metal*, were used by the ancients for mirrors, but the art of tinning iron does not appear to have been discovered until a much later date.

Occurrence of tin.—Tin occurs in comparatively few localities, never in the native state, and in but few forms of chemical combination. The most important one is *tinstone* or *cassiterite*, tin dioxide (SnO_2), which is met with in two principal forms, crystallised and massive. The crystals are of the regular prismatic or tetragonal system, isomorphous with those of rutile, and are frequently well formed and of large size. Tinstone in the usual or massive form is a dark reddish-brown or slaty-coloured very heavy mineral, which occurs in Cornwall in veins usually running nearly east and west, and in which the tin ore is associated with arsenical pyrites, copper sulphide, wolfram, and a great variety of other minerals. Tin usually occurs in plutonic or metamorphic rocks, such as granite, felspar, porphyry, or clay slate, but by the action of denudation on these older rocks grains of tinstone are frequently met with in the neighbouring alluvial deposits, and this variety of ore, which is of special purity and now almost entirely exhausted in this country, is known as 'stream tin.' The metal also occurs in small quantities as *tin pyrites* (SnS_2). The largest quantities of tin are now produced in the island of Banca ('Straits tin'). Smaller though considerable quantities are met with in Britain, Germany, Siberia, China, South Australia, New South Wales, Nigeria, and Bolivia. Among the newer sources of tin may be mentioned the Waterberg district, to the north of Pretoria, in the Transvaal, the present monthly output of which is valued at about £30,000, and is likely to increase. Cassiterite has been met with over an area comprising Helderberg, between Stellenbosch and Somerset West, and the Kuits River Mills in the Koeberg District of South Africa. The Malay States are the chief producer, contributing over 36 p.c. of the world's output; then follow Bolivia and the Dutch East Indies, with about 20 and 15 p.c. respectively. At present the production and consumption of tin appear to balance. Normally the United Kingdom imports about 35,000 tons of tin ore, about 8000 tons being from British possessions, and 40,000 tons of metal, which, with the excep-

tion of 2000–3000 tons, is derived from British possessions. The re-exports in a normal year are about 3000 tons of ore, and 40,000 tons of unwrought tin. The balance, about 32,000 tons of tin ore, together with the domestic production, which in 1913 was 8355 tons, was apparently sufficient to meet the domestic requirements of the United Kingdom. Few new sources of tin have been discovered in recent years, although it appears probable that the Belgian Congo is likely to become an important producer in the not far distant future. It would seem that unless really extensive deposits are discovered, tin will be one of the first base metals to be exhausted. The smelting of tin ore is concentrated in few hands, although the tin-smelting capacity of the world is well in excess of the annual supplies of ore. In this respect the Straits Settlements heads the list with a capacity of about 58,000 tons of metal, Great Britain following with a capacity of about 34,000 tons, and the United States with a capacity of 30,000 tons, the total world smelting capacity being about 175,000 tons per annum (Sir R. Redmayne, *J. Soc. of Arts*, 1923; *J. Soc. Chem. Ind.* April 27, 1923, 425). Promising reports are received in connection with tin mining in Texas. In parts of Nigeria tin occurs distributed over wide areas, but in relatively small proportions. The present world's output of tin is about 115,000 tons per annum.

Production of tin.—The metallurgy of tin is in its main features simple, but the mechanical preparation of the ore involves more skill and labour than is the case with any of the other common metals. So much, in fact, is this true that success in the extraction of tin frequently depends more upon the captain of the mine, who superintends the dressing of the ores, than upon the smelter. On account of the high price of tin, and the relatively high density of tinstone, it is found practicable to work ores which in the first place contain comparatively little tin, ores which contain only 0.5 p.c. of tinstone being sometimes profitably worked. The principle adopted in the mechanical separation of tinstone is very simply illustrated in the operation of 'vanning,' which is frequently used in Cornwall and elsewhere as an approximate test of the richness of an ore. A quantity of the crushed material is placed in a miner's shovel of special shape, known as a vanning shovel, water is added, and then by means of a circular motion which is imparted to the shovel by the hands, aided by a peculiar jerk of the wrist, the ore is ultimately almost completely separated from the earthy matter, and can be dried and weighed. On the large scale the ore is first picked and assorted, and then broken by suitable stone breakers and rolls. The roughly-powdered ore is carefully assorted, and then fed into a mill containing a battery of stamps, of which there are many varieties in use. Each stamp weighs 3 cwt. or upwards, the face of the stamp being either steel or chilled cast iron. By means of suitable cams on a revolving wheel the stamp is raised at regular intervals, and allowed to fall upon the ore which is contained in the box or coffer of the stamp. A supply of water flows through the boxes and escapes through perforations, carrying away the finely-crushed ore, while the larger pieces remain in the box to be further crushed by the stamp.

The finely-powdered ore now passes to some form of buddle, or to a concentrating table, which more or less completely separates the earthy matter. Probably the simplest form of such apparatus, of which there is an endless variety, is the inclined plane with ridges or 'riffles' placed at right angles to its length. On such a plane the heavier particles naturally remain, the richer fragments being deposited principally at the upper part of the buddle, whilst the earthy matter, with some ore, passes away. But such a simple form of buddle is now seldom used, and a considerable number of improvements have been from time to time adopted. Thus the inclined plane is made movable, and either a jerking or a rocking motion is imparted to it, and this is found to give better results than the fixed form. But buddles of a circular shape have met with considerable favour in late years, one form (Borlase's) being a circular concave buddle fed from the outside and discharging the slimes from the middle; but the variety generally preferred in Cornwall is that of a very flat cone, the water and ore being distributed either by a revolving spout, near the apex of the cone, or by means of a smaller and more acute distributing cone. The waste liquid from the buddle is led into a succession of tanks or pools, where it is allowed to settle in order to recover the finer portion of the ore, which would otherwise be lost, and the slimes thus obtained are worked over again in order to recover the finely-divided tin ores.

In dressing tin ores it is important that they should not be too finely crushed, or the gangue will be removed with greater difficulty. The ore should be, as far as possible, separated into parcels, the fragments in each being of uniform size, and the method of treatment is varied with the fineness of the material; in no case should the ore be crushed more than is necessary to separate the matrix. These facts form the basis of all successful ore dressing.

Reduction of tin.—From the point of view of the tin smelter, ores of tin may be divided into two classes, first those of tolerable purity, which may be directly smelted in the furnace, and secondly a less important class of ores, which from the fact that they contain notable proportions of copper, arsenic, sulphur, or tungsten, require to be further treated, after dressing, before smelting. Ores which contain arsenic or sulphur are roasted at a low temperature, usually in calciners with a bed which is mechanically rotated in a horizontal plane, and which is supplied with mechanical rabbles. The greater part of the arsenic and sulphur is thus removed. The mass is then withdrawn, and, after being exposed for some time to the action of the atmosphere, is washed to remove the oxide of iron and other lighter matters from the heavy oxide of tin. Ores which contain much tungsten are heated with sodium sulphate or carbonate in a reverberatory furnace, by which means soluble sodium tungstate is produced, and can be removed by washing from the unaltered oxide of tin. This process (Oxland's) is not carried on now to any considerable extent. The ore having been purified by one or other of these processes is ready for smelting in the ordinary way. The reduction of the metal from the ore is always accomplished by heating

with carbon, which operation may be performed either in a reverberatory furnace, as is the custom in this country, or in small blast furnaces such as are used to a limited extent in Germany. Shaft furnaces also are used in China, Sumatra, Nigeria, and by natives in many other localities.

Tin smelting in England.—The furnace employed for the smelting of tin in this country, and in fact pretty generally elsewhere, is a reverberatory, with a fireplace at one end and a stack at the other. At the front is a single working door, while at the back is a tapping hole which is closed during the smelting, but which when the operation is concluded serves to convey the metal into a 'float' or circular iron pot lined with clay. The bed of the furnace is about 18 ft. long by 9 ft. broad, and slopes to the tapping hole. The fireplace is about 2 ft. broad, and the firebridge is of firebrick and some 14 ins. high. The roof is low, and slopes uniformly from the firebridge to the stack.

The charge of ore, which weighs 20–25 cwts., is mixed with rather less than one-fifth of its weight of anthracite powder, and spread uniformly over the furnace bottom. If the ore is refractory, a little fluorspar or lime is added as a flux. The door is then closed and luted up, and the temperature gradually raised for 5–6 hours, when the door is opened, the mass rabbled, and a quantity of powdered anthracite or 'culm' is thrown on the surface of the charge. After heating for about another hour, and a further rabbling, the metal is tapped. Part of the slag produced is thick and is raked out of the furnace, while the remainder is more fluid, flowing out with the metal, and is called 'glass' by the smelter. The slag consists essentially of ferrous silicate, and as it frequently contains a considerable amount of tin it is melted again when the furnace is at liberty.

As tin is a valuable metal any considerable loss in smelting would result in commercial failure. The boiling-point of tin is high, in the neighbourhood of 2000°C., so the loss by volatilisation is very small. Practically the chief source of loss, in the smelting process, is in the slags. Tin oxide readily passes into solution in fused silicates yielding enamels. Hence the slag should be as small in quantity as possible, and should not be oxidised. The first requirement is met by employing ores of high concentration, and by mixing them so that the basic gangue of one will neutralise the acid gangue of another, so far as possible. Thus the use of fluxes is kept at a minimum, and the bulk of slag diminished. The slags are collected, and are generally smelted in a water-jacketed blast furnace, for the recovery of the tin they contain.

Small blast furnaces, which were previously used in Cornwall, have survived longer in southern Germany, and are also employed by the natives of India. The waste of metal is much greater than in the reverberatory furnace, whilst the cost of fuel (charcoal) is also greater than in England, but the tin obtained is stated to be of excellent quality.

Refining.—The refining process consists of two parts, a preliminary liquation, and the refining proper. The liquation is conducted in a furnace of similar shape to the reverberatory furnace above described, and about 10 tons are

operated upon at once. The temperature is carefully regulated so as just to melt the purer tin, which gradually flows away into a separate pot or 'kettle,' while the impurities, consisting of iron, arsenic, sulphur, and traces of many other elements, together with some 20 p.c. of tin, remain in the form of a hard, brittle, white, semi-metallic mass known as *hard-head*. For the composition and properties of hard-head, see Levy and Ewen, *Trans. Inst. Min. & Metallurgy*, 1908-9, 466. The purer metal which has collected in the kettle (which is heated by a small separate fire) is now refined by plunging billets of green wood under the surface of the melted tin. A quantity of gas is evolved from the wood, and violently agitates the metal, gradually separating a scum which contains the impurities originally present in the crude tin. The same result is sometimes attained by 'tossing' the melted metal in ladles from a height of several feet and allowing it to fall into the kettle; in this way the metal is also exposed to atmospheric influences, and a scum separates as before. The refined metal is sold as *grain*, *refined*, or *common tin*, according to its quality, though all tin met with in commerce has been more or less refined. For *refined tin* purer ores are employed, the refining is continued longer, and after polishing the metal is allowed to stand some time, and only the upper or purer portions are used. The second or ordinary quality, when cast in suitable moulds, is known as *block tin*. A simple test of the commercial quality of tin is to melt the metal at a moderate temperature, and to pour it into an ingot mould. The ingot, if of good quality, should be smooth, bright, and rounded, and should retain this appearance on solidification; if impure it will have more or less sharp edges, and will 'frost' over on solidifying, while very impure metal will be tinged with yellow or purple, according to the amount and nature of the impurities. *Grain tin* is produced by heating blocks of refined tin to a temperature a little below the melting-point of the metal, at which point it becomes very brittle, and is broken either by dropping from a height or by a blow of a hammer. For further particulars of the properties and metallurgy of tin, see H. Louis, *Metallurgy of Tin*, London, 1911.

Electrolytic refining of tin.—After liquida- tion, to remove iron, crude tin has been successfully refined on the large scale by electrolysis in solutions containing (a) 20 p.c. of hydrofluosilicic acid, 0.1 p.c. of sulphuric acid, and 6 p.c. Sn; (b) 5 p.c. of hydrofluosilicic acid, 8 p.c. of sulphuric acid, and 3 p.c. Sn; (c) 8 p.c. of sulphuric acid, 4 p.c. of cresol- or phenol-sulphonic acid, and 3 p.c. Sn; (d) 13.7 p.c. of sulphuric acid, 21.2 p.c. of crystallised sodium sulphate, and 1.5 p.c. Sn. The electrolysis is preferably carried out at 35° with a current of 10 amp. per sq. ft. at 0.3 volt. With electrolytes (a), (b), (c), which contain the tin as a stannous salt, an emulsion of 1 lb. of glue and 8 lb. of cresylic acid is added per ton of metal deposited, to assist in producing smooth deposits, and 0.3 p.c. of hydrochloric acid is added to bring about uniform corrosion of the anode and to make the slimes soft and porous. Electrolyte (d) contains the tin as stannic sulphate, and 0.2 p.c. of Cuprasol slimes is added to obtain

a smooth deposit. The slimes from Bolivian crude tin containing 97 p.c. Sn usually assay about 20 p.c. Pb, 5 p.c. Cu, 3 p.c. As, 5 p.c. Sb, 20 p.c. Bi, and 30 p.c. Sn, together with 130 ozs. Ag per ton, and traces of Au. Two methods of treating this material have been used: the first involves fusion of the slime with sodium hydroxide under oxidising conditions to obtain a lead-bismuth-silver bullion, which is refined electrolytically, and a soda slag from which crude tin is again obtained by reduction. In the second process the slimes are melted and reduced to metal, which is cast into anodes: these are electrolysed in 18 p.c. hydrochloric acid, which dissolves 90 p.c. of the tin and bismuth, 45 p.c. of the antimony, and 35 p.c. of the copper. The bismuth is precipitated by crude tin and refined by fusion with soda and sulphur, and the tin is precipitated by lime. The slimes are smelted to give a base lead bullion, which is softened and desilverised (J. R. Stack, *Trans. Amer. Electrochem. Soc.* 1924, 45, 279; *J. Soc. Chem. Ind.* 1924, 43, B. 521).

Brands of tin. In 1911 a committee of the London Metal Exchange drew up a new form of contract for the purchase of tin. This provided for the recognition of two classes of tin: Class A. includes Straits or Australian tin of good merchantable quality, and also refined tin of good merchantable quality, assaying not less than 99.75 p.c. of tin. Class B includes common tin of merchantable quality, and assaying not less than 99 p.c. of tin. The official brands include the following: Straits, Australian, Banca, Billiton, English, German, and Chinese. In connection with this classification a number of brands and descriptions were assayed, and tabulated analyses prepared.

It will thus be seen that some of the best brands of commercial tin are of remarkable chemical purity.

Properties of tin. Tin is a white lustrous metal which exhibits a fibrous structure, and when bent emits a creaking sound owing to its crystalline character. When melted and allowed partially to solidify, and the still liquid portion poured away, needle-shaped crystals are formed in the remainder. The metal is deposited in tetragonal prisms when stannous chloride is decomposed by a weak electric current. Tin is capable of existing in different allotropic forms depending upon the temperature. At ordinary temperatures it is in a metastable condition, but on exposure to great cold it falls to pieces forming a coarse grey powder. Between 18° and 170° the stable form of tin is tetragonal, above 170° it is rhombic. Tin has a sp.gr. of 7.312 and melts at 232° (Heycock and Neville). It expands 2.8 p.c. during melting. The change of density of melted tin with temperature may be represented by the formula

$$d = 7.01 - 0.00074(t - 232)$$

(Hogness, *J. Amer. Chem. Soc.* 1921, 43, 1621). Tin suffers little change when exposed to air, either dry or moist, at ordinary temperatures. When melted it slowly oxidises to the dioxide. It is readily attacked by acids: hydrochloric acid converts it into stannous chloride with evolution of hydrogen, nitric acid forms meta-stannic acid. It dissolves in aqueous solutions

of the alkalis with evolution of hydrogen, forming meta-stannates.

For passive tin, see Steiner (Z. Elektrochem. 30, 279, June, 1924; Sci. Abstr. 1924, 27, 832).

Uses of tin.—The manufacture of tin plates absorbs more tin than any other industry, and of this a separate account will be given. Tin is also largely used for alloying with copper to produce bronze, bell metal, and speculum metal, while in combination with other metals tin produces a number of useful alloys, to be afterwards described, among which may be mentioned pewter, Britannia metal, plumber's (or soft) solder, Queen's metal, type metal, fusible metal, &c. Though tin is comparatively brittle at ordinary temperatures, it becomes very malleable at about 100°, and can then be rolled into thin sheet or foil, for which there is a considerable application, and which was formerly much used, in the form of an amalgam, for the 'silvering' of mirrors.

Tin foil containing small quantities of aluminium gradually becomes brittle, owing to the slow oxidation of the aluminium. On account of its power of resisting atmospheric influences and the action of vegetable acids, tin is also used for the manufacture of pipes for brewers, distillers, and other purposes. For similar reasons lead pipes are sometimes tin-lined. Pots, pans, kettles, and other culinary utensils are frequently *tinned* inside. The process is very ancient, and extremely simple. The surface of the vessel to be tinned (which may be of copper, brass, or iron) is carefully cleaned and brightened, and a little ammonium chloride (patented for this purpose by John Bootie in 1768) is often rubbed over the surface. Some tin and a little powdered resin is now melted in the vessel, and is wiped over the surface with tow. By this means a skilful workman rapidly produces a uniform coating of tin, which resists considerable wear, and yet weighs, according to the experiments of

	Tin	Anti- mony	Arsenic	Lead	Bis- muth	Copper	Iron	Silver	Sul- phur
Banca tin	99.950	0.007	nil	trace	nil	0.018	0.045	nil	trace
Billiton	99.960	0.006	nil	nil	nil	0.023	0.018	nil	nil
Penang	99.939	trace	0.013	trace	nil	0.016	0.028	nil	0.004
Singapore tin	99.870	0.008	0.045	0.034	0.003	0.052	0.003	0.006	0.005
M. Bischoff	99.795	0.005	0.063	0.037	0.005	0.035	0.042	trace	0.008
Pymont tin	99.938	0.017	0.019	trace	nil	0.022	trace	nil	0.004
Irvine Bank	99.580	0.062	0.034	0.221	0.025	0.125	0.002	0.018	0.004
Williams Harvey & Co., No. 1	99.860	0.015	0.040	0.004	0.005	0.047	0.003	nil	0.006
" " No. 2	99.560	0.166	0.037	0.162	0.007	0.050	0.005	trace	0.013
" " No. 2a	99.350	0.245	0.065	0.223	0.015	0.042	0.016	trace	0.013
" " No. 3	99.200	0.300	0.037	0.396	0.007	0.100	0.013	0.014	0.006
" " No. 4	99.941	0.011	0.022	trace	0.001	0.020	trace	trace	0.005
Penpoll, No. 1	99.720	0.118	0.054	0.041	0.007	0.052	0.001	0.009	0.007
" " No. 2	98.710	0.569	0.042	0.546	0.055	0.103	0.007	0.015	0.004
" " No. 3	99.300	0.325	0.056	0.212	0.050	0.088	0.002	0.021	0.009
Redruth	99.160	0.178	0.053	0.177	0.017	0.445	0.014	0.006	0.008
Th. Goldschmidt, No. 1	99.860	0.004	nil	0.102	nil	0.043	trace	nil	trace
" " No. 2	99.400	0.015	nil	0.425	nil	0.069	trace	nil	trace
" " No. 3	99.150	0.122	0.046	0.143	0.112	0.352	0.007	0.003	trace
Chinese, No. 1	99.343	0.031	0.040	0.434	0.007	0.052	0.010	trace	0.011
Wing Hong & Co., No. 2	98.602	0.039	0.035	1.035	0.042	0.134	0.014	trace	0.011
" " No. 3	95.280	0.381	0.050	3.995	0.020	0.106	0.028	0.018	0.008

Bayen, less than a milligramme per square inch of surface. No wonder that Pliny states, with surprise, that copper when tinned 'does not increase in weight! Tin salts are also used for tinning brass and copper wire, and as mordants in dyeing.

Alloys of tin. The alloys of tin are of great practical importance, and have naturally attracted considerable attention, although accurate information is still wanted in respect of many of their physical and other properties. For convenience of study the alloys of tin may be divided into two classes, the first in which the properties of the resulting alloy are entirely different from the mean of the constituents, while the second class includes those alloys some of the most important properties of which agree very closely with what might be anticipated from the properties of the constituent metals. The first class is typically represented by the alloys of copper and tin, which include the important alloys known as *brasses*, *gun metal*, *bell metal*, &c.

Tin itself is weak, soft, readily fusible, and of a nearly white colour, while copper is strong, tough, moderately hard, and of a characteristic red colour. On adding tin to copper, however, in gradually increasing proportions a succession of alloys is obtained with properties which are utterly different alike from those of each other and from their constituent metals. Thus an addition of about 5 p.c. of tin to copper produces a tough strong alloy, which still retains a fairly characteristic copper colour, but which is much harder than copper, and is suitable for medals or coinage, but the hardening effect of tin is so great that already the practical limit has been reached for coinage purposes. On adding 5 p.c. more tin we have an alloy which is still harder, so much so that it has to be cast instead of being rolled or drawn, and the alloy possesses a rich yellow colour. With a little more tin an alloy suitable for the hardest bearings is produced, and with still more tin we have the alloy used for small bells, and which is

sonorous, but shows considerable brittleness when cold, but though it be worked at a low red heat. With still more tin an alloy suitable for the largest bells is obtained; brittleness is more marked, and the fracture is dull earthy grey, and it is only when the metal has been worked or burnished that a yellow colour is visible. But on continuing the addition of tin, which is one of the softest of the common metals, the alloys become more and more brittle, until with about 33 p.c. the alloy can easily be pounded in a mortar, and possesses a white colour, with a more or less pronounced blue shade. This alloy is thus utterly different alike from its constituents and from either of the other alloys previously mentioned. As examples of the second class of alloys of tin, in which the properties of the alloy are approximately what would be expected from the characters of the constituents, the combination with zinc or with lead may be taken. Tin and zinc unite in all proportions, and the colour, hardness, ductility, &c., of the alloys are what would be anticipated from a mixture of the two constituents. Tin and lead also unite in all proportions to form a series of alloys, all of which are nearly white in colour, and are soft, malleable, and readily fusible, like the metals themselves. Tin-lead alloys, however, furnish a characteristic illustration of the fact that the melting-point of mixtures or alloys is very commonly lower than the mean calculated from the melting-points of the pure substances. This rule is very generally observed, both in salt solutions, with mixtures of salts, and with mixtures of organic substances (Guthrie, *Phil. Mag.* [iv.] 59, 1, 206, 266; [v.] 1, 49, 354, 446; 17, 462; 6, 35). Common, or soft, solder is an alloy of tin and lead, the best proportions being very nearly 2 parts of tin to 1 of lead. The melting-point of this alloy, calculated from the melting-points of its constituents ($Pb=327^{\circ}$, $Sn=228^{\circ}$), would be 261° , but the lowest melting-point in this series of alloys actually observed is 180° (Turner, *B'ham. Phil. Soc.* [iv.] 318), and the composition of the alloy was very nearly 2 parts of tin to 1 of lead. A number of investigators have examined these alloys of tin and lead, including Küpffer, Pillichody, Laurie (*Chem. Soc. Trans.* 1889, 678), and more recently Rosenhain and Tucker (*Phil. Trans. Series A.* 1908, 89), and the results of the determination of the composition of the lowest melting-point alloy vary from about 60 to 65 p.c. of tin (62.93 p.c. tin, Rosenhain and Tucker). There appears to be no indication of a definite alloy of tin and lead in atomic proportions, though, on very slow cooling, there is evidence of the existence of a solid solution, at the lead end of the series. There is also an inversion at 150° with alloys containing 18–63 p.c. of tin. In addition to their use for solders the tin-lead alloys have an important application in the form of *pewter* , the toughest and hardest variety of which contains about 3 parts of tin to 1 of lead. The hardness of lead-tin alloys is altered completely by prolonged re-heating of the alloy (C. di Capua and M. Arnone, *J. Soc. Chem. Ind.* 1924, 43, B. 580; Atti R. Accad. Lincei, 1924, 33, i. 293). Alloys of tin and antimony belong to the same class as those previously mentioned, and a mixture of 4 parts of tin with 1 of antimony is used for one

kind of type metal. Tin also enters into the composition of Britannia metal, the proportions being as follows (Greenwood), *Metallurgy*, i. 211):—

	Britannia metal			Queen's metal
	For spinning	For rolling	For casting	
Tin . . .	94	90	84	75
Antimony . . .	5	7	10	8.5
Copper . . .	1	3	4	—
Bismuth . . .	—	—	2	8.4
Lead . . .	—	—	—	8.5

A Birmingham manufacturer's mixture for Britannia metals is as follows: tin, 1 cwt.; antimony, 12 lbs.; copper, $\frac{1}{2}$ lb.

Britannia metal has a somewhat considerable application on account of its white colour, and the fact that it takes a good polish and resists the influence of the atmosphere; its low conductivity for heat also renders it very suitable for some purposes. This manufacture was introduced by Jessop and Hancock about 1770.

Type metal varies considerably in composition, consisting essentially of antimony and lead; but for small type tin is commonly added, and in some cases considerable proportions of tin are employed.

The following illustrates the composition of type metal of excellent quality, and suitable for different sizes of type. It will be noted that large type is made of a softer and cheaper mixture.

	Tin	Lead	Antimony
Large type . . .	7.5	78	14.5
Medium type . . .	9.0	73	18
Small type . . .	14.5	57	28.5

From 1 to 1.5 p.c. of copper is also added in some cases to improve the wear of the type.

White bearing metals for heavy machinery contain the same constituents as type metal. At least 10 p.c. of antimony is required; with above 20 p.c. the alloy is brittle. The limit of tin, on account of price, is usually about 45 p.c. (Hague, *Bearing Metals*, South Staffs. Iron & Steel Inst. Jan. 1909; Hiorns, *Anti-friction Alloys*, Birm. Metallurgical Soc. Feb. 1909). For special purposes larger proportions of tin are employed, as shown in the following analyses (G. Hughes, *Non-ferrous Metals in Railway Work*, Journ. Inst. of Metals, Sept. 1911):—

	A	B	C
Tin . . .	82.0	11.5	80
Antimony . . .	14.0	13.5	10
Copper . . .	4.0	3.0	10
Lead . . .	—	72.0	—

Alloy B is a fairly typical soft bearing metal. A and C are harder, the former being used for bearings, &c., in steam locomotives, and the latter for high-class axle bearings on the pinion and commutator ends of electrical rolling stock.

Tin is also a constituent of the various fusible alloys, one of the best known being Wood's alloy, which consists of 4 parts of tin with 4 of lead, 8 of bismuth, and a little cadmium; it fuses at 63° .

The tin-lead-bismuth eutectic melts at 94° . It can be prepared by melting together 4 parts of tin, 8 of lead, and 13 of bismuth. The alloy with 4 of tin, 8 of lead, 10 of bismuth, and 4 of cadmium melts at about 71° .

Fusible alloys are used chiefly for taking rapid impressions of objects which would fre-

quently be injured by the use of metal melting at a higher temperature, and also for safety plugs in steam boilers, &c.

For the equilibrium of the ternary system bismuth-tin-zinc, see Sheikh D. Muzaffar (J. Chem. Soc. 1923, 123, 2341).

Hardness of tin-cadmium and tin-bismuth alloys.—The hardness of tin is increased by addition of cadmium to a maximum for about 6 p.c. of the latter. With further addition of cadmium, the hardness falls rapidly until the eutectic point is reached at 28 p.c. of cadmium, remains constant over the region 28-97 p.c. Cd, and then falls to the value for pure cadmium. This behaviour is changed markedly by annealing the alloys in paraffin wax at 150° for 330 hours, the two branches of the curve in the neighbourhoods of 0 p.c. and 100 p.c. of cadmium then revealing the solid solubility of each metal in the other; about 3 p.c. of tin dissolves in cadmium and about 8 p.c. of the latter in tin (cf. Bucher, A., 1917, ii. 211).

With tin-bismuth alloys the maximum hardness corresponds with the eutectic point, but annealing causes the disappearance of this maximum and renders the curve normal, the maximum hardness being then shown by crystals of tin saturated with bismuth, and the limit of solid solution being extended from 4 p.c. to 7 p.c. of bismuth (C. di Capua, Atti R. Accad. Lincei, 1924 [v.] 33, i. 141; Chem. Soc. Abstr. 1924, 126, ii. 414).

Tin-copper alloys. History.—Copper is one of the few metals which have been known from prehistoric periods, and, like silver and gold, is in the pure condition too soft and ductile for many useful applications. The ancients, therefore, prepared various hard copper alloys or bronzes, which were used for many purposes to which iron and steel are now applied. The elements added to give hardness were arsenic, iron, or, preferably, when obtainable, tin. A very ancient Egyptian knife-blade (1400 B.C.) examined by Dr. Percy (Metallurgy, i. 504) consisted of copper with 2.29 p.c. of arsenic and 0.43 p.c. of iron; such a material would, of course, form an indifferent cutting tool.

The Hindoos have for many centuries produced a variety of bronze for coins and statues, which was hardened by the presence of iron. Dr. Percy mentions an ancient Indian coin which contained 5.06 p.c. of iron, the remainder being copper (l.c.), while in the Birmingham Art Gallery there is one of the earliest known images of Buddha, which is believed to be 2500 years old, and which was found by Daniel Forbes to contain 91.50 p.c. of copper and 7.59 p.c. of iron. With the introduction of tin by the Phoenicians came the use of bronze in Egypt, Assyria, Greece, and all the important countries of the ancient world. Of these bronzes, numerous examples are preserved, and the composition recommended for various purposes was very similar to that which is used at the present day. Thus Pliny states (Thomson, Hist. Chem. i. 57) that the Romans made their pans for boiling from a mixture of 100 lbs. of copper and 3-4 lbs. of tin, while for statues to every 100 lbs. of copper, consisting of one-fourth old copper and three-fourths new metal, 12½ lbs. of tin was added. Brass was not known, or at all events was not in general use, until shortly before the

Christian era, and the references to brass which so frequently occur in the Old Testament have to do either with copper or bronze, and not with alloys of copper and zinc. See further on the early history of copper and copper alloys, W. Gowland, Presidential Address, Institute of Metals, 1912.

Constitution of copper-tin alloys.—Previous to the researches of Matthiessen, it was customary to regard alloys as examples of chemical combination, and most experimenters prepared and studied alloys of definite atomic proportions. An example of this method of working is to be found in the researches of Mallet on the tin-copper alloys (Brit. Assoc. Rep. ix., Construction of Artillery, p. 82). The remarkable change in properties which results when tin and copper are alloyed was used as an argument in favour of the view that definite chemical compounds were produced. The result of more recent investigations, however, tends to show that although in some cases definite atomic combinations actually do occur, still these are comparatively few (see C. H. Desch, Intermetallic Compounds, Journ. Institute of Metals, vol. i. 227); while the other alloys, which constitute the vast majority of those in use, are either solid solutions of a metal in an excess of one of the constituent metals, or are simply mixtures of the two or more metals present in the alloy. The equilibrium of the copper-tin series has been studied by Heycock and Neville, Phil. Trans. 202A, 1; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 209; Shepherd and Blough, J. Phys. Chem. 1906, 10, 630; Haughton and Turner, Jour. Institute of Metals, 1911, part ii.; Ishihara, Chem. Soc. Abstr. 1925, ii. 122; Stockdale, Chem. Soc. Abstr. 1925, ii. 973. For a discussion of the equilibrium diagram, see art. METALLOGRAPHY. In the tin-copper series there is good evidence of the existence of a definite alloy Cu_2Sn containing 61.64 p.c. of copper, while there is considerable reason to believe that Cu_3Sn , containing 68.18 p.c. of copper, also exists. Thus Calvert and Johnson (Phil. Trans. 1858), in investigating the conductivity for heat of these alloys, found a maximum conductivity corresponding to Cu_2Sn , and a minimum conductivity corresponding to Cu_3Sn . Some very interesting determinations by Riche (Compt. rend. 55, 1862, and more completely Ann. Chim. [iv.] 30, 361) show two maxima, corresponding to Cu_2Sn and Cu_3Sn . These experiments have also received strong support from the induction balance curve of Roberts-Austen (Phil. Mag. 1879, [ii.] 57), which shows two distinct breaks corresponding to Cu_2Sn and Cu_3Sn . The determination of relative electric conductivity by Lodge (*ibid.* 1879, [ii.] 554) also show a very distinct maximum at Cu_2Sn and a minimum conductivity corresponding to Cu_3Sn . Laurie examined these alloys from the standpoint of the electro-motive force produced in a standard cell, and concluded that there was very definite evidence of the existence of Cu_2Sn , but failed in this way to obtain any proof of the existence of Cu_3Sn (Chem. Soc. Trans. 1898, 109; 1899, 678).

The evidence in favour of Cu_2Sn is therefore exceedingly strong, while that in favour of Cu_3Sn , though not quite so complete, is still good, and at present there is hardly sufficient evidence

in support of any other atomic combinations. Farther evidence on this point will be found in C. H. Desch's paper on Intermetallic Compounds, *Journal Institute of Metals*, 1, 1909, 227, above cited. These facts, when considered in connection with the known characters of the two alloys in question, give a key to the peculiar characters of the useful tin-copper alloys. The two definite alloys are white, hard, and brittle, and practically all the alloys used in the arts, except speculum metal, contain more copper than $\text{Cu}_3\text{Sn}=68.18$ p.c. Cu. Hence the useful bronzes may be regarded as mixtures of one of two definite alloys with an excess of a solid solution of tin in copper, and these tend to separate more or less completely during solidification. This separation is particularly marked with large castings rich in copper, as in *gun metal*, which was in former times largely used for ordnance. Microscopical examination shows clearly that at the copper rich end of the series of alloys the first constituent to separate out on cooling the fluid alloy is a solid solution of tin in copper. This forms a dendritic, or fir-tree like structure, giving cores which increase in tin from the centre outwards. This copper-rich solid solution is called the α constituent, and is relatively soft and ductile; as the proportion of tin increases harder constituents separate out, the first of them being designated by the symbol β . It is harder and more brittle than α .

Copper retains a maximum of 13.9 p.c. of tin in solid solution, but tin can retain only traces of copper. The compound Cu_3Sn exists in two modifications: the α -form is stable up to 676° , above which the β -form is the stable modification and melts unchanged at 720° . The existence of the compound Cu_3Sn has been definitely proved, and a new compound, Cu_5Sn_3 , has been found in and isolated from alloys containing more than 60 p.c. of tin. It is stable below the eutectic point at 225° in all alloys containing more than 61 p.c. of tin (cf. *J. Soc. Chem. Ind.* 1923, 42, 227A) (O. Bauer and O. Vollenbruck, *Z. Metallk.* 1923, 15, 119-125, 191-195; *J. Chem. Soc.* 1923, 124, ii. 640).

The production of bronze castings requires special precautions, which cannot be described here. For details, see Mallet On the Construction of Artillery, 1856; also Reports of the United States Chief of Ordnance, 1880, 126, 189; 1884, 369. These latter reports contain some important observations with regard to this variety of bronze. It is stated that the best proportion for such purposes is 91 of copper to 9 of tin. This is best cast in a mould or 'chill' of cast iron, and 100 tests of metal so prepared gave an average tensile strength of 21.9 tons per square inch, the maximum being 24.8 tons and the minimum 16.5 tons. It should be mentioned that these values are higher than those usually obtained in this country, where the metal is generally cast in sand moulds.

Composition of principal tin-copper alloys.—The following list is based on that given by Holtzapffel (*Mechanical Manipulation*, i. 270).

Tin, 0.5 p.c. A small quantity of tin is sometimes added to copper for engraver's purposes to give crispness. About 5 p.c. was used by the Romans for pans, and for ancient flexible bronze nails. A similar alloy is now used for bronze coinage and medals, often with

a little of the tin replaced by zinc; also for engineers' soft gun metal or 'brasses.'

7 p.c. Slightly harder alloy; suitable for mathematical instruments, &c.

8.5 p.c. Rather harder; fit for wheels to be cut with teeth.

8-12 p.c. Soft bronze statues of the ancients. These alloys are harder than the preceding, and mark the extreme limit for coinage purposes. Also used for brass ordnance, 9 or 10 p.c. of tin being preferred. Medium engineers' 'brasses' contain 10-12 p.c. of tin.

12-14.5 p.c. Hard bronze of the ancients, used for weapons and tools. These proportions are also used for engineers' hard bearings.

16 p.c. Soft musical bells.

18-20 p.c. Chinese gongs and cymbals.

20 p.c. Small house bells; Indian gongs.

22 p.c. Large house bells.

24 p.c. Limit for large church bells.

About 33 p.c. Speculum metal (v. Phil. Trans. 1840, 503).

About 66 p.c. 'Temper,' an alloy used for addition to tin and lead to harden pewter.

It has already been mentioned that the addition of a small quantity of tin to copper prevents it rolling well when hot, and the addition of a little more tin destroys its malleability when cold. Bronze is tempered by an exactly opposite process from that used in the case of steel, namely, the alloy is heated to redness and then rapidly cooled in water.

Admiralty bronze consists of 88 parts copper, 10 zinc, and 2 tin. It is a very useful and important alloy, which has received considerable attention in recent years. Its properties are largely influenced by temperature of casting and rate of cooling (see Carpenter and Elam, *J. Institute of Metals*, 1918, xix. 155).

For the majority of purposes bronze is melted in crucibles of fireclay or plumbago, the charge being about 90 lbs. For large castings a reverberatory furnace is often employed, though such work is sometimes performed by means of a large number of crucibles. It is recommended that the copper should be well melted and kept in fusion for some time before the tin is added, if strong castings are required. Founders also prefer to use some new metal in every charge, and not merely to re-melt scrap. The oxidation which takes place during melting removes some 3 or 4 parts of copper to 1 of tin; the result is, therefore, that the alloy, which contains about 9 parts of copper to 1 of tin, tends to get poorer in tin by remelting, and due allowance must be made for this loss, even though it may appear to be slight, as small differences in composition often exert a most important influence in tin-copper alloys.

Bronze bearing metal.—According to Dudley (*Jour. Franklin Inst.* 133, 81, 161; *J. Soc. Chem. Ind.* 11, 460), the following composition is very suitable for bearings for locomotives and similar purposes: copper, 77; tin, 8; lead, 15. The presence of lead in bearings very much diminishes the loss of metal caused by wear, and also reduces the local heating of the journals. Phosphor bronze and other varieties of bearing metal for similar purposes to the above often contain about 10 p.c. of lead, and the wearing properties of the alloy is chiefly connected with the proportion of copper and tin to lead. The presence

of tin is necessary in order to obtain a uniform alloy, as lead and copper alone do not unite well. With too much tin the alloy wears more rapidly and becomes more heated. The presence of phosphorus and arsenic gives solidity to the castings, but with suitable proportions of tin and lead, as above, alloys are obtained which wear even better than standard phosphor bronze with the following composition: copper, 79.7; tin, 10; lead, 9.5; phosphorus, 0.8 p.c.

Phosphor bronze is an alloy containing copper and tin in various proportions, and which also contains a small quantity of phosphorus, introduced in the form of phosphor tin. Occasionally small quantities of zinc or lead are also added. The phosphorus varies from a mere trace, added chiefly to ensure soundness in casting, to about 1.75 p.c. with hard alloys. The results of the analyses and mechanical tests of 99 samples of phosphor bronze, as received by the British Admiralty, have been given by A. Philip, *Journ. Inst. of Metals*, 1, 164, while the constitution and microstructure have been dealt with by O. F. Hudson and E. F. Law, *Journ. Inst. of Metals*, iii. 1910, 161. This alloy has met with considerable favour where special power of resisting wear (as with gears and bearings for quick-running machinery) is required. Similar alloys containing manganese, which is added in the form of ferro-manganese, have also met with considerable application, and are known as *manganese bronzes*. **Silicon bronze**, made by the addition of copper silicide, is used for conductivity wire, though many of these so-called bronzes contain very little or no tin. They are usually alloys which closely resemble Muntz metal in composition, and contain about 60 p.c. of copper, 38 p.c. of zinc, and the remainder of specially added elements, such as manganese, and impurities.

The structure of a tin amalgam corresponding approximately with the formula $HgSn$ is found to consist, like that of tin bronzes, of large granules which are built up of a crystalline skeleton solidifying at a higher temperature and of a component still liquid at the ordinary temperature. The crystalline skeleton consists of acicular, tabular, and granular particles, which are comparatively loosely united and are composed of very small crystalline granules. Centrifugation of the amalgam allows of the separation of the liquid component from the crystalline skeleton (F. Hauser, *Zeits. f. Physik*, 1923, 13, 1 and 2, 1-6; *Sci. Abstr.*, 1923, 26, 680-681).

Detection of tin and mercury by means of a spot test.—A black stain is produced if a mercuric chloride test paper is treated with one drop of a solution containing stannous tin and then with one drop of aniline. The stannous ion is the only cation in the five analytical groups that will reduce mercuric chloride to metallic mercury in the presence of aniline, and the test can therefore be used in the presence of any of the ordinary metals. If the tin is present in the stannic condition, it is first reduced to the stannous form by means of magnesium and hydrochloric acid. By using a test paper soaked in a solution of stannous chloride, the same reaction serves for the detection of mercury (Tananaev, *Zeitach. anorg. Chem.*, 1924, 133, 222; *Chem. Soc. Abstr.*, 1924, 19, 871).

Dry assay of tin ores.—Hofman finds that Winkler's method of assaying black tin stone gives results averaging 65.96 p.c., or 1.88 p.c. too low, the figures disagreeing amongst themselves up to over 3 p.c. The process consists of reducing together 5 grms. each of cassiterite and cupric oxide with 15 grms. of black flux, 1.25 grms. of borax, and a little salt as a cover. A similar experiment is conducted without the cassiterite, and the copper obtained in the one case deducted from the alloy in the other gives the amount of tin. The following modifications of this method were tried: increasing the amount of charcoal, using chalk-lined crucibles, omitting the salt and increasing the potassium carbonate, and Rickett's modification of adding argol; but they all gave worse, and in some instances very variable, results.

The iron method—reduction with hæmatite, charcoal, and potassium cyanide or fluorspar—gave unsatisfactory results. The same may be said when a mixture of ferrocyanide and cyanide was used, and also when any of the Cornish methods were employed. So far, with fairly pure cassiterite only two methods have proved satisfactory, viz. the German and the pure cyanide methods. Hofman has attempted to prove which of these two methods gives the best results when the cassiterite is mixed with those minerals likely to be naturally associated with it. The minerals used were quartz, felspar, mica, tourmaline, garnet, and columbite. Mixtures of the purified cassiterite ore with varying proportions of each of these minerals were assayed by both methods, the percentage of tin being calculated on the cassiterite ore present. The charges were so regulated that the flux in the German assay was always equal to three times the quantity of ore plus the mineral, and in the cyanide assay to six times the quantity. In the latter case 4 parts of cyanide were mixed with the ore; 1 part was used to coat the crucible bottom, and 1 part as a cover. In all cases the cyanide method gave more concordant, and less prejudicially affected, results than the other. The results of the German assays fluctuated greatly as the amount of mineral present increased. Thus, in the case of quartz and albite the results were lower as the quantity of mineral was increased, the respective figures being, with 37.5 p.c. of each mineral, 60.7 and 60.2 p.c.; the corresponding cyanide figures being 63.90 and 65.30 p.c. (the real percentage of tin was 67.84). The tin buttons, moreover, in the German assay with albite contained iron, while those by the cyanide process were free, the temperature of fusion being too low to cause decomposition of the albite.

With muscovite, tourmaline, garnet, and columbite the results with the German method were very unreliable, being sometimes too high and very ferruginous, and sometimes too low, varying from 82 p.c. with 50 p.c. of garnet to 46 p.c. with 44 p.c. of tourmaline. The cyanide method gave fairly good results in all the above cases, very little iron getting into the buttons, except in the case of garnet, when the result was 69.89 p.c., with 37.5 p.c. of mineral present. With the same quantity of muscovite, tourmaline, and columbite the assays were respectively 63.3, 64.7, and 66.0 p.c. Consequently, where anything like a true result is

required the cyanide assay is by far the most to be relied upon, and should be employed in cases of buying and selling, although in concentration works, where comparative results and large numbers of assays are required, the question of cost must be considered, and the cheaper German method might be adopted.

Hofman emphasises the importance of properly preparing the ore for assay, and states that the ordinary method of grinding the whole sample to a uniform size is not suited to the tin ores of the Black Hills, chiefly on account of the preponderance of mica. Hence a preliminary sizing is advantageous. The ore while being pulverised is screened through a series of sieves Nos. 20, 40, 60, and 80, the different-sized screenings being then washed. This method gives purer concentrates, and necessitates less loss of cassiterite, as the material has been washed without excessive grinding, which in the present process reduces the brittle cassiterite to a slime, while some of harder associated minerals are only converted into sand. The subsequent treatment of the concentrates mentioned in the first part of the paper is recommended, as the roasting renders the cassiterite more friable and more readily reducible, the assays in some cases showing a difference of 0.5 p.c. between the raw and roasted ores in favour of the latter (Part II, H. O. Hofman, Technol. Quarterly, 3, 261-280; J. Soc. Chem. Ind. 9, 1154; v. Rennie and Derrick, *ibid.* 1892, 662).

For analysis of tin ores by wet methods, cf. Craig, J. Ind. Eng. Chem. 1919, 11, 750; Analyst, 1919, 359.

The following figures, issued by the Imperial Mineral Resources Bureau, show the world's production of tin ore in terms of metal and the world's smelter production of tin in 1921:—

	Output of tin ore. Long tons.	Smelter output of tin. Long tons.
United Kingdom . . .	679	14,000
Nigeria . . .	5,057	—
Swaziland . . .	234	—
Union of South Africa . . .	720	—
Southern Rhodesia . . .	—	4
India . . .	1,362	172
Straits Settlements . . .	1	41,917
Federated Malay States . . .	34,490	—
Unfederated Malay States . . .	1,611	—
Australia . . .	2,650	2,985
Bolivia . . .	18,804	60
Germany . . .	—	4,000 ²
United States . . .	—	10,305
China . . .	11,200	6,134
Siam . . .	6,181	—
Dutch East Indies . . .	26,911	—
Other Countries . . .	900	500
	110,800	95,000

¹ Figures not available.

² Estimated.

In the volumetric determination of tin, stannous chloride solutions may be titrated directly with potassium bichromate, using diphenylamine sulphate as internal indicator, the end-point being marked by the development of a blue colour; or indirectly in a similar manner after addition of excess of ferric chloride (J. G. F. Bruce, Chem. News, 1924,

184, 273; J. Soc. Chem. Ind. 1924, 43, B. 540; Analyst, 1924, 49, 402).

The small quantities of tin present in canned foods are determined volumetrically by titration with standard iodine after preliminary ignition to remove organic matter and precipitation as sulphide. A special apparatus is used in which the tin is reduced to stannous chloride by zinc and hydrochloric acid and titrated as such in an atmosphere of carbon dioxide. By means of an arrangement of three flasks and three 2-way taps the reduced liquid is blown by the carbon dioxide into another flask containing starch solution, the reducing flask is rinsed out by water saturated with carbon dioxide, and the wash-water driven as before to the main solution, which is then titrated with standard iodine, the solution being kept mixed by means of the gas content (E. J. B. Willey, J. Soc. Chem. Ind. 1924, 43, 70 T.; J. Soc. Chem. Ind. 1924, 43, B. 273).

T. T.

COMPOUNDS OF TIN.

According to Paneth and Fürth (Ber. 1919, 52, [B] 2020) an alloy of tin and magnesium Mg_2Sn when acted upon by dilute hydrochloric or sulphuric acid evolves minute quantities of a gaseous *hydride of tin* which is decomposed on passing through a heated glass tube. The gas can be condensed by liquid air and re-evaporated without decomposition.

Oxides. A monoxide, *stannous oxide* SnO , and a dioxide, *stannic oxide* SnO_2 , each of which gives rise to a distinct series of salts, are known, the former acting as a base and the latter acting as either base or acid. Oxides of the composition Sn_2O_3 , $SnO \cdot 3SnO_2$, $2SnO_2 \cdot H_2O$, SnO_2 , and others have also been said to exist, but it is probable that, with the exception of SnO_2 , they are mixtures of the other two oxides.

Stannous oxide SnO is obtained as an olive-brown anhydrous powder, when stannous oxalate is heated out of contact with the air; or as a white precipitate of the composition $2SnO \cdot H_2O$, with evolution of carbon dioxide, when stannous chloride and an alkaline carbonate or hydroxide are mixed in solution. If the precipitate is washed with air-free water, and the lixiviated product is heated in the absence of air, nearly pure dark grey stannous oxide is obtained (Enequist, Eng. & Mining J. 1895, 219; see also Hantzsch, Zeitsch. anorg. Chem. 1902, 30 289).

It may also be obtained as a bluish-black anhydrous powder by heating a mixture of 4 parts of stannous chloride with 7 of sodium carbonate, and lixiviating the resultant mixture of stannous oxide and sodium chloride (Sandall, J. exp. Chem. [i.] 254). The anhydrous oxide may also be obtained from the hydrated form as follows: (1) as a black powder by heating it out of contact with the air; (2) in minute cubes by digestion with acetic acid at 56°; (3) of a brilliant scarlet colour, which becomes brown on rubbing, by evaporating a dilute solution of ammonium chloride containing stannous chloride in solution until the chloride commences to crystallise (Fremy, Berz. J. 24, 133; 5, 172; Ann. Chim. [iii.] 12, 460); (4) as small black shining crystals, which, when heated to 58°, decrepitate and swell up, with production

of soft olive-green laminae, by prolonged digestion with a weak solution of caustic potash at the ordinary temperature (Fremy, *l.c.*). A stronger solution dissolves the oxide and ultimately deposits it in crystals, the deposit from a solution of 4 parts of potassium hydroxide in 10 of water containing potassium stannate and tin, the former produced by absorption of atmospheric oxygen. Fremy also describes various red, black, brown, and other forms of this oxide.

The following method is given by Fraenkel and Snipischsky (Zeitsch. anorg. Chem. 1922, 125, 235): Stannous chloride is dissolved in the least possible amount of hot concentrated hydrochloric acid and sodium hydroxide solution added gradually until the solution reacts alkaline towards phenolphthalein; the resulting milky liquid is then kept boiling in a bath of saturated sodium chloride solution. In a few hours a blue lustrous powder is obtained which is washed and dried (J. Soc. Chem. Ind. 1923, 101 A).

Stannous oxide becomes incandescent, and forms stannic oxide, when heated in the air. It is violently oxidised by nitric acid, and other oxidising agents. Carbon or hydrogen reduces it to metal at a red heat. It dissolves in acids, with production of stannous salts, and in caustic potash or soda, but not in ammonia. The soda solution is employed in calico printing and dyeing under the name *sodium stannite*, and is prepared as described under *sodium stannate*.

Stannous oxide and tin salts are used as reserves under pararosaniline red and other diazo colours (Bull. Soc. Ind. Mulhouse, 1900, 45).

Stannous oxide is sometimes recommended for use in glass and enamel manufacture, but it is too costly, and the results are not very satisfactory.

A so-called *sesquioxide* Sn_2O_3 is obtained as a slimy grey precipitate by the action of recently-precipitated ferric hydroxide on a solution of stannous chloride (v. Fuchs, Kastner's Archiv. für Chemie und Meteorologie, 23, 368; J. pr. Chem. 5, 318; and Berzelius, Pogg. Ann. 28, 443; Berz. J. 13, 110).

This substance is readily soluble in ammonia and in concentrated hydrochloric acid. It does not appear to form definite salts. Its hydrochloric acid solution acts like a mixture of stannous and stannic chlorides. An orange-yellow oxide of the composition $\text{SnO} \cdot 3\text{SnO}_2$ is obtained by digesting metastannic acid in cold aqueous stannous chloride (Fremy, J. Pharm. [ii.] 1, 344).

Hydrated stannous oxide, according to Ditte (Ann. Chim. 1882, [v.] 27, 145), is prepared by adding the hydroxides of sodium or potassium to a solution of stannous chloride, and was described as a brownish-yellow powder of the formula $\text{SnO} \cdot 2\text{H}_2\text{O}$ (cf. Schaffner, Annalen, 1844, 51, 168). According to Bury and Partington (Chem. Soc. Trans. 1922, 121, 1998) the more probable formula is $3\text{SnO} \cdot 2\text{H}_2\text{O}$. It is stable at 110° and slowly loses water on standing under water, forming stannous oxide.

Stannic oxide SnO_2 occurs as *caesilerite* or *stannos*, varieties of which are known as *stream tin*, *wood tin*, *toad's eye*, &c. Daubrée (Ann. Mines, 20, 65) has pointed out that, with the exception of quartz, the minerals most frequently associated with tin ore are fluorine compounds.

Stannic oxide is obtained as an anhydrous

white powder of sp.gr. 6.7122 at 4° (Joule and Playfair, Chem. Soc. Trans. 1849, 1, 128) when tin is heated until it burns in the air. The powder is converted into microscopic quadratic crystals resembling the native oxide when heated in a current of hydrogen chloride (Deville, Compt. rend. 1861, 53, 161; see also Abel, Chem. Soc. Trans. 1858, 119). The oxide may also be obtained in trimetric crystals, and is therefore dimorphous (v. Daubrée, Pharm. Zentr. 1849, 821; Levy and Bourgeois, Compt. rend. 94, 1365.)

It has also been obtained in oblong and rhombic plates of sp.gr. 7.0096 and approaching the form of anatase (Emich, Monatsh. 1893, 14, 345).

Metallic tin may be heated electrically or otherwise to 1700° out of contact with air, and the resulting tin vapour is then burnt in a current of air or oxygen. The stannic oxide thus produced is said to be more homogeneous and in a better state of subdivision for enamelling than the ordinary oxide (Eng. Pat. 9231, 1900).

Stannic oxide is obtained from its ores or from dross, waste, &c., by heating the ore or waste with or without an admixture of coke, chalk, or dolomite and acting upon the liberated molten tin with hot air or oxygen (Fr. Pats. 392805, 392806, 1908; 370640, 1906; 409157, 409485, 1909; also Eng. Pats. 12910, 1899; 28565, 1908; U.S. Pats. 695939, 1912; 780984, 1905; 880873, 1908; J. Soc. Chem. Ind. 1900, 448; *ibid.* 1905, 197; *ibid.* 1908, 335; *ibid.* 1909, 21; *ibid.* 1910, 352; see also *ibid.* 1904, 1239; *ibid.* 1907, 696, 1094).

The dioxide may also be formed by electrolysis a solution of sodium chloride using a tin plate as anode and a platinum plate as cathode (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436).

Stannic oxide is reduced to metal when heated with hydrogen, carbon monoxide, carbon, potassium, or sodium (Doeltz and Graumann, Metallurgie, 1907, 4, 420). It dissolves in fused potassium disulphate, but separates from the mass when treated with water. When fused with sulphur, stannic sulphide is formed, with evolution of sulphur dioxide.

The anhydrous oxide is insoluble in acids, except in concentrated sulphuric acid, with which it forms a syrup decomposed by dilution, with precipitation of the oxide. It dissolves in aqueous or fused alkalis, with formation of stannates.

Treated with hydrochloric acid in presence of tin both stannous and stannic oxides form stannous chloride, and this is used as a method for the recovery of tin from the waste liquors of the dye house (Vignon, Textile Colourist, 18, 333; J. Soc. Chem. Ind. 1893, 762).

With chloroform stannic oxide chiefly reacts thus:



(Renz, Ber. 1906, 39, 249).

When heated with hypophosphorous acid over a Bunsen flame for 30 mins., *stannous phosphate* or *pyrophosphate*, is formed; since these are readily soluble in hydrochloric acid, stannic oxide can thus be separated from silica which is not affected by this treatment (Dott, Pharm. J. 1908, 81, 585).

Stannic oxide, in the form of *pure powder*,

which is a mixture of tin and lead oxides, or a stannate of lead, is used as a polishing material for glass. To avoid any possibility of danger from the use of this powder it has been recommended to mix 1 part of putty powder with 2 of metastannic acid (Gueroult, *Compt. rend.* 1892, 115, 757). Stannic oxide is an important factor in the manufacture of glazes and of enamels, the latter assuming an intensely white colour on the addition of a small quantity of the oxide. It is also the best material known for making opaque glaze or glass, and is employed in glaze brick and tile manufacture (Enequist, *l.c.*; Burt, *Trans. Amer. Ceramic Soc.* 1902, 4, 139).

Tin oxide is also said to be useful for the purification of water (*J. Soc. Chem. Ind.* 1894, 56).

Perstannic oxide SnO_5 . W. Spring (*Bull. Soc. chim.* [iii.] 1, 180) has obtained a substance of the composition $\text{H}_2\text{Sn}_2\text{O}_7$, probably a hydrate of this oxide, by dialysing the turbid solution obtained by adding hydrated barium peroxide in excess to a solution of stannous chloride in hydrochloric acid, and evaporating the solution of the colloid on the water-bath.

Stannic acids. Two isomeric stannic hydroxides are known, each of which behaves as an acid and exists in various degrees of hydration between the limits H_2SnO_3 and H_4SnO_4 . They are both colloidal modifications of hydrated stannic oxide, only differing in the size of their particles, the α -acid consisting of relatively small, the β -acid of relatively large particles (Mecklenburgh, *Zeitsch. anorg. Chem.* 1909, 64, 368; 1912, 74, 207; 1914, 84, 121; *see also* Fremy, *Ann. Chim.* 1844, [iii.] 12, 466; *ibid.* 1848, 23, 385; Musculus, *Compt. rend.* 1867, 65, 961; Vignon, *ibid.* 1889, 103, 1049; *ibid.* 109, 372; Kleinschmidt, *Monatsh.* 1918, 39, 149; Kreis, *Schweiz. Chem. Zeit.* 1919, 389; Tian, *Compt. rend.* 1921, 172, 1402; Collins and Wood, *Chem. Soc. Trans.* 1922, 441).

Stannic acid, α - or ortho-stannic acid H_2SnO_3 , is obtained by precipitating stannic chloride with ammonia, or by addition of calcium or barium carbonate to a solution of stannic chloride in quantity insufficient to precipitate the whole.

It is also formed by treating an alkali stannate with a mineral acid (Kühl, *Pharm. Zeit.* 1908, 53, 49) and by electrolysis of an alkali chloride, nitrate or sulphate solution, using platinum as cathode and tin as anode (Lorenz, *Zeitsch. anorg. Chem.* 1896, 12, 436), and by other methods (Engel, *Compt. rend.* 1897, 125, 851; Neumann, *Monatsh.* 12, 518; Coppadoro, *Chem. Zeit.* 1907, 31, Rep. 336).

Its composition varies with its mode of drying, and it is converted into anhydrous SnO_2 at 630°–655°. It forms a gelatinous substance, or white voluminous, amorphous precipitate, slightly soluble in water and of acid reaction. When dried spontaneously, it forms translucent lumps, resembling gum arabic.

When boiled with phenosafranine in the presence of sodium sulphate, stannic acid forms an intense red lake; metastannic acid under the same conditions only forms a pale rose tint (Vignon, *Compt. rend.* 1891, 112, 580).

A colloidal stannic acid is known (*v. Graham, Phil. Trans.* 151, 213; Van Bemmelen, *Rec. trav. chim.* 7, 87; Schneider, *Zeitsch. anorg.*

Chem. 1894, 5, 83; *ibid.* 1900, 23, 111; Lottermoser, *J. pr. Chem.* 1899, [ii.] 59, 489; Biltz, *Ber.* 1902, 35, 4431). It can be prepared by the dialysis of an alkali solution of tin chloride or of a hydrochloric acid solution of potassium stannate. Colloidal stannic acid is the most important constituent of purple of Cassius (*v. GOLD PURPLE*).

Stannic acid forms a large and important series of salts, most of which are crystalline. The alkaline stannates are soluble, and may be prepared by dissolving the precipitated oxide in the alkaline hydroxide. The others are mostly insoluble, and are best obtained by double decomposition. The potassium and sodium salts are the only ones of technical importance. The stannates have been investigated by Fremy (*Ann. Chim.* 1844, [iii.] 12, 462; 1848, [iii.] 23, 393), Moberg (*J. pr. Chem.* [i.] 28, 230), Marignac (*Ann. de Mines*, [iii.] 15, 277), Ordway (*Amer. J. Sci.* [ii.] 40, 173), Ditte (*Compt. rend.* 1882, 94, 1114; 1883, 96, 701), and Bellucci and Parravano (*Atti R. Accad. Lincei*, 1904, [v.] 13, ii. 324, 339; *ibid.* 1905, 14, i. 457).

According to the last-mentioned authors they are isomorphous with the plumbates and platinates.

Sodium stannate Na_2SnO_3 usually occurs in six-sided tables of the composition $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ (Moberg, Marignac, Ordway, *l.c.*), which are less soluble in hot than in cold water. According to Ordway, 100 parts of water dissolve 67.4 parts at 0°, and 61.3 parts at 20°.

According to Bellucci and Parravano, the water is present not merely as water of crystallisation but in a more intimate form, namely, as $\text{Na}_2\text{Sn}(\text{OH})_6$.

Crystals of the above composition are deposited from a hot alkaline solution, but the salt may also be obtained with 8, 9, or 10 molecules of water. The form crystallising with 9 molecules is said to be obtained in oblique rhombic prisms by recrystallising the commercial salt (Jonas, *Chem. Zentr.* 1865, 607); while, according to Haefely (*Dingl. poly. J.* 144, 66), crystals of the composition $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ are deposited from hot concentrated solutions of 1.3 sp.gr., but re-dissolve on cooling to a solution of 1.35 sp.gr., from which crystals containing 8 molecules of water are gradually deposited.

Copper is readily tinned by immersion in a solution of the salt.

Sodium stannate is largely used, under the name of 'preparing salt,' as a mordant in dyeing and calico-printing, the fabric being first passed through a solution of the stannate, and then through weak sulphuric acid, which precipitates the hydrated oxide on the fibres.

For preparing this salt on the large scale, the original processes patented by J. Greenwood, J. Mercer, and J. Barnes (*Eng. Pat.* 10757, 1845), J. Young (*Eng. Pats.* 12359, 1848; 12744, 1849), and Haefely (*Eng. Pat.* 603, 1854), are still used with some modifications. A number of other processes are mentioned in the list of patents relating to tin salts (*infra*).

The process of Greenwood, Mercer, and Barnes consists in heating 22 lbs. of caustic soda in an iron crucible until evolution of water ceases, and then adding 8 lbs. of sodium nitrate and 4 lbs. of sodium chloride, followed, when the mass is nearly fused, by 10 lbs. of feathered

tin, with constant stirring until deflagration ensues. The mixture then becomes white hot, and pasty, and is wholly converted into the stannate.

For preparing sodium 'stannite' a mixture of 4 lbs. of sodium chloride, 1 gallon (13.5 lbs.) of caustic soda, 1 lb. of sodium nitrate, and 4 lbs. of tin is heated in an iron crucible, and the dry powder finally obtained is stirred so long as ammonia is evolved.

Young's processes—most of which are described below—consist mainly in the preparation of the stannate directly from the ore, thus avoiding the cost of obtaining and re-oxidising the metal.

By one process the native or prepared oxide is boiled in an iron pot with a quantity, varying with the tin value of the ore, of 22 p.c. soda lye, the temperature being gradually raised to about 600°F., at which combination takes place. When the operation is completed, which is ascertained by removing a portion and seeing how much dissolves, the mass is cooled in another vessel and is dissolved, filtered, or decanted, and recrystallised or sold in solution.

In another process, the ore is heated to redness with one and a half parts of sodium nitrate in a current of steam with constant stirring. The stannate is produced, with evolution of nitrous fumes and nitric acid. The nitrate may be replaced by 1 part of salt, hydrochloric acid being then obtained as the by-product.

'Stannite' of soda is obtained by heating the metal with its own weight of caustic soda, with constant stirring, or by electrolysis a concentrated solution of sodium hydroxide, using a rotating tin anode and a platinum cathode. The current must not be too strong, and the solution must be protected from oxidation by a stream of hydrogen (Goldschmidt and Eckardt, *Zeitsch. physikal. Chem.* 1906, 56, 385). The solution of the stannite may be used in dyeing and printing operations as it is, or it may be converted into stannate, with precipitation of tin as a black powder, by boiling.

The stannate may be obtained direct from the metal by heating a mixture of 20 parts of tin, 16 of sodium hydroxide, and 3 of manganese dioxide to redness, with constant agitation and free exposure to the air. The dioxide appears to act as a carrier of oxygen, and is obtained unchanged at the end of the operation.

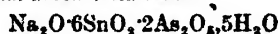
In another process, calcium stannate is obtained by roasting in a reverberatory furnace a mixture of the ore with slaked lime. The product is treated with sufficient hydrochloric acid to precipitate the tin as oxide, but not to redissolve any of it, and the precipitate is dissolved in boiling soda lye. The salt may also be obtained by boiling barium stannate, obtained similarly to the lime salt, with sodium sulphate, until all the barium is converted into sulphate.

Haeffely's process consists in the preparation of a solution of 'plumbate of soda' by dissolving 54 lbs. of red lead or 70-80 lbs. of litharge in a solution of 45 lbs. of caustic soda of 70°Tw. The solution is diluted, and 16 lbs. of tin is suspended in it while boiling, so that in 4 or 5 hours the lead is obtained as a deposit, which may be readily oxidised for re-use, while sodium stannate remains in solution.

The following process has also been employed (*Chem. Zeit.* 9, 851):—Ten boilers, arranged in horseshoe form, and each having a central tube, the lower end of which forms a perforated funnel, are almost filled with granulated tin, and six of them are charged with soda lye of 15°Bé. The liquor is drawn off from each, after a suitable amount of boiling, through a siphon passed into the central tube, and is passed from boiler to boiler until of 30°Bé, when it is allowed to settle in a tank. For preparing 'sodium stannate liquor' enough common salt is dissolved in the solution to reduce the proportion of tin to 5 p.c.; and for producing the solid the liquid is evaporated and calcined, and mixed with enough sodium chloride to reduce the tin to 42 p.c.

Sodium stannate is used in order to render cotton goods, such as flannelette, fireproof (W. H. Perkin). The flannelette is impregnated with a solution of sodium stannate of about 45°Tw., squeezed, dried on heated copper drums, passed through a solution of ammonium sulphate of about 15°Tw., in order to precipitate tin oxide, again squeezed, dried, and finished in the usual manner. The tin oxide is probably present in actual combination with the fibre, for the fire-proofing is not destroyed by repeated washing with hot water and soap.

A sodium arsenio-stannate



occurring in shining needles, is sometimes used instead of the ordinary stannate, and is said to give brighter colours and to be more economical. It is prepared by adding nitric acid to a boiling solution of sodium stannate and sodium arsenate, and treating the resulting precipitate of $2\text{SnO}_2 \cdot \text{As}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ with excess of soda (v. Haeffely, *Dingl. poly. J.* 140, 290; J. Mercer and W. Blythe, *Eng. Pat.* 12807, 1849). In the latter process a sodium phospho-stannate is also employed for the same purposes. Another sodium arsenio-stannate



has been obtained by Prandtl (*Ber.* 1907, 40, 2133).

Potassium stannate K_2SnO_3 is obtained similarly to the sodium salt, and is sometimes employed in dyeing and calico-printing. It crystallises from spontaneously evaporated solutions in transparent oblique rhombic prisms of the composition $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ (Marignac, *Ann. de Mines*, [v.] 15, 277; Moberg, *J. pr. Chem.* [i] 28, 230; Ordway, *Amer. J. Sci.* [ii.] 40, 173). It becomes anhydrous when heated to redness.

Potassium stannate is insoluble in alcohol, but dissolves in water to an alkaline solution, 100 parts of water dissolving 106.6 parts at 10° and 110.5 parts at 20° (Ordway, *l.c.*).

Cupric stannate CuSnO_3 has been employed as a green pigment. It is prepared for this purpose by precipitating sodium stannate with copper sulphate, or by addition of a solution of 118 parts of tin in *aqua regia* to a solution of 250 parts of copper sulphate, with subsequent addition of sodium hydroxide in excess.

Chromium-tin compounds. A so-called chromium stannate or 'pink colour' used for producing a blood-red colour in pottery glass,

is prepared by heating a mixture of 10 parts of stannic oxide, 34 parts of calcium carbonate, parts of silica, 1 part of alumina, and 3-4 part of crystallised potassium chromate for several hours in a closed crucible. The red compound produced gives a fine rose-coloured product when washed with dilute hydrochloric acid.

A substance known as *mineral lake*, possessing a fine lilac colour, is used in colouring paper-hangings and for oil painting. It consists of mixture of chromium oxide and excess of stannic oxide, and can be prepared by igniting together 1 part of the former with 50 of the latter (Leykauf, J. pr. Chem. 1892, 19, 127), or by dissolving potassium chromate in 5 or 6 parts of water, and adding this solution to a solution of stannous chloride until precipitation ceases. The damp, washed precipitate is ground with half its volume of nitre, and dried, and the finely-powdered mixture is thrown in small portions into crucible heated to redness and containing some potassium nitrate. After pouring off the supernatant fused salt, the pale-yellow residue is washed free from alkali, and is calcined at a strong heat in a luted crucible until it becomes dense and acquires the desired colour.

A series of 'pinks' have been prepared by moistening equal portions of calcium stannate or mixtures of tin dioxide and whiting with varying proportions of a solution of ammonium dichromate. The mixtures are then dried, fired, cooled, and washed with hot water. The products all contain a more or less constant quantity of chromium, and it is probable that they consist of the colouring agent, chromium oxide, resting on a base of stannic oxide (Lethbridge, Trans. Engl. Ceramic Soc. 1903-1904, 9; see also Hull, Trans. Amer. Ceramic Soc. 1902, 4, 230).

Stannates of many other metals and thio-stannates have also been obtained.

The powdery product of oxidation of tin with hot nitric acid, commonly described as metastannic acid, is a nitrate of metastannic acid, which on washing with water gives rise to metastannic acid as a secondary hydrolytic product. Metastannic acid obtained by the action of nitric acid (sp. gr. 1.40) on tin and careful washing with water, dried in air at ordinary temperature, has the composition $5\text{H}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$. It loses its water *in vacuo* over sulphuric acid. It is an amorphous powder, combining with hydrochloric and sulphuric acids with development of heat forming easily hydrolysable compounds. The action of hydrochloric acid on metastannic acid yields a stannyl chloride $5\text{SnO}_2 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ or $\text{Sn}_2\text{O}_3(\text{OH})_2\text{Cl}_2$. According to Weiser (J. Phys. Chem. 1922, 26, 654), stannic and metastannic acids are not acids, but are hydrated stannic oxides, the composition and properties of which are determined by conditions of formation. There are no definite hydrates of stannic oxide. Hydrated stannic oxide adsorbs colloidal gold, silver, and platinum, forming purple masses, the most common of which is the purple of Cassius.

Application to purple of Cassius of Debye and Scherrer's X-ray method yields an impression, analysis of which shows that this substance does not contain gold in chemical combination, but consists of a mixture of colloidal gold and colloidal stannic acid (A. Huber, Phys. Zeits. 1924, 25, 35; Sci. Abstr. 1924, 27, 457).

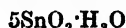
It is also obtained by the ready isomerisation of stannic acid, as when a hydrochloric or hydrobromic acid solution of the latter is allowed to stand (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 376).

It is insoluble in ammonia, except when freshly precipitated from a cold solution of a metastannate by an acid, but dissolves in alkaline hydroxides and carbonates, with formation of metastannates.

A colloidal metastannic acid is known (v. Graham, Phil. Trans. 151, 213; Van Bemmelen, Rec. trav. chim. 7, 87; Liebschutz, Chem. News, 1910, 102, 213; Kreis, Schweiz. Chem. Zeit. 1919, 389.)

The meta-acid is said to have a tendering effect on silk fibres (Heermann, Färber-Zeit. 1908, 19, 318; Bayerlein, *ibid.* 1908, 18, 241).

The salts of metastannic acid appear to indicate that the acid has the formula



The metastannates are difficultly crystallisable. When strongly heated, they decompose into stannic oxide and the base. Potassium metastannate $5\text{SnO}_2 \cdot \text{K}_2\text{O} \cdot 4\text{H}_2\text{O}$ is a strongly alkaline salt obtained by dissolving the acid in potash. It is precipitated from aqueous solution by a neutral alkaline salt or by ammonium chloride. Sodium metastannate



is a slightly soluble granular salt obtained like the potassium salt. A hard gummy precipitate of the composition $\text{Na}_2\text{Sn}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$ is obtained by addition of caustic soda to a solution of the above compound of hydrochloric acid and metastannic acid.

Thiometastannates are also known.

Perstannic acid $\text{HSnO}_4 \cdot 2\text{H}_2\text{O}$ is formed when stannic acid is treated with excess of 30 p.c. hydrogen peroxide and the mixture heated to about 70° . On heating to 100° it yields the acid $\text{H}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The alkali stannates when similarly treated form the salts corresponding to these acids (Tanatar, Ber. 1905, 38, 1184). When concentrated alkali stannates are electrolysed at low temperature with a low current density they also form perstannates (Coppadoro, Gazz. chim. ital. 1908, 38, i. 489, and *l.c.*).

Salts of tin with oxyacids. These salts, although numerous, are of little technical importance, but a number of solutions containing them are used in dyeing and calico-printing. Stannous sulphate SnSO_4 is obtained as a crystalline powder by evaporating *in vacuo* a solution of tin or stannous hydroxide in dilute sulphuric acid. Stannic sulphate $\text{Sn}(\text{SO}_4)_2$ is obtained as a white salt, soluble in dilute sulphuric acid but mostly precipitated on dilution, by dissolving the hydroxide in sulphuric acid. According to Litte (Compt. rend. 1887, 104, 172), a solution of stannic hydroxide in warm dilute sulphuric acid (1-8) deposits, on concentration, first radiating needles, then rhomboidal lamellae, and finally hexagonal prisms, all colourless and all possessing the composition $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. He has obtained the same product by the action of sulphuric acid on metastannic acid. The crystals deliquesce to a clear liquid. The solution is decomposed, on dilution, with precipitation of the hydroxide. A number of double tin sulphates are known (Weinland and Köhl, Ber.

1906, 39, 2951; *Zeitsch. anorg. Chem.* 1907, 54, 244). *Stannous nitrate* $\text{Sn}(\text{NO}_3)_2$ is obtained by dissolving tin or stannous hydroxide in dilute nitric acid (R. Weber, *J. pr. Chem.* [ii.] 26, 121; Walker, *Chem. Soc. Proc.* 1893, 114; *Engel. L.c.*; Kleinschmidt, *Monatsh.* 1918, 39, 149).

Metastannic nitrate $5\text{SnO}_2 \cdot 2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Sn}_2\text{O}_5(\text{OH})_2(\text{NO}_3)_2$ is prepared by the action of hot nitric acid on tin; the compound obtained from tin and cold nitric acid consists of a mixture of stannyl nitrate $\text{SnO}(\text{NO}_3)_2$ and metastannic nitrate.

A basic salt of the composition $2\text{SnO} \cdot \text{N}_2\text{O}_5$ is obtained as a white crystalline precipitate by adding a solution of sodium carbonate to the neutral salt in quantity insufficient for complete precipitation. It may also be obtained by digesting the normal salt with stannous hydroxide. It deflagrates at 100° , or on friction. *Stannic nitrate* $\text{Sn}(\text{NO}_3)_4$ crystallises in silky tablets from a solution of stannic hydroxide in nitric acid.

It is also formed by dissolving tin in 70 p.c. nitric acid (Montemartini, *Gazz. chim. ital.* 1892, 22, 384). Even at the ordinary temperature it slowly changes into the meta-salt, and for this reason the white bulky precipitate which it yields with aqueous sodium hydroxide may not dissolve completely in an excess of the reagent; at 45° the change in the stannic nitrate is so rapid that the solution suddenly gelatinises; the transformation is complete by prolonged heating at 100° .

The so-called 'nitrate of tin' or 'physic' used by dyers is a mixture of stannous and stannic chlorides (*v. Stannous chloride, infra*). A solution of tin in nitric acid is, however, also used in dyeing (*v. Crookes, Handb. of Dyeing and Calico Printing*, 1874, 527).

Stannous sulphide SnS is obtained as a tough, crystalline, bluish-grey fusible mass by heating tin with sulphur, or in crystalline scales by fusing the sulphide so obtained with stannous chloride and treating the product with dilute hydrochloric acid. The crystalline sulphide may also be obtained by heating the amorphous form in the electric furnace (Mourlot, *Compt. rend.* 1897, 124, 768). It is obtained as a brown powder, which blackens on drying, by precipitating stannous chloride with sulphuretted hydrogen.

Stannous sulphide is insoluble in normal ammonium sulphide, but dissolves in the yellow sulphide and in alkaline polysulphides (*v. Ditte, Compt. rend.* 1882, 94, 1419), and, with evolution of sulphuretted hydrogen and formation of stannous chloride, in hot hydrochloric acid. Hydrogen chloride acts similarly on the warmed, but not on the cold, sulphide (Ditte, *ibid.* 1883, 97, 42).

Stannous sulphide is sometimes soluble, at other times insoluble, in sodium hydroxide, the cause of this variation being unknown (Perkin, *J. Soc. Chem. Ind.* 1901, 425).

Pure stannous sulphide has m.p. 880° (Pélabon, *Compt. rend.* 1906, 142, 1137). It is slightly radioactive (Campbell, *Proc. Cambridge Philos. Soc.* 1906, 13, 282).

Orthorhombic crystals of stannous sulphide are occasionally met with in tin furnaces, and were supposed at one time to be an allotropic form of tin (*cf. Spencer, Min. Mag.* 1921, 19, 113).

Stannic sulphide SnS_2 cannot be prepared by simply heating tin and sulphur together, because the heat generated is sufficient to reduce the disulphide to monosulphide, but it may be so obtained when sufficient ammonium chloride or other volatile substance is present to moderate the action. Woulfe (*Phil. Trans.* 1771, 61, 114; also Gmelin's *Handbook*, 5, 79) describes a number of methods of preparing this compound, which is used as a bronze powder for bronzing articles of gypsum, wood, &c.

Various mixtures of tin chloride and sulphur, or tin, sulphur, and ammonium chloride, or tin amalgam or tin sulphide with sulphur and ammonium chloride, are heated in retorts or covered crucibles, at first gently for a few hours, then more strongly, but not quite to redness. On cooling the greater portion of the sulphide is at the bottom, but the purer and finer crystals are found sublimed at the top.

Crystalline stannic sulphide, sp.gr. 4.425, is often known as 'Mosaic gold,' *aurum mosaicum*, or *musivum*. For a reddish shade, 50 grms. of 50 p.c. tin amalgam, 25 of crystallised stannous chloride, 35 of ammonium chloride, and 35 of sulphur are finely powdered together and ignited gradually in a glass retort covered with asbestos, in the flame of a large blow-pipe, which is moved about periodically. During the operation the colour of the mass should be dark brown. If it becomes black owing to the formation of stannous sulphide, the flame should be lowered. For yellowish shades, 50 grms. of crystallised stannous chloride and 25 grms. of flowers of sulphur are employed. The yield is 57 p.c. of the theoretical (Langutt, *Zeitsch. angew. Chem.* 1897, 557). V. GOLD, MOSAIC.

When heated, stannic sulphide sublimes, with partial decomposition into sulphur and stannous sulphide. It dissolves readily in alkalis, but not in acids, except *aqua regia*. It fuses in a current of chlorine, and absorbs 6 molecules of the gas, forming a yellow crystalline compound of the composition $\text{SnCl}_4 \cdot 2\text{SnCl}_2$ (Rose, *Pogg. Ann.* 42, 517). When heated with iodine in a current of carbon dioxide it gives a brown, crystalline, fusible mass of the composition $\text{SnS}_2 \cdot \text{I}_2$ (Schneider *J. pr. Chem.* [i.] 79, 419).

The dirty-yellow precipitate obtained by passage of sulphuretted hydrogen through a solution of a stannic salt consists of a mixture of stannic sulphide and stannic hydroxide; this dissolves in alkaline sulphides, with formation of thiostannates (Kühn, *Annalen*, 1852, 84, 110), and also in alkalis and hydrochloric acid. Ditte (*Compt. rend.* 1882, 95, 641) describes several double sulphides or thiostannates and also seleniothio-stannates.

Hydrogen chloride or bromide convert the sulphide into the corresponding halide (Kelley and Smith, *Amer. Chem. J.* 1896, 18, 1096).

When stannic sulphide is allowed to remain in contact with ammonia, filtered, and the filtrate acidified, a white mass of an amorphous stannic sulphide is formed. It dissolves readily in ammonia to an orange-red solution, and becomes yellow on drying (Schmidt, *Ber.* 1894, 27, 2739; *Chem. Zentr.* 1907, i. 397; *Materne, ibid.* 1906, ii. 557; Lang and Carson, *J. Soc. Chem. Ind.* 1902, 1018). When dried in air it loses a little sulphur and becomes dark brown, hard, and brittle. This sulphide behaves like a

colloidal sulphide. Colloidal stannic sulphide has been obtained (Spring, Ber. 1883, 16, 1142; Schneider, Zeitsch. anorg. Chem. 1894, 5, 83; see also Biltz, Chem. Zentr. 1904, i. 1040).

Tin sesquisulphide Sn_2S_3 is obtained by gentle ignition of 3 parts of stannous sulphide and 1 of sulphur in a retort. It forms a yellowish-grey mass of metallic lustre (Antony and Niccoli Gazz. chim. ital. 1892, 22, ii. 408). A sub-sulphide, Sn_3S_2 , of a grey colour, and crystalline, has been observed to occur (Epprecht, Chem. Zeit. 1915, 39, 341).

Stannous selenide SnSe is obtained with incandescence when selenium is heated with tin as a light-grey lustrous body of crystalline fracture, not reducible by hydrogen. It is obtained as a dark-brown precipitate, which becomes nearly black on drying, by passing seleniuretted hydrogen into stannous chloride solution. It dissolves in alkalis and alkaline sulphides (v. Uelsmann, Annalen, 1860, 116, 124; Pélahor l.c.).

Stannic selenide SnSe_2 is obtained by passing seleniuretted hydrogen into stannic chloride solution as a yellowish-red precipitate which dries to a brown powder, soluble in caustic alkalis and alkaline sulphides, and forming stannous selenide when heated in hydrogen.

According to Little (Annalen, 1859, 112, 213), it is obtained as a tin-white, lustrous, easily-fusible mass, unaffected by hydrochloric acid, but readily decomposed by nitric acid, by heating tin in selenium vapour. Ditte (Compt. rend. 1882, 95, 641; *ibid.* 1887, 104, 174) describes some double selenides corresponding with the thiostannates (v. *Stannic sulphide*).

A telluride is also known.

Stannous chloride SnCl_2 is obtained in the anhydrous condition by heating tin in hydrogen chloride, or by heating a mixture of equal weights of 'feathered' (i.e. granulated) tin or filings and mercuric chloride; and in monoclinic prisms of the composition $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (O. Henry, J. Pharm. 12, 134) by evaporating a solution of tin in hydrochloric acid.

Stannous or stannic chloride may be obtained as desired by the following process: Stannous chloride, formed by the action of a solution containing chlorine on tin, is subjected to the action of a gaseous or fluid mixture containing free chlorine, hydrochloric acid, and air or oxygen (Young, J. Amer. Chem. Soc. 1901, 23, 119, 450). Stannic chloride is thus formed which when made to react with tin reforms stannous chloride (U.S. Pats. 810454, 810455, 810456, 810897, 1906; Df. R. P. 184494). For other methods, see D. R. PP. 176456, 176457, 181876, 188018.

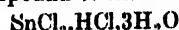
The crystals melt at 40° , and at 100° lose most of their water, together with a little hydrochloric acid. When dried *in vacuo*, or over sulphuric acid, they become anhydrous.

The anhydrous chloride fuses at 249.3° to an oil which boils at $617^\circ\text{--}628^\circ$ (Carmelley and Carleton Williams, Chem. Soc. Trans. 1879, 563), or, according to Biltz and V. Meyer (Ber. 1888, 21, 22), at 606.1° . The anhydrous chloride is sometimes called 'butter of tin,' although that term is usually applied to the hydrated tetrachloride. Stannous chloride is soluble in water and alcohol. On dilution, the aqueous solution becomes turbid, from precipitation, with separation of hydrochloric acid, of a basic chloride

$2\text{SnO} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, which is also formed when the clear solution is exposed to the air. Mallet (Chem. Soc. Trans. 1879, 524) has observed a gelatinous deposit of the composition $\text{SnO}_2 \cdot \text{HCl}$, to which he has applied the term *chlor-stannic acid*, in a solution of stannous chloride after long standing. Donath (Rep. Anal. Chem. 7, 77) considers that this compound is produced, together with stannic hydroxide, by the action of light on aqueous stannous chloride.

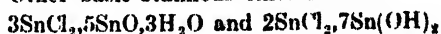
Keller (J. Amer. Chem. Soc. 1917, 39, 2354) found a crystalline deposit of $\text{SnCl}_2 \cdot \text{SnO}$, in cavities in a piece of tin found in an aboriginal cemetery in Florida.

R. Engel (Compt. rend. 1888, 106, 1398) has obtained a compound of the composition



which he calls *chlorostannic acid*, by passing chlorine over the hydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The crystals fuse to a clear liquid having the above composition, and depositing, when cooled to -40° , slender silky needles which melt at about -27° . According to Ditte (*ibid.* 1883, 97, 42), however, the liquid contains a chloride of the composition $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, which is also formed by the action of concentrated hydrochloric acid on the chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Other basic stannous chlorides are



(Carson, J. Amer. Chem. Soc. 1919, 41, 1969).

When stannous chloride is electrolysed crystalline tin can be obtained (Saposhnikoff, J. Russ. Phys. Chem. Soc. 1905, 37, 153).

Stannous chloride forms crystalline double chlorides with the alkalis (v. Benas, Chem. Zentr. 1884, 957, forming salts of the composition $\text{SnCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$). Similar compounds are formed with NH_4Cl (Rimbach and Fleck, Zeitsch. anorg. Chem. 1915, 94, 139). It absorbs dry ammonia, with formation of a compound of the composition $\text{SnCl}_2 \cdot \text{NH}_3$, and also $\text{SnCl}_2 \cdot 2\text{NH}_3$ (Naumann, Ber. 1910, 43, 313).

A third compound, $3\text{SnCl}_2 \cdot 2\text{NH}_3$, is formed by the action of gaseous ammonia on stannous chloride between 120° and 300°C . It is a crystalline mass of reddish-brown colour, powerfully double-refractive, and appears to be the most stable of the compounds of ammonia and stannous chloride (Sofianopoulos, Compt. rend. 1911, 152, 865).

Stannous chloride is soluble in alcohol and in ether, the latter solution gives a brownish-red ring when added to hydrochloric acid containing 1/50 mgrm. of arsenious acid (Jong, Zeitsch. anorg. Chem. 1902, 41, 596).

Like other stannous salts, stannous chloride is a strong reducing agent and is employed as such, both for the reduction of organic and inorganic compounds. It is also used in the analysis of a number of substances (Henriet, Compt. rend. 1901, 132, 966; Weil, *ibid.* 1902, 134, 115).

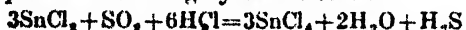
A small quantity of stannous chloride is said to increase the yield of alcohol in fermentation processes; it also accelerates the revivification of the yeast sown in must, and cultures taken from the yeast so formed retain a similar property for a certain length of time (Gimel, Compt. rend. 1908, 147, 1324).

Stannous chloride and other stannous salts

are largely used in dyeing and calico-printing under the name 'tin-salts' or 'tin crystals' (Dreher, *Färber-Zeit.* 7, 145; Reisz, *ibid.* 221, 222; Binder, *Bull. Soc. Ind. Mulhouse*, 1900, 92; Paterson, *J. Soc. Dyers Col.* 1906, 22, 188; Coberti, *J. Soc. Chem. Ind.* 1899, 829).

Stannic chloride SnCl_4 was first prepared by Libavius in 1605, who obtained it by distilling a mixture of tin or its amalgam with excess of mercuric chloride; he termed the product *Spiritus argenti vivi sublimati*. It may also be prepared by the action of chlorine (Lorenz, *Zeitsch. anorg. Chem.* 1895, 10, 44; Beckmann and Geib, *ibid.* 1906, 51, 96); or phosphorus pentachloride on tin (Goldschmidt, *Chem. Zentr.* 1881, 489); or by the action of chloroform on stannic oxide (Renz, *Ber.* 1906, 39, 249). Technically, it is generally prepared by the action of chlorine or hydrochloric acid on tin-plate waste or tin waste residues from dye works and a large number of patents have been registered for this purpose (see *Fr. Pats.* 371067, 1906; 392615, 401125, 405851, 406300, 1909; Heermann, *Färber-Zeit.* 1907, 18, 34; *U.S. Pats.* 884756, 877261, 877248, 1908; 976990, 958986, 1910; *D. R. P.* 222838; *J. Soc. Chem. Ind.* 1907, 253; *ibid.* 1908, 160; *ibid.* 1909, 21, 1087; *ibid.* 1910, 424, 1105; see also *U.S. Pats.* 883140, 883141, 1908; *Fr. Pats.* 386594, 388089, 1908).

Stannic chloride may also be prepared by the action of sulphur dioxide upon stannous chloride in presence of strong hydrochloric acid



(Smythe and Wardlaw, *Proc. Durham. Phil. Soc.* 1914, 5, 187).

The chloride distils over as a colourless mobile liquid, boiling at 113.89° at 760 mm. pressure (Thorpe, *Chem. Soc. Trans.* 1880, 37, 331), and solidifying at -33° to small white crystals (Besson, *Compt. rend.* 1889, 109, 940).

The liquid has sp.gr. 2.2788 at $0^\circ/4^\circ$ (Thorpe, *l.c.*), and, owing to its high refractive index, presents a very brilliant appearance.

When exposed to the air, it emits dense white fumes, and is finally converted into a crystalline hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Lewy, *Compt. rend.* 1845, 21, 369), which is also obtained, with evolution of heat, by mixing stannic chloride with one-third its weight of water. This hydrate is sometimes known as 'butter of tin,' or, by the dyers, as 'oxymuriate of tin.' Hydrates of the composition $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ are also known. For the sp.gr. of various solutions of this salt, see Heerman (*Chem. Zeit.* 1907, 31, 680).

On hydrolysis, it first forms the intermediate compound SnCl_3OH , and then stannic acid; by alcoholysis it gives the compound SnCl_3OEt (Pfeiffer, *Ber.* 1905, 38, 2466; von Biron, *J. Russ. Phys. Chem. Soc.* 1906, 37, 963).

Stannic chloride forms crystalline double chlorides, sometimes called *chloro-stannates* or *stannichlorides* with the alkaline chlorides (Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, v. 13, ii. 307; von Biron, *J. Russ. Phys. Chem. Soc.* 1904, 36, 489, 933; *ibid.* 1905, 37, 963, 994, 1036; Weinland and Bames, *Zeitsch. anorg. Chem.* 1909, 62, 250; Druce, *Chem. News*, 1918, 117, 193); thus, $\text{SnCl}_4 \cdot 2\text{KCl}$ and



the latter forming the 'pink salt' formerly much used by dyers.

Stannic chloride dissolves phosphorus and iodine, and mixes with bromine and carbon disulphide. It converts mercury into calomel, and is itself decomposed by nitric acid, with precipitation of metastannic acid. Among the substances produced by direct combination with other compounds may be mentioned $\text{SnCl}_4 \cdot 2\text{NH}_3$, a soluble volatile solid (Rose, *Pogg. Ann.* 16, 63); $3\text{SnCl}_4 \cdot 2\text{PH}_3$, a yellow fuming solid (Rose, *ibid.* 24, 159); $\text{SnCl}_4 \cdot \text{N}_2\text{O}_5$, a yellow amorphous mass; $\text{SnCl}_4 \cdot \text{SO}_2$, a white solid (Rose, *ibid.* 44, 320); $\text{SnCl}_4 \cdot \text{PCl}_5$ and $\text{SnCl}_4 \cdot \text{POCl}_3$ (Casselmann, *Annalen*, 1852, 83, 257); $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, a white crystalline compound (Coldridge, *Phil. Mag.* [v.] 29, 383, 480). A yellow crystalline substance $\text{SnCl}_4 \cdot 2\text{SCl}_2$, fusing below 30° , is obtained by the action of chlorine on stannic sulphide (Rose, *Pogg. Ann.* 42, 517).

When a cooled solution of stannic chloride in chloroform is treated with nitric peroxide, the compound $3\text{SnCl}_4 \cdot 4\text{NOCl}$ is formed (Thomas, *Compt. rend.* 1896, 122, 32), whilst if such a solution is treated with nitrogen sulphide dissolved in chloroform, red crystals of the substance $\text{SnCl}_4 \cdot 2\text{N}_2\text{S}_2$ are deposited (Davis, *Chem. Soc. Trans.* 1906, 1576).

Stannic chloride absorbs large quantities of chlorine at low temperatures, with considerable increase in volume and lowering of the melting-point (Besson, *Compt. rend.* 1889, 109, 940).

Stannic chloride is used in dyeing as a mordant, and silk is weighted with it before dyeing (Froenkel and Fasal, *J. Soc. Chem. Ind.* 1898, 148; *ibid.* 1904, 899). Its use for this purpose is said to have been discovered by the Dutch chemist, Drebbel, in 1630, who found that cochineal gives a permanent brilliant red dye in the presence of dilute stannic chloride.

A patent was taken out in England as early as 1748 by O. Pawl (Specification No. 630, 1748) for the use of tin dissolved in *aqua fortis*, with addition of ammonium chloride, for dyeing scarlet.

The older methods of preparing tin salts for this purpose, whereby tin is dissolved in excess of hydrochloric acid, and the solution is oxidised by means of chlorates, have the disadvantage of producing a very impure product. The mordanting and weighting is due only to the stannic chloride and the impurities tend to weaken the fibres, to make the latter more sensitive to light, and to bring about the gradual deterioration in the strength of the material. To avoid this, Sperry has devised a special apparatus whereby pure anhydrous stannic chloride may be prepared by the treatment of impure tin-bearing materials with ordinary commercial chlorine (*J. Soc. Chem. Ind.* 1908, 312, 404, 628, 749, 978; *Eng. Pat.* 389188; *U.S. Pats.* 882354, 887538, 885391. For Fig. and description of apparatus, see *J. Soc. Chem. Ind.* 1908, 313). From the pure stannic chloride thus prepared all the compounds of tin needed by dyers may be obtained in pure condition.

According to Fiehler and Müller (*Arch. Sci. phys. nat.* 1916, [iv.] 42 123), the weighting of silk by steeping it in a solution of stannic chloride is due to a true chemical combination between the stannic chloride and the fibroin and its component amino-acids, followed by hydrolysis

during the washing process. After the hydrolysis the stannic acid is precipitated in the silk and the fibroin is regenerated and is capable of taking up more stannic chloride.

A solution consisting of stannic and stannous chloride, obtained by dissolving tin in *aqua regia*, is used in the preparation of fuchsine under the name 'nitrate of tin' or 'physic' (see above).

It is now more usual, however, to employ the crystalline pentahydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

A solution consisting of stannic chloride, containing more or less stannous chloride, and used in dyeing under the name 'oxychloride of tin' or 'pink cutting liquid,' is prepared by adding 1 part of stannous chloride to $1\frac{1}{2}$ parts of nitric acid of sp.gr. 1.31 in portions, with constant stirring, to prevent boiling over from the violence of the action; or by dissolving 337 parts of stannous chloride in 300 parts of hydrochloric acid (20°Tw.), with the aid of a minimum of water, and adding gradually 58 parts of potassium chlorate.

In small quantities stannic chloride may be added to the sizing mass for cotton warps in order to prevent the too rapid decomposition of the size (Textile Colorist, 1893, 15, 7).

For the detection of tin in mordanted cloth, see Paterson (J. Soc. Dyers, 1906, 22, 189); Silbermann (Bull. Soc. chim. Mulhouse, 1906, 76, 357).

A rapid and delicate method for detecting sodium chloride in commercial stannic chloride, consists in precipitating the former with 99.5 p.c. alcohol saturated with hydrogen chloride (Heermann, Chem. Zeit. 1907, 31, 27).

Stannous bromide SnBr_2 is obtained in solution by dissolving tin in hydrobromic acid (Balard, Ann. Chim. 1826, [ii.] 32, 337). It may be obtained as an anhydrous, pale-yellow, crystalline mass by heating tin in hydrobromic acid vapour and re-distilling the product (Freyer and Meyer, Zeitsch. anorg. Chem. 1892, 2, 1).

According to Rayman and Preis (Annalen, 1884, 223, 323), it melts at 215.5° to a pale-yellow oily liquid, of sp.gr. 5.117 at 17° . According to Carnelley and Carleton Williams (Chem. Soc. Trans. 1879, 564), it melts at 259° , and boils at 617° – 634° .

A hydrate $\text{SnBr}_2 \cdot \text{H}_2\text{O}$ separates in needles or thin plates from the greenish solution of tin in warm concentrated hydrobromic acid. It loses its water in dry air, or when heated to 70° – 80° . It dissolves in a little water, but is decomposed by excess, with precipitation of a gelatinous precipitate (v. Benas, Chem. Zentr. 1884, 957).

A hydrate $\text{SnBr}_2 \cdot 2\text{H}_2\text{O}$, crystallising in large monoclinic tables, is also obtained from the solution of tin in hydrobromic acid (Benas, l.c.).

Benas, Rayman and Preis have also described compounds of stannous bromide with potassium and ammonium bromides.

Stannic bromide SnBr_4 was discovered in 1826 by Balard (Ann. Chim. [ii.] 32, 337). It is obtained by adding bromine drop by drop to strips of tin, the temperature being kept between 35° and 59° (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 366); or preferably, on account of the violence of the action with pure bromine, by gradually adding the tin to a solution of bromine in carbon disulphide, or by passing

the vapour of bromine over heated tin (Carnelley and O'Shea, Chem. Soc. Trans. 1878, 55).

Stannic bromide forms a white iridescent deliquescent mass, which, by distillation, is obtained in small, well-formed, highly lustrous crystals, melting at 30° and boiling at 210° (uncorr.) (Carnelley and O'Shea, l.c.), or at 203° (corr.) (Rayman and Preis, Chem. Zentr. 1882, 773), and having a sp.gr. of 3.349 at 3.5° (Rayman and Preis, l.c.).

It fumes in the air, and dissolves readily in water. The solution deposits stannic hydroxide on heating or after standing. A hydrate $\text{SnBr}_4 \cdot 4\text{H}_2\text{O}$ is obtained in colourless transparent, fuming crystals, by exposing the anhydrous bromide to moist air, or by dissolving in a little water and evaporating over sulphuric acid. Oxybromides $\text{Sn}_2\text{Br}_2\text{O} \cdot 12\text{H}_2\text{O}$ and $\text{SnBr}_2\text{O} \cdot 10\text{H}_2\text{O}$, obtained from stannic bromide, and a compound $\text{SnBr}_4 \cdot 2\text{NH}_3$, obtained by absorption of ammonia by the warmed bromide, are also known (Rayman and Preis, l.c.).

Stannic bromide unites with ether to form a deliquescent crystalline body $\text{SnBr}_4(\text{C}_2\text{H}_5)_2\text{O}$ (Nickles, Compt. rend. 1861, 52, 869). By evaporating solutions of the mixed bromides, Raymond and Preis (l.c.) have obtained the following double bromides or stannibromides: $2\text{NaBr} \cdot \text{SnBr}_4 \cdot 6\text{H}_2\text{O}$, in pale-yellow, soluble crystals; $\text{CaBr}_2 \cdot \text{SnBr}_4 \cdot 6\text{H}_2\text{O}$, in slender deliquescent needles; $\text{MgBr}_2 \cdot \text{SnBr}_4 \cdot 10\text{H}_2\text{O}$, in pale-yellow, deliquescent tables; $\text{MnBr}_2 \cdot \text{SnBr}_4 \cdot 6\text{H}_2\text{O}$, in large, pale-yellow, deliquescent crystals; $\text{FeBr}_2 \cdot \text{SnBr}_4 \cdot 6\text{H}_2\text{O}$, in greenish, granular crystals; $\text{NiBr}_2 \cdot \text{SnBr}_4 \cdot 8\text{H}_2\text{O}$, in apple-green, granular, deliquescent crystals; and



in yellowish-red, deliquescent tablets (see also Leteur, Compt. rend. 1891, 113, 540).

Stannous iodide SnI_2 is obtained by dissolving tin in concentrated hydriodic acid. At the ordinary pressure solution is extremely slow, but it proceeds more rapidly in a sealed tube at 120° – 150° (Wöhler and Dünhaupt, Annalen, 1853, 86, 374). It may also be obtained in yellowish-red needles, slightly soluble in water, and readily soluble in solutions of alkaline chlorides and iodides, and in hydrochloric acid, by addition of potassium iodide in slight excess to a concentrated solution of stannous chloride (Warden, Pharm. J. 1897, 58, 61). The aqueous solution is decomposed by much water, with separation of hydriodic acid and a yellow, insoluble body the composition of which varies with the amount of water present (Personne, Compt. rend. 1862, 54, 216).

The formation of the iodide may be used as a delicate test for tin. One c.c. of the solution to be tested is treated with 0.5 c.c. of 5 p.c. potassium iodide solution and 0.5 of strong sulphuric acid added through a pipette reaching to the bottom of the test-tube. In presence of tin a yellow precipitate is produced at the plane of contact of the two layers (Heller, Zeitsch. Chem. 1922, 61, 180).

Stannous iodide melts at 316° (Carnelley and Carleton Williams, Chem. Soc. Trans. 1879, 564) and volatilises at a red heat. It absorbs dry ammonia, with formation of a white body having the composition $2\text{NH}_3 \cdot \text{SnI}_2$ (Rammelsberg, Pogg. Ann. 48, 169; Ephraïm and Schmidt,

Ber. 1909, 42, 3856). It unites with other metallic iodides, with hydrogen iodide (Young, J. Amer. Chem. Soc. 1897, 19, 851), and with stannous chloride.

Stannic iodide SnI_4 is obtained in yellowish-red octahedra by heating tin filings, preferably moistened with carbon disulphide or tetrachloride, with iodine to a temperature above 50° .

It has sp.gr. 4.696 at 11° (Bödeker, Die Beziehung zwischen Dichte und Zusammensetzung, &c., Leipzig, 1860), m.p. 146° and b.p. 295° (Personne, J. 1862, 172), m.p. 143° , b.p. 341° (corr.) (Emich, Monatsh. 1904, 25, 907). It sublimes at 180° .

It dissolves in carbon disulphide, carbon tetrachloride, alcohol, chloroform, and benzene. Water decomposes it into stannic hydroxide and hydriodic acid.

Its formation under certain conditions may be used as a delicate test for tin (Mazuir, Ann. Chim. anal. 1919, [ii.] 2, 9).

By the action of ammonia on stannic iodide, dissolved in carbon disulphide, a white substance $\text{SnI}_4 \cdot 8\text{NH}_3$, insoluble in water, is formed (Ephraim and Schmidt, l.c.).

Stannous fluoride SnF_2 is obtained in small, opaque, white, monoclinic tables of sweetish astringent taste, by evaporating a solution of stannous hydroxide in hydrofluoric acid.

Stannic fluoride SnF_4 is obtained in aqueous solution by dissolving the hydrated dioxide in hydrofluoric acid; or as a hygroscopic, white crystalline substance by the action of anhydrous hydrofluoric acid on stannic chloride (Ruff and Plato, Ber. 1904, 37, 673). It has sp.gr. 4.78 at 19° , b.p. 705° , but sublimes below this temperature. It combines with other fluorides forming a characteristic series of crystalline double salts, the *stannifluorides*, which are isomorphous with the corresponding fluorides of titanium, germanium, zirconium, and silicon (Marignac, J. 1859, 110; Emich, Monatsh. 1904, 25, 907; Ruff and Albert, Ber. 1905, 38, 55; Hall and Smith, Chem. Zentr. 1905, ii. 1462).

A number of mixed halogen compounds, such as SnCl_2Br , SnCl_2I , SnBr_2I , &c., have been described (Besson, Compt. rend. 1897, 124, 683; Lenormand, J. Pharm. Chim. 1898, [vi.] 8, 249; *ibid.* 1899, 10, 114). According to Anger (Compt. rend. 1909, 149, 860), most of these compounds are only mixtures, thus, $2\text{SnBr}_2\text{I} = \text{SnBr}_4 + \text{SnI}_4$, &c.

Phosphides.—Tin combines directly with phosphorus, forming a series of phosphides, which are used for the production of phosphor-bronze (Emmerling, Ber. 1879, 12, 155; Natanson and Vortmann, *ibid.* 1877, 10, 1460; Künzel, Dingl. poly. J. 1888, 270, 166; D. R. P. 103966; Stead, J. Soc. Chem. Ind. 1897, 206).

Tin phosphide Sn_3P_2 has a silver-white colour, crystallises in spangles, sp.gr. 5.18, and begins to dissociate at 480° .

The phosphide SnP is also a crystalline substance, sp.gr. 4.10. It has a metallic appearance, begins to dissociate into phosphorus and Sn_3P_2 at 415° , and is attacked violently by fuming nitric acid (Jolibois, Compt. rend. 1909, 48, 636). Other phosphides have also been described.

Tin hydride.—According to Vaubel (Chem. Zeit. 1924, 48, 351), a 5 p.c. solution of acetic

acid or a 1 p.c. solution of oxalic acid in contact with tin-plate containing rusty spots causes the evolution of tin hydride. The same effect is produced with pure tin in contact with metallic Zn , but the amount of hydride formed is much smaller. It is suggested that the formation of tin hydride in solution may account for cases of poisoning by eating tinned foods that show rust-spots (J. Soc. Chem. Ind. 1924, 43, B. 560).

Tin hydride is formed invariably when nascent hydrogen is liberated in the presence of tin; its production when tin is dissolved rapidly in hydrochloric acid accounts for the peculiar odour of the gas (Kastner, 1821).

The compound obtained by the action of tin hydride on silver nitrate solution has approximately the composition SnAg_4 .

During the dissolution of polished tin in hydrochloric acid, a black powder is deposited which dissolves only very slowly even in the concentrated acid; it is suggested that this is a peculiar modification of the metal which is produced by the reduction of stannous chloride by nascent hydrogen (W. Vaubel, Ber. 1924, 57, (B) 515; cf. Paneth and Fürth, Chem. Soc. Abstr. 1923, 124, ii. 41; 1924, 126, ii. 414; Paneth and Rabinovitch, Ber. 1924, 57, [B] 1877; Chem. Soc. Abstr. 1925, 128, ii. 59).

An unstable tin carbonate Sn_2CO_3 is also known (Deville, Ann. Chim. 1852, [iii.] 35, 4, 48; see also Moissan, Compt. rend. 1897, 125, 840).

Quadrivalent tin and trivalent arsenic in dilute sulphuric or hydrochloric acid may be completely separated by treatment with hydrogen sulphide after the addition of a little hydrofluoric acid. The separation is effected by treating the solution in a platinum dish with 2.5 c.c. of 48 p.c. hydrofluoric acid, heating for a few minutes, and when cold diluting to 300 c.c. The solution is then treated with a rapid stream of hydrogen sulphide for 30 minutes, when arsenious sulphide alone is precipitated. The separation is both rapid and quantitative (Le R. W. McCay, J. Amer. Chem. Soc. 1923, 45, 1187–1191; J. Soc. Chem. Ind. 1923, 42, 680 A.).

ORGANIC COMPOUNDS OF TIN.

Stannous acetate, oxalate, citrate, and tartrate are employed in dyeing and calico-printing, being generally prepared by addition of an alkaline salt of the acid to a solution of stannous chloride, or by dissolving the precipitated hydroxide in the acid. Liechti and Schwitzer (Mittheilungen des Tech. Gew. Museums, 1886, 41) have indicated the value of some of these as mordants (Platsch, Zeitsch. anorg. Chem. 1899, 20, 308; Rosenheim and Aron, *ibid.* 1904, 39, 171; Paterson, l.c.; Henderson, Orr, and Whitehead, Chem. Soc. Trans. 1899, 555).

The ancient Egyptians are believed to have used basic tin citrates (prepared by the action of lemon juice or citric acid on tin), as a mordant, in dyeing the tapestries discovered in the tombs of Antinoë (Gillieron, Bull. Soc. Mulhouse, 1907, 77, 148). Basic tin citrate forms a very efficient mordant for yellow dyes on wool, giving pure intense colours.

Stannous formate is prepared by dissolving precipitated stannous hydroxide in dilute formic acid. It forms white anhydrous crystals, which decompose above 100° (Goldschmidt, Chem. Zeit. 1907, 31, 608).

Tin forms a number of alkyl derivatives of the type SnR_4 , $\text{SnR}^1\text{R}^2\text{R}_2$, &c. (Letts and Collie, Chem. Soc. Proc. 1886, 166; Pope and Peachy, *ibid.* 1903, 290; Polis, Ber. 1889, 22, 2915; Pfeiffer and Schnurmman, *ibid.* 1904, 37, 319; Werner, Zeitsch. anorg. Chem. 1898, 17, 99; Pfeiffer, *ibid.* 1910, 68, 102).

Methyl-stannic acid or methyl-stannoxylic acid $\text{MeSnO}\cdot\text{OH}$ is formed when a mixture of methyl iodide, stannous chloride, and potassium hydroxide is allowed to stand for a day or two and the alkali is then removed by passing carbon dioxide into it. It can also be obtained pure by treating methyl-stannic bromide or iodide with ammonia. It is an odourless white powder, insoluble in water and organic solvents, but soluble in mineral and some organic acids, and in alkali hydroxides. With hydrobromic acid it yields *methyl-stannic bromide* or methyl stannibromoform SnMeBr_3 , m.p. 53° , which has also been obtained by other methods. The corresponding *iodide* or *iodoform*, MeSnI_3 , m.p. 86° , and the compounds SnMe_2Br_2 ; SnMe_2O ; SnMe_2SH and methyl-stannichloroform, m.p. 105° – 107° , b.p. 179° – 180° , have also been prepared (Pfeiffer and Lenhardt, Ber. 1903, 36, 1054, 3027; Pope and Peachy, Proc. Roy. Soc. 1903, 72, 7; Chem. Soc. Proc. 1900, 42, 116; Pfeiffer, Ber. 1904, 37, 4618; Shukoff, Ber. 1905, 38, 2691).

The potassium salt of *ethylstannic acid* is formed by the interaction of stannous chloride, ethyl bromide, and potassium hydroxide:



On treatment with dilute hydrochloric acid ethylstannic acid is formed as a white amorphous gelatinous substance, becoming yellowish-brown, transparent and horny on drying. For its salts, see Druce, Chem. Soc. Trans. 1921, 760).

The tin halogen compounds form a number of double compounds with aliphatic and aromatic amines (Cook, Amer. Chem. J. 1899, 22, 435; Richardson and Adams, *ibid.* 446; Slagle, *ibid.* 1898, 20, 633).

Pyridine stanni-iodide $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{SnI}_2$ is formed when an alcoholic solution of pyridine hydriodide is added to stannic iodide dissolved in alcoholic hydrogen iodide. It forms bluish-black glistening needles. The analogous *quinoline salt* $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{SnI}_2$ forms black needles. Both these compounds decompose gradually, liberating iodine (Rosenheim and Aron, Zeitsch. anorg. Chem. 1904, 39, 170). Similar chlorides, bromides and alkyl derivatives have also been prepared (Pfeiffer, Annalen, 1910, 376, 310; see also Hayes, J. Amer. Chem. Soc. 1902, 24, 360).

A number of other organic compounds of tin have also been prepared (Fischer, Monatsh. 5, 426; Werner and Pfeiffer, l.c.; Thiele and Dimroth, Annalen, 1899, 305, 102; Pfeiffer and Lenhardt, l.c.; Dilthey, Ber. 1903, 36, 925; Rosenheim and Levy, *ibid.* 1904, 37, 3662; Rosenheim and Schnabel, *ibid.* 1905, 38, 2777; Weinland and Barnes, l.c.; Pfeiffer, Annalen, 1910, 376, 285; Druce, Chem. Soc. Trans. 1921, 758; Chem. Soc. Abstr. 1925, i. 798; Kraus and Gress, Chem. Soc. Abstr. 1925, i. 1394; Kraus, *ibid.* 1925, i. 1253, 1254; Vorländer, *ibid.* 1925, i. 1256).

According to Miak (Compt. rend. 1923, 176, 138) tin exists normally in the human organism; the liver has the highest content, followed by the stomach, kidneys, lungs, and brain. 0.03–0.04 grm. in 100 grms. of human viscera is not excessive in amount.

TINCAL v. BORAX.

TIN MORDANTS v. DYING.

TIN PLATES. *History.*—Although the art of tinning brass and copper was well known to the Romans (*v. supra*), the production of sheet iron coated with tin, or 'tin plate,' is of a considerably later period. The art was probably of German origin, and existed in Bohemia prior to 1620. About this time the manufacture was introduced into Saxony, and speedily developed into a thriving industry. Unsuccessful attempts, with which M. Réaumur was connected, were made to introduce the manufacture into France. About 1670 an English company was formed to start a tin-plate works in this country, and Mr. Yarranton was sent to Germany to learn the art. Works were started at Pontypool, and met with some success, but were stopped, owing to the grant of a patent for the manufacture to E. Hemming in 1691. Works were, however, once more started in 1720 at Pontypool, and these were gradually followed by others, particularly in South Wales, which gradually became the most important seat of the manufacture in the world. In the earlier processes of manufacture the plates were hammered by hand from iron made in the charcoal hearth, while the surface was cleaned from scale by immersion for several days in sour barley-water, instead of for a few minutes in dilute sulphuric acid, as at present.

In 1728, the *rolling* of sheets was introduced by Hanbury, of Pontypool, while sulphuric acid was substituted for barley-water in 1806. The rolling of tin plates as they leave the tin pot, which saves metal and improves the surface, was introduced by Morewood (who took out many patents for coating metals) in 1866, since which time a great variety of machines have been introduced for use in the tinning process.

Pickling, machines have superseded hand labour, while iron made in the old-fashioned open-hearth refinery (or puddling furnace for second qualities) has been generally replaced by steel. Siemens' steel was used about 1875, Bessemer steel about 1880, and basic steel was introduced a few years later (*v. P. W. Flower, Origin and Progress of the Manufacture of Tin Plates, J. Iron and Steel Inst.* 1886; C. Vogel, Stahl und Eisen, 29, 1097).

The M'Kinley Tariff, which came into force on July 1, 1891, led to a rapid development of the tin-plate industry in the United States, and a corresponding depression in South Wales. Other markets for Welsh tin plates were, however, gradually found, so that the industry has more than made up for the ground lost.

Production of tin plate.—The metal used for rolling into sheets was formerly, as above stated, wrought iron of special quality, which was made in refineries using only charcoal. At present very mild steel is employed, Siemens' steel being in most demand for this purpose. The bars are cut into suitable lengths, and each length is heated to redness, and then passed through 'chilled' rolls until its length is about

doubled; the plate is then folded across the middle, re-heated, and again rolled. The reheating, folding over, and rolling is repeated until a sheet of the proper thickness is obtained, sometimes as many as thirty-two thicknesses being rolled together as one piece in this way. The sheets are then cut to size with shears and separated, when they should part readily if the operation thus far has been successfully conducted. The 'rough black plates' so produced should be free from streaks or 'spilly' places, and should be uniformly coated over with a black scale of oxide. This is now removed by 'pickling' in warm dilute sulphuric acid for about 20 mins., and by subsequent washing and rubbing with sand and water. The sheets are next annealed in wrought-iron boxes, which are usually about 2 ft. square, but vary in size; the upper part is in the form of a bell for ready removal, and to prevent the entry of air the joint is stopped by being covered with sand. The annealing requires about 10 hours, and is conducted in a large furnace maintained at a cherry-red heat. The pots are then withdrawn and allowed to cool, after which the sheets are cold-rolled, to improve the surface and give the smoothness and uniformity which is necessary to produce a good tin plate. The cold-rolling renders the plates somewhat hard, and they are therefore annealed once more, usually in cast-iron pots, as it is not necessary in the second annealing to use so high a temperature or as long a time as in the first case. The sheets are now finally pickled in weaker sulphuric acid then was used in the previous pickling, and after being again rubbed with sand are immersed in water preparatory to tinning.

The tinning apparatus, or 'stow,' varies somewhat with the size and quality of the plates; with very large plates the bath of tin is contained in a basin-shaped pot, while for large sizes and ordinary qualities the plates are manipulated entirely by machinery during the tinning process.

The form of apparatus which was general in S. Wales until nearly the end of the nineteenth century, and which is still occasionally employed for purposes where a specially good tin plate is required to withstand atmospheric and similar influences, consists of five baths or pots, called respectively (1) the grease pot, (2) the tin-man's pot, (3) the washing pot, (4) the dipping pot, (5) the grease pot. Formerly two other pots were used, but these have been rendered unnecessary by the introduction of rolls. The grease pot contains melted grease, such as tallow or palm oil, and in this the sheets are dipped until all moisture has been removed, and they are uniformly coated with grease. They are next dipped into the tin pot, which contains melted tin covered with a layer of grease, the latter being now usually replaced by a bath of zinc chloride or 'killed spirits.' The sheet now receives its first coating of tin, which, however, is not perfect, and to complete the tinning the sheet is dipped into the first compartment of the washing-pot, where it remains until a uniform coating is produced. The plate is now taken out and rapidly examined by the workman, who wipes over the surface with a brush, and to remove the marks of the brush rapidly dips the plate into the second compartment of the same

pot, which contains the best tin, and then transfers it to the grease pot, where it passes through a pair of rolls, which squeeze off the excess of tin and improve the surface. Formerly the plate remained for about 10 mins. in the grease pot, during which time the excess of tin drained off. The plate was afterwards transferred to the 'cold pot,' after which the lower part was inserted in the 'list' pot, which contains a little tin at a comparatively high temperature, and which rapidly removes the thick edge of tin which had accumulated at the bottom of the plate. The plates, after coating with tin, are then cleaned from grease, usually by rubbing with bran and finishing with the woolly skin of a sheep; they are afterwards separately examined for defects, and, after classification, are packed in the familiar flat wooden boxes and branded for market (*v. E. Trubshaw, J. Iron and Steel Inst. 1883, i. 252*).

For a description of the process of manufacture of tin plates in Germany, which does not materially differ from that above described, *v. Dingl. poly. J. 250, 231*.

For the method of tinning cast iron in Germany, *v. Schott, Stahl u. Eisen, 1919, 39, 119*.

In modern tin-plate works mild steel bars are reheated and rolled into 'black plates' by passing successively through two pairs of rolls for 'roughing' and 'finishing' respectively. In the United States sometimes only one pair of rolls is used; or two pairs of finishing rolls may be served by one pair of roughing rolls. The plates, after being separated, are pickled in diluted sulphuric or hydrochloric acid with the aid of pickling machines; they are then annealed under cover in iron or steel boxes, cold rolled, re-annealed at a lower temperature and again pickled, this time in weaker acid. The plates are then swilled in water and introduced, without drying, into the tinning machine. Of such machines there are various modifications. A typical form consists of two divisions connected with each other at the lower part of the pot which contains molten tin. The tin in the first division is coated with a tinning flux of zinc chloride, while that in the second division is covered with hot grease. The plate passes through the flux into and through the tin, emerging through the grease, and passing through rolls which remove the surplus tin, and give a smooth, bright, and even surface. For further details and drawings, see G. B. Hammond, *The Manufacture of Tin Plates, J. Iron and Steel Inst. 1897, 2, 24*; also papers by R. B. Thomas (*Proc. Inst. Mech. Eng. 1906, 490*) and T. L. Bailey (*J. Soc. Chem. Ind. 1918, 114 T*).

The occurrence of blisters in the thin sheets of steel used in the manufacture of tin plates is not infrequently a cause of considerable trouble. The origin of these has been studied by E. F. Law (*J. Iron and Steel Inst. 1906, 1, 134*), who concludes that oxidised steel will give rise to blistered sheets, and the defect is more likely to arise with Bessemer than with open hearth steel. Brittleness in sheets may arise from excess of sulphur or phosphorus. In metal of good chemical purity a peculiar form of weakness, sometimes called 'rectangular brittleness,' may result from annealing at an improper temperature, or for too long a time.

According to E. Mayer (*Stahl u. Eisen, 1918*)

38, 960) there is no proof that molten tin really alloys with the iron, and the time of dipping is too short to admit of diffusion of the tin into the iron. A metallographic study of tinfoil shows that there is always a sharp demarcation line between the tin and iron.

See also Chemistry in relation to Tinfoil Manufacture (H. J. Bailey, J. Soc. Chem. Ind. 1923, 362). T. T.

TIN PYRITES v. STANNITE.

TIN SALTS or **TIN CRYSTALS**. *Stannous chloride* v. *Tin salts and oxides*, art. **TIN**.

TIN STONE. *Native oxide of tin* v. **CASSITERITE**.

TINTOMETER v. **COLORIMETER**.

TIN WHITE COBALT. *Smaltine, Cobalt arsenide* v. **COBALT**.

TIODINE. Trade name for thiosinamine ethyl iodide $C_2H_5NHCSNH_2C_2H_5I$ v. **THIOSINAMINE**.

TITANIC IRON-ORE v. **ILMENITE**.

TITANITE v. **SPHENE**.

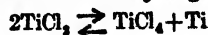
TITANIUM. Sym. Ti. At. wt. 48.1 (Thorpe); 47.9 (Baxter and Fertig, J. Amer. Chem. Soc. 1923, 45, 1228). Experiments to determine the ratio $TiCl_3:4Ag$ gave a mean value of 0.43957, the extremes being 0.43940 and 0.43967, which leads to the mean value 47.85 for the atomic weight of titanium, the extreme values being 47.89 and 47.78 (Baxter and Fertig, J. Amer. Chem. Soc. 1923, 45, 1228-1233; J. Chem. Soc. 1923, 124; Abstr. ii. 498). According to Aston, Titanium is simple. Titanium is not found in the free state, but occurs as oxide in three minerals of different crystalline form: *rutile*, *anatase*, and *brookite*. It is found as *titaniferous iron ore* or *ilmenite* $(FeTi)_2O_3$, and in smaller quantities as *sphenoid titanite* $CaTiSiO_6$, *perovskite* $(CaFe)TiO_3$, *schorlomite* $Ca(TiFe)SiO_6$, and *keilhaute* $CaY(TiAlFe)SiO_6$. It occurs in magnetic iron ores, and is thus frequently found in slags and pig iron; and in other minerals, in soils, clays, certain mineral waters, and in the sun's atmosphere (Barnes, J. Soc. Chem. Ind. 1896, 421; Riecke, *ibid.* 1908, 901; Becker, Zeitsch. Kryst. Min. 1903, 38, 317; Hall and Smith, Chem. Zentr. 1905, ii. 1161; H. R. Adam, J. S. Afr. Chem. Inst. 1923, 6, 3). The presence of titanium oxide in clays considerably reduces their refractibility. Titanium is said to be diffused throughout all primitive granite rocks (Dieulafoy).

It has also been found in human and in ox flesh and bone (Baskerville, J. Amer. Chem. Soc. 1899, 21, 1099); in the ash of many plants (Wait, *ibid.* 1896, 18, 402; Lippmann, Ber. 1897, 30, 3037); and in many peats (Baskerville, *l.c.* 402). It is more abundant in nature than has hitherto been supposed, but it is only within the last few years that the metal and many of its compounds have become important industrially.

Various titanium compounds have been suggested for use as pigments as far back as 1846. Ferro-titanium has been utilised in the iron industry since 1895, and titanium white, a pigment consisting essentially of titanium dioxide, is now being made.

Titanium can be extracted from its oxide by electrolyzing a solution of the latter in dry halogen salts of the alkaline earth metals heated to moderate redness. After cooling, the titanium is separated from the electrolyte by lixiviation

with water and with dilute hydrochloric acid (Fr. Pat. 344099, 1904; J. Soc. Chem. Ind. 1904, 1998; cf. also Moissan, Eng. Pat. 3073, 1895; Sternberg and Deutsch, Eng. Pat. 13117, 1893; Borschers, U.S. Pat. 930344, 1909; J. Soc. Chem. Ind. 1909, 986). In a somewhat impure form it can be obtained by the reduction of potassium titanium fluoride with sodium (Weiss and Kaiser, Zeitsch. anorg. Chem. 1910, 65, 345). Very pure titanium has been obtained in moderately large quantities by heating pure titanium tetrachloride with about half its weight of sodium in a steel bomb to a low red heat (Hunter, J. Amer. Chem. Soc. 1910, 32, 330; Lely and Hamburger, Zeitsch. anorg. Chem. 1914, 87, 209), or by passing the vapour of $TiCl_4$ over sodium hydride. Also by heating the dichloride at 1100° in hydrogen:



Titanium in a very pure state is obtained by passing the vapour of the iodide over a heated tungsten filament. Thus obtained it is ductile (van Arkel and de Boer, Zeitsch. anorg. Chem. 1925, 148, 345; Chem. Soc. Abstr. 1925, ii. 1193.)

Titanium has the appearance of polished steel. It is hard and brittle in the cold, but can be readily forged when raised to a low red heat. It has sp.gr. 4.50 and melts at 1800° - 1850° (Hunter); see also Moissan (Compt. rend. 1906, 142, 673).

For crystalline structure (hexagonal), see Patterson (Physical Rev. 1925, [ii] 26, 56; Chem. Soc. Abstr. 1925, ii. 845).

It is less ductile than thorium, zirconium, or uranium, and can be obtained in rod-form only with special precautions, owing to its ready oxidisability.

Titanium burns in oxygen, in nitrogen, and in the halogens, dissolves readily in sulphuric or hot concentrated hydrochloric acid, more slowly in nitric acid, and decomposes steam at 700° - 800° .

Titanium readily forms alloys with various metals; some of those with iron having been employed for the manufacture of pencils for arc lights (Ladoff, J. Ind. Eng. Chem. 1909, 711).

Aluminium-titanium alloys with up to 30 p.c. of the latter metal contain hard crystals of the compound Al_3Ti , m.p. 1325° , and immiscible with aluminium (E. van Erckelen, Metall und Erz. 1923, 20, 206.)

For alloys with carbon and iron, see *Tamara*, (Chem. Soc. Abstr. 1925, ii. 787).

Filaments of metallic titanium having a high melting-point and high resistance, and as used for incandescent electric lamps, are manufactured by treating titanic oxide with ammonia in the cold. The product is heated in a vacuum to 1200° , and is then mixed with an organic binding material such as a solution of casein in ammonia. The mixture is formed into threads and then heated in an electric furnace to 1300° . Finally the filament is subjected to the action of a high tension electric current in a vacuum (Trensen, Eng. Pat. 14652, 1906; J. Soc. Chem. Ind. 1906, 877).

Titanium is used in metallurgy, its addition to steel increasing greatly the transverse strength and elasticity of the steel (Ladoff, *l.c.* 642; Venator, Stahl und Eisen, 1910, 20, 666).

Its value in steel manufacture seems to be related to its power as a deoxidant. It is mainly applied in the form of 'Ferro carbon-titanium,' containing from 15-20 p.c. Ti, and consisting of microscopic particles of titanium carbide held in a matrix of grey cast iron. When added to molten steel the matrix dissolves and the titanium carbide is diffused through the mass when it reacts on the oxygen, the titanium oxide acting as a flux for silicates and other slags. (For the effect of wear on titanium treated rails, see Comstock, J. Soc. Chem. Ind. 1915, 55.)

Aluminium-titanium alloys containing up to 30.7 p.c. of titanium consist of a mixture of hard, needle-shaped crystals of Al_3Ti in a softer ground mass of aluminium. The compound Al_3Ti melts at 1325° and forms neither eutectic nor solid solution with aluminium. Addition of titanium, in amounts not exceeding 1 p.c., to aluminium removes the combined nitrogen and oxygen, and consequently improves the tensile properties; at the same time, the resistance of the metal to attack by salt solutions and by organic acids is appreciably increased (cf. J. Soc. Chem. Ind. 1923, 721 A; Eugen van Erckelens, Metall. und Erz. 1923, 20, 206-210; J. Chem. Soc. Abstr. 1923, 124, ii. 569).

A protective coating on iron and steel is said to be formed by mixing a titanium ore with 10-50 p.c. of asphalt, and if the product is to be used as a paint, adding turpentine. These coatings can also be formed by heating the metal to be treated with a layer of titanic mineral mixed with carbonaceous material in a furnace for several hours (Johnson, Eng. Pat. 15500, 1893; J. Soc. Chem. Ind. 1893, 1046).

The arc spectrum of titanium has been analysed with the object of ascertaining the regularities of this spectrum. It is shown that two different sets of multiplets of six or seven lines occur. These sets have respectively the differences 170.1 and 2.167, and are similar to the multiplets of the alkaline-earth metals. There are also multiplets of eleven to thirteen lines, with differences 42.0, 62.3, 81.7, and 100.2, similar to the multiplets of manganese, chromium, and molybdenum. The majority of the lines classified belong to King's temperature classes I. and II., although a few belong to the classes III. and IV. (Astrophys. J. 1914, 39, 139). About 10 p.c. of the arc lines of titanium are thus classified. Long tables of the classification are given in the paper (C. C. Kiess and Harriet K. Kiess, J. Washington Acad. Sci. 19; J. Chem. Soc. 1923, 124, ii. 596; 1924, 126, ii. 510; see also Behner, Zeitsch. wiss. Phot. 1925, 23, 325; Chem. Soc. Abstr. 1925, ii. 1100; Crew, Chem. Soc. Abstr. 1925, ii. 335).

Compounds of titanium.—Titanium hydride appears to exist. When the gases from a titanium electrode are passed through a heated glass tube a deposit of titanium is formed as a black metallic mirror. The gaseous hydride is colourless and tasteless, and is condensed at the aperture of liquid air. Titanium forms four oxides. The monoxide TiO forms black prisms, obtained by heating the dioxide in the electric furnace, or with magnesium powder (Winkler, Ber. 1890, 23, 3058; Moissan, Compt. rend. 1892, 115, 1034; J. Soc. Chem. Ind. 1892, 963). The sesquioxide Ti_2O_3 (Moissan,

Compt. rend. 1895, 120, 290; Braun, Min. Mag. 1892, ii. 37) is obtained by strongly igniting the dioxide in hydrogen and allowing the product to cool in this gas. In sulphuric acid it forms a violet solution, this being the characteristic colour of all the solutions of trivalent titanium compounds. The corresponding hydroxide is obtained by digesting a solution of titanic acid in hydrochloric acid with metallic copper at 20° - 40° , or by treating the trichloride with alkalis. The sesquioxide and the corresponding salts are readily oxidised to the dioxide or the trioxide and their salts (Manchot and Richter, Ber. 1906, 39, 320, 488).

Titanium dioxide TiO_2 , is the most important of the four oxides. It is trimorphous, occurring as the three distinct minerals mentioned above. It can be obtained by the decomposition of aqueous titanium chloride by ammonia or by fusing rutile with three times its weight of potassium carbonate.

Titanium oxide can be prepared by mixing crushed ilmenite or other titanium ore with carbon and heating to about 1800° . The resulting mass is crushed and the iron is removed by magnetic separation and treatment with acid (U.S. Pat. 921886, 1909; J. Soc. Chem. Ind. 1909, 657).

For the occurrence of titanium in Nile silt, see E. Griffiths-Jones (Analyst, 1923, 48, No. 568, 320).

The following results, expressed as percentage of TiO_2 , calculated on the silt dried at $100^\circ C.$, were obtained:—

	Titanium dioxide. Per cent.
Nile silt collected from the river bank at Maadi, near Cairo	2.35
Silt from the River Atbara taken 10 miles upstream from the junction with the main river—	
No. 1, a grey silt of fine texture	2.2
No. 2, a coarse sand	1.3
Silt from Nile at Hassanat Discharge site about 5 miles upstream from the junction with the Atbara—	
No. 1, fine silt; brown in colour	2.4
No. 2, fine silt, grey in colour	2.55
No. 4, fine sand, brown in colour	1.7

Amorphous titanium dioxide is a white, tasteless powder which becomes lemon yellow when gently heated, and brown when ignited strongly. It has a sp.gr. 3.89-4.25. It is insoluble in water and dilute acids, resembles silicon dioxide closely in chemical properties, and when fused with alkalis or alkali carbonates forms the titanates.

Titanium dioxide finds application as a paint material and is extracted on the large scale from a variety of ilmenite found near Egersund, Norway. The concentrated ore containing 47.5 p.c. of titanium oxide is reduced to fine powder and mixed to a paste with concentrated sulphuric acid. On heating the mineral is converted into soluble sulphates of iron and titanium. On treating with water and heating nearly to boiling-point the titanic oxide is precipitated, dried, and calcined. The product is mixed with barium sulphate, carbonate and calcium phosphate, and comes into commerce as 'titanium white.'

Titanox consists of titanium dioxide precipitated upon a base of finely divided *blanc fixe*. In colour it is far whiter than white lead, but not quite so white as French process zinc oxide or the best grades of lithopone. Its hiding power is twice that of white lead and is the greatest of any white pigment. Its inertness towards varnish liquids enables it to be used in compositions that can be kept without danger of livering or thickening. 100 p.c. titanox in oil dries very slowly to a soft film, and a fair quantity of a metallic drier should be used, while for interior work an addition of about 30-50 p.c. of zinc oxide is advantageous, this causing it to give a firm dust-resisting film. Titanox appears to be very resistant to sunlight and to all atmospheric conditions and to hydrogen sulphide fumes. Experiments on rabbits showed that titanox is non-toxic and physiologically inert (H. A. Gardner, U.S. Paint Manuf. Assoc., Govt. No. 199, Feb. 1924, 256; J. Soc. Chem. Ind. 1924, 43, B. 303).

Green pigments containing titanium were first manufactured about 1861. White titanium pigments are now chiefly made in America and Norway, and are usually sold in two forms containing 65-90 p.c. and 25-35 p.c. TiO_2 , respectively. Ilmenite ($\text{FeO} \cdot \text{TiO}_2$, containing 51 p.c. TiO_2) is now the chief raw material used for these pigments, since it is cheaper than rutile (containing 90-98 p.c. TiO_2), which was formerly used. Pure white pigments are microcrystalline, and have sp.gr. 4.0 and refractive index 2.1-2.3. White titanium pigments are only soluble in the concentrated acids and alkalis, and are inactive towards the oils and pigments used in the paint and varnish industries. The resinates and linoleates of cobalt and manganese are particularly suitable siccatives for use with titanium paints, 0.2 p.c. of manganese or 0.03 p.c. of cobalt being recommended as suitable quantities. Paints containing titanium pigments are elastic and do not crack or scale after prolonged weathering. Titanium pigments have a high covering and oil-absorption power, and a ready-to-use paint contains 52-62 p.c. of white titanium pigment and 48-38 p.c. of oil (E. O. Rasser, Chem. Zeit. 1923, 47, 460-461; J. Soc. Chem. Ind. 1923, 42, 729 A).

The following volumetric method of estimating titanium in titanium pigments is not affected by other elements likely to be present, and is convenient when a number of samples have to be analysed. The reagent used is prepared by dissolving 30 grms. of ferric ammonium sulphate in 300 c.c. of water containing 10 c.c. of sulphuric acid, adding permanganate solution drop by drop as long as the pink colour disappears, diluting to a litre, and standardising in terms of iron; 0.5 gm. of the pigment is mixed with 20 c.c. of concentrated sulphuric acid and 7 to 8 grms. of sodium sulphate in a 250 c.c. beaker, which is heated on a hot plate until fumes of sulphur trioxide are evolved and then boiled over a flame for 5 minutes or until solution is complete. The cold liquid is mixed with 100 c.c. of water and boiled, the barium sulphate and silica being filtered off and washed with 5 p.c. sulphuric acid solution. As reductor a 500 c.c. pyrex glass dispensing burette, 22 by 1 inches, is used. Into this is introduced a platinum gauze covered with a $\frac{1}{2}$ -inch mat of

fibrous asbestos supporting, in the order mentioned, a 1-inch layer of 10-mesh and a 6-inch layer of 20-mesh amalgamated zinc and a 5-inch layer of amalgamated stick zinc. The reductor is connected with a litre flask for receiving the reduced titanium solution through a 3-holed rubber stopper, which carries also an inlet tube for carbon dioxide and an outlet tube joined to the suction pump. The reductor is prepared by passing through it a little hot dilute sulphuric acid followed by hot water, sufficient of which is left to cover the zinc. The hot filtrate from the barium sulphate is now introduced, about 100 c.c. of water being drawn from the reductor into the original beaker to bring the solution to about the top of the zinc; the water withdrawn may be acidified with 10 c.c. of sulphuric acid and kept on a hot plate for washing after the reduction. The titanium solution is left in the reductor for 10 minutes, the receiving flask being meanwhile connected with the reductor and the air displaced by carbon dioxide. When reduction is complete the receiving flask is joined to the suction pump, and, with carbon dioxide still flowing, the reduced solution is drawn out and is followed by the acid washing liquor and three or four quantities of 100 c.c. of hot water, the zinc being kept covered. The suction is then gradually released and the flask disconnected, 5 c.c. of saturated potassium thiocyanate solution being added and the liquid titrated at once with the ferric ammonium sulphate solution until a brownish colour persists for at least a minute; the burette reading is to be corrected by an amount which each operator must determine by means of several blank tests. As the composition of titanium oxide is always very nearly 25 p.c. of titanic oxide and 75 p.c. of barium sulphate, the percentage of the pigment is obtained nearly enough for all practical purposes by multiplying the percentage of titanic oxide by four. If only an occasional estimation is to be made, the following gravimetric method is useful. The filtrate from the barium sulphate (see above) is treated with excess of ammonia and filtered, the precipitate being dissolved in hydrochloric acid (1:1) and again precipitated with ammonia. The precipitated titanium hydroxide is filtered off and washed with hot water, the filtrate being added to that from the previous filtration. The residue is dissolved in hydrochloric acid (1:1), the volume of the solution, which is received in a 500 c.c. beaker, being kept below 150 c.c. To the solution, heated to 50°C., ammonium hydroxide is added gradually until the precipitate formed just redissolves, ammonium carbonate solution being then added, drop by drop, until a slight permanent precipitate forms. This is dissolved in hydrochloric acid, and an excess of 2 c.c. of the acid (1:1) added, the solution being treated with sulphur dioxide gas or solution until it smells strongly, diluted to about 400 c.c. and boiled until only a slight odour remains. The liquid is filtered while hot, and the precipitate washed with hot water, dried, calcined at not lower than 900°C. for 30 minutes, and weighed as TiO_2 .

With a mixed pigment containing titanic oxide, 1 gm. is heated on a hot plate in a 400 c.c. pyrex glass beaker with 10 grms. of sodium sulphate and 40 c.c. of sulphuric acid (93 p.c.)

for 30 minutes, and then boiled for about 10 minutes, cooled, diluted to 300 c.c., boiled for 30 minutes, and filtered while hot. The residue is washed with 5 p.c. sulphuric acid solution; it contains silica, undecomposed silicates and all the lead and barium as sulphates. The hot filtrate, containing the titanium, iron, aluminium, zinc, and calcium, is treated with excess of ammonia, and filtered, the precipitate being washed with hot water, redissolved in hydrochloric acid (1:1), and again precipitated with ammonia. The precipitate is filtered off and washed with hot water, the filtrate being united with that from the first separation; if desired, this filtrate may be tested for aluminium and used for estimating the calcium and zinc. The precipitate is dissolved in dilute hydrochloric acid, and the titanium separated and estimated as described above, the filtrate being used for estimating the iron and aluminium (L. E. Barton, *Chem. Trade J.* 1923, 357, 358; *Analyst*, 1923, 48, 403).

For the volumetric estimation of titanium, see also Morley and Wood (*J. Chem. Soc.* 1924, 125, 518; *Abstr.* 1924, 126, ii. 351); Lundell and Jones (*J. Amer. Chem. Soc.* 1923, 45, 2620-2623; *J. Soc. Chem. Ind.* 1924, 43, B. 38).

Titanium oxide is used as a mordant, and in at least two cases it has an advantage over alumina; thus alizarin yellow produces with titanium as bright but a much faster colour than with alumina, whilst the scarlet obtained from alizarin orange on a titanium mordant is the fastest scarlet that can be obtained on wool.

For this purpose the titanium mordant must be freed from iron, and this can be done by dissolving freshly precipitated titanium hydroxide, containing iron, in tartaric acid, making alkaline with ammonia and precipitating the iron by the addition of the requisite amount of ammonium sulphide. The filtered solution is then warmed until most of the free ammonia has been expelled (Barnes, *J. Soc. Chem. Ind.* 1899, 15).

According to Sabatier and Mailhe (*Compt. rend.* 1910, 150, 823) the dioxide forms a very efficient catalyst in the esterification of acetic acid.

According to E. L. Nichols (*Physical Rev.* 1923, [ii] 22, 420), cathode rays but not ultraviolet light from an iron spark excite a very faint, orange-red fluorescence in titanium oxide, or, after fusion of the surface layer, a fine blue fluorescence, with rapid fatigue. A thin layer of the oxide, when heated, gave a very feeble greyish-blue fluorescence up to 425°, strong red from 425° to 677°, and strong yellow from 677° to 1000°. When the oxide is heated directly with an oxygen-hydrogen flame, two distinct phases are observed, according as the oxygen or the hydrogen is in excess (*cf.* Nichols and Wilber, *Chem. Soc. Abstr.* 1922, ii. 105; 1924, 126, ii. 81).

Like silicic acid, titanous acid forms a number of hydrates known as ortho- and meta-titanous acids (Wagner, *Ber.* 1888, 21, 960; Pfordten, *Anzeig.* 1887, 237, 218; Tamann, *Zeitsch. anorg. Chem.* 1905, 43, 370; Bornemann and Schramm, *Chem. Zentr.* 1910, ii. 1870). Many titanates are known. The two compounds $\text{Na}_2\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{TiO}_3 \cdot 4\text{H}_2\text{O}$ described by Demsky in 1909 have been shown by Collenberg and Sandved not to exist (*Zeitsch. anorg. Chem.* 1923, 120, i. 1; *Chem. Soc. Abstr.* 1924, 126, ii. 52).

Tetramethyl titanate prepared from methyl alcohol, sodium, and titanium tetrachloride crystallises at 210° and boils at 243° corr. at 52 mm. Tetraethyl-, tetraisopropyl-, and tetra-*n*-butyl titanates have also been prepared (Bischoff and Adkins, *J. Amer. Chem. Soc.* 1924, 46, 256; *Chem. Soc. Abstr.* 1924, 126, i. 259).

Chloro-acetate compounds of titanium have been prepared from TiCl_4 and acetic acid (Gins and Monath, *Zeitsch. anorg. Chem.* 1925, 143, 383; *Chem. Soc. Abstr.* 1925, i. 531).

Titanium peroxide TiO_2 (Classen, *Ber.* 1888, 21, 370) resembles hydrogen peroxide very closely in its reactions in solution. Faber (*Zeitsch. anal. Chem.* 1907, 46, 277) has prepared the hexavalent acetate and phosphate



both of which are stable at low temperatures, but, particularly the acetate, are explosive on heating. Hypertitanates of potassium and sodium have also been prepared (Melikoff and Pissarjewsky, *Ber.* 1898, 31, 678).

According to Billy (*Compt. rend.* 1921, 172, 1411) all salts of the oxide TiO_2 are really complexes of hydrogen peroxide and pertitanic salts corresponding with the peroxide Ti_2O_3 .

Halogen compounds.—Titanium tetrachloride TiCl_4 can be obtained readily by passing dry chlorine over a mixture of the dioxide with carbon; by passing the vapour of chloroform over titanium dioxide (Renz, *Ber.* 1906, 39, 249), and by heating the latter with sulphur monochloride (Hall, *J. Amer. Chem. Soc.* 1904, 26, 1235; Bourion, *Ann. Chim.* 1910, [viii.] 20, 547; *ibid.* 21, 49), or by passing sulphur dioxide into a warm, strongly acid solution of titanium trichloride (Smythe and Wardlaw).

Titanium tetrachloride is best prepared from industrial ferro-titanium by treating the latter with hydrochloric acid to remove most of the iron. It is then levigated to remove titanous anhydride, and after drying the mass is introduced into a porcelain tube, heated to dull redness, and subjected to the action of a current of dry chlorine. The ferric chloride is separated by filtration, and the filtrate is fractionally distilled when the pure substance is obtained. It boils at about 136°, is colourless, and does not fume in air (Vigouroux and Arrivaut, *Compt. rend.* 1907, 144, 485).

The tetrachloride can also be prepared from rutile by igniting the latter with aluminium and then heating the mixture in a current of chlorine (Ellis; *Chem. News*, 1907, 95, 122).

It is a mobile, transparent, colourless liquid of sp. gr. 1.7604 at 0/4° (Thorpe), which solidifies at -23° and boils at 136.4° under 760 mm. pressure (Thorpe). It is decomposed by an excess of water yielding titanous acid and combines with ammonia, forming a number of solid addition compounds (Rosenheim and Schütte, *Zeitsch. anorg. Chem.* 1901, 26, 239; Stähler and Wirthwein, *Ber.* 1905, 38, 2618). When the latter are extracted with liquid ammonia, dark yellow titanamide $\text{Ti}(\text{NH}_2)_4$ is formed. Titanium tetrachloride, like stannous chloride, yields a large number of crystalline compounds with other chlorides (Rosenheim and Schütte, *loc. cit.*; Rast and Ipsen, *Ber.* 1903, 36, 1777). Is reduced to the trichloride by heating with aluminium, antimony, arsenic or tin in a sealed tube at 400°.

A solution in concentrated hydrochloric acid deposits, on evaporation in the cold over sulphuric acid, large, colourless, rhomboidal plates of $\text{TiCl}(\text{OH}) \cdot 2\text{H}_2\text{O}$, decomposed in moist air (Collenberg and Sandved, l.c.).

Titanium trichloride TiCl_3 is formed when a mixture of titanium tetrachloride vapour with hydrogen is passed through a red-hot tube (Georges and Stähler, Ber. 1909, 42, 3200; Stähler and Bachran, Ber. 1911, 44, 2906), and can be prepared by electrolysis of a solution of the tetrachloride and then evaporating the solution to the sp.gr. 1.5 at $60^\circ\text{--}70^\circ$ (Spence, U.S. Pat. 723217, 1903; J. Soc. Chem. Ind. 1903, 495, 628; D. R. P. 154542). As prepared by the latter process, it forms violet crystals of the composition $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, which decompose into the tetra- and di-chloride on heating, the latter also being formed when the trichloride is heated in hydrogen (Georges and Stähler, l.c.). Titanium trichloride may be prepared by reduction of the tetrachloride by means of hydrogen, provided that the reaction products are quickly cooled and the hydrogen chloride is removed by means of metallic titanium. The trichloride so prepared consists of large violet crystals, which are fairly stable in the air. The reduction is not direct, but three reactions, $\text{TiCl}_4 + \text{H}_2 = \text{TiCl}_3 + 2\text{HCl}$; $\text{TiCl}_4 + \text{TiCl}_3 = 2\text{TiCl}_3$; $2\text{TiCl}_3 + 2\text{HCl} = 2\text{TiCl}_2 + \text{H}_2$, may proceed simultaneously (F. Meyer, A. Bauer, and R. Schmidt, Ber. 1923, 56, 1908–1914; J. Soc. Chem. Ind. 1923, 42, 1067 A). When titanium tetrachloride is heated with magnesium, zinc, aluminium, arsenic, or antimony it is reduced to trichloride, the reaction being accelerated by aluminium chloride. Phosphorus and sulphur reduce the tetrachloride only in presence of aluminium chloride. Reduction with aluminium and aluminium chloride in absence of air is the best method of preparing titanium trichloride. The trichloride can be sublimed at 425°C . at 1 mm. pressure. At 475°C . it decomposes into dichloride and tetrachloride. Titanium dichloride is a black powder, stable at least to 600°C . in absence of air, but catching fire at once in moist air. It decomposes water immediately with evolution of hydrogen (O. Ruff and F. Neumann, Zeitsch. anorg. Chem. 1923, 128, 81–95; J. Soc. Chem. Ind. 1923, 42, 1220 A).

Investigation of the reduction of the tetrachlorides of titanium and zirconium by sodium amalgam, magnesium, zinc, aluminium, tin, arsenic, phosphorus, etc., has shown that reduction by aluminium at about 250° affords a convenient means for the preparation of the trichlorides, from which excess of tetrachloride and aluminium chloride can be removed by distillation. Titanium trichloride thus prepared is a bright violet, non-crystalline powder subliming at $425^\circ/\text{1 mm.}$ to form dark violet, prismatic crystals; it is very sensitive to oxygen and moisture, and dissociates at 450° to form the volatile tetrachloride and a black residue of the dichloride, which is very reactive, takes fire in moist air, and decomposes water with evolution of hydrogen (O. Ruff and F. Neumann, Zeitsch. anorg. Chem. 1923, 128, 81).

The trichloride is a powerful reducing agent. It liberates sulphur from sulphurous acids, sulphites, and thiosulphates, and selenium from selenious acid, many metals, such as gold, silver

the platinum metals, mercury, and copper from solutions of their salts, and reduces nitric acid and nitrates to ammonia. It reduces ferric salts quantitatively to the ferrous condition, reacts with a gold solution like stannous chloride, producing colloidal gold, analogous to purple of Cassius, organic nitro compounds to amines, gives characteristic coloured precipitates or colorations with many organic acids or their salts. The intense violet coloration with solutions of alkali citrates is a characteristic and sensitive test, and can be employed in the analysis of many dyes (Knecht, Ber. 1903, 36, 166; Knecht and Hibbert, *ibid.* 1549; *ibid.* 1905, 38, 3318; 1907, 40, 3819; J. Chem. Soc. 1924, 125, 1537). This reducing property has also been made use of in cloth printing (D. R. P. 138503; *Frld.* 1902–4, 477). Titanium trichloride forms double compounds with the chlorides of rubidium and caesium (Stähler, Ber. 1904, 37, 4405), and also with nitrogen sulphide (Davis, Chem. Soc. Trans. 1906, 1576).

The use of titanous chloride in the titration of iron is discussed by Brandt (Chem. Zeit. 1924, 48, 265, 270; J. Soc. Chem. Ind. 1924, 43, B. 469).

The standardisation of titanous chloride solutions, using the potentiometric method, has been studied by Zintl and Rauch (Zeitsch. anorg. Chem. 1925, 146, 281; Chem. Soc. Abstr. 1925, ii. 1003; see also Tomicek, Chem. Soc. Abstr. 1925, ii. 243).

A brown polymorphic modification of titanium trichloride, obtained by the action of the silent discharge on a mixture of hydrogen and the vapour of the tetrachloride, has been described by Böck and Moser (Monatsh. 1913, 34, 1825).

Titanium dichloride TiCl_2 , prepared as above, is a hygroscopic light-brown powder.

Titanium tetrabromide (Ruff and Ipsen, l.c.), and tribromide (Stähler, l.c.), the triiodide (Stähler, l.c.), tetra-iodide and the diiodide (Defacqz and Copaux, Compt. rend. 1908, 147, 65), the tetra- and tri-fluorides (Ruff and Ipsen, l.c.; Ruff, Plato and Graf, Ber. 1904, 37, 673), and a number of alkali titanofluorides (Marchetti, Zeitsch. anorg. Chem. 1895, 10, 66; Piccini, *ibid.* 438; Ebler and Schott, J. pr. Chem. 1910, [ii.] 81, 552) have been prepared.

Titanium forms three sulphides TiS_2 , Ti_2S_3 , and TiS (Müller, Chem. Zentr. 1910, ii. 1195), and also a chlorosulphide.

Titanium sesquisulphate $\text{Ti}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is obtained when the metal is dissolved in dilute sulphuric acid. It is decomposed by heat and forms alums and double salts with the alkali sulphates.

The electrolytic reduction of many organic compounds is greatly facilitated by the addition of a small quantity of a titanium salt, such as the sulphate (D. R. P. 168273; *Frld.* 1905–7, 115). Titanous sulphate is also recommended for detecting copper in dyed fabrics (Knecht, J. Soc. Dyers, 1904, 20, 97). The electrometric titration of chlorate, bromate, iodate, and ferricyanide with titanous sulphate is discussed by Hendrixson (J. Amer. Chem. Soc. 1923, 45, 2013; Sci. Abstr. 1924, 27, 53).

Titanous sodium sulphate $\text{Ti}_2\text{Na}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ is obtained by electrolysis of a solution containing titanous sulphate, sodium sulphate, and sulphuric acid. The electrolysis is carried out with a

low-current density in a lead-lined vessel, the solution being finally evaporated to a sp.gr. of 1.145, when the salt crystallises out.

It is a powerful reducing agent, and can be applied in the preparation of other titanous salts (Peter Spence and Sons, D. R. P. 149602, 1904).

Titanium disulphate $Ti(SO_4)_2 \cdot 3H_2O$ forms double salts with the sulphates of the alkalis and alkaline earths (Weinland and Kühl, *Zeitsch. anorg. Chem.* 1907, 54, 253). A number of basic sulphates (Blondell, *Bull. Soc. chim.* 1899, [iii.] 21, 262; Roseheim and Schütte, *l.c.*) and titanousulphuric acid (Reichard, *Chem. Zeit.* 1904, 28, 16) have also been prepared. The preparation of solutions of titanyl sulphate $TiOSO_4$ is described by Weizmann and Blumenfeld (E. P. 209480, 210033; *J. Soc. Chem. Ind.* 1924, 43, B. 256).

Titanium forms a number of nitrides and also a chloro- and bromo-nitride (Ruff and Eiser, *Ber.* 1908, 41, 2250; *J. Soc. Chem. Ind.* 1908, 809; Ruff, *Ber.* 1909, 42, 900; Ruff and Treidel, *ibid.* 1912, 45, 1364). The mononitride Ti_2N_3 is a bronze yellow mass of sp.gr. 5.18, and is hard enough to cut rubies and diamonds (Moissan, *Compt. rend.* 1895, 120, 290).

According to Shukoff, however (*J. Russ. Phys. Chem. Soc.* 1910, 42, 40), titanium only forms solid solutions with nitrogen, but no definite compounds.

Titanium also forms a carbide (Shimer, *Chem. News*, 1887, 55, 156; Moissan, *l.c.*; and *Compt. rend.* 1897, 125, 839); a carbide of titanium, m.p. 3400° – 3500° Abs. was prepared by Friederich (*Z. Physik.* 1925, 31, 813; *Chem. Soc. Abstr.* 1925, ii. 374); Titanium forms a cyanonitride $Ti(CN)_2 \cdot 3Ti_2N_3$ (Wöhler, *Annalen*, 1850, 73; *ibid.* 34, 74, 212; Franck, *Chem. Zeit.* 1897, 21, 520; *J. Soc. Chem. Ind.* 1908, 809); and a silicide $TiSi_2$ (Hönigsamid, *Compt. rend.* 1906, 143, 224; *J. Soc. Chem. Ind.* 1909,

double double pyrophosphates of titanium and alkali are prepared by mixing together alkali pyrophosphates and basic titanium sulphate (Barnes and Spence, *Eng. Pat.* 6329, 1906; *J. Soc. Chem. Ind.* 1907, 93).

Titanium phosphide TiP forms a brittle mass with a metallic lustre. It burns when heated in air, is a conductor of electricity, is insoluble in dilute and in concentrated alkalis and acids (Gewecke, *Annalen*, 1908, 361, 79).

Titanic acid forms crystalline *thiocyanates* of the type $K_2TiO(SCN)_2 \cdot H_2O$ and double salts with pyridine (C_5H_5N), $H_2TiO(SCN)_2$, and quinine (Rosenheim and Cohn, *Zeitsch. anorg. Chem.* 1901, 28, 167).

Double fluorides of titanium, with some alkaloids are described by Schaeffer (*J. Amer. Chem. Soc.* 1906, 30, 1862).

Complex azo-salts of titanium have been prepared by Mazzucchelli and Pantanelli (*Gazz. chim. Ital.* 1910, 40, i. 666). Other titanium organic compounds are described by Dilthey 57, 588; *Annalen*, 1906, 344, 300), and Schnabel (*Ber.* 1905, 38, 2777), Gropmann (*Chem. Zeit.* 1906, 30, 907), Mazzucchelli (*Atti R. Acad. Lincei*, 1907, [v.] 16, ii 263), Pantanelli (*Chem. Soc. Trans.* 1906, 1004).

The possibility of using titanium compounds was first demonstrated by

Barnes in 1877. For the behaviour of titanic acid towards dyes, see A. M. Morley and J. K. Wood (*J. Soc. Dyers and Col.* 1923, 39, 100–105). The salts used are: the sulphate, chlorides, fluoride, oxalate, tartrate, lactates, and the double alkali derivatives of these salts. The salts for this purpose are obtained by the following process.

The ore is melted with sodium hydroxide and the mass is lixiviated with water; the residue is then washed free from alkali, dissolved in hydrochloric acid, and the solution is treated with alkali to precipitate titanium as hydroxide. The product is freed from iron by the addition of sodium sulphide, the precipitate washed and treated with sulphurous acid. It is then converted into titanium oxalate by treatment with ammonium oxalate and oxalic acid (Erban, *Chem. Zeit.* 1906, 30, 145; *cf.* also Dreher, *Eng. Pat.* 1835, 1903; *J. Soc. Chem. Ind.* 1904, 18; Spence, *ibid.* 1900, 246).

The *lactates* are conveniently prepared by dissolving titanic acid in hydrochloric acid and pouring the solution into a warm solution of an alkali or alkaline earth lactate (Dreher, *Farber-Zeit.* 1902, 13, 293; D. R. P. 149577; *Frdl.* 1902–4, 43; *J. Soc. Chem. Ind.* 1902, 988, 1245; 1903, 908).

The soluble salts of titanium, such as the oxalate, are very efficient fixing agents for the tannates of the basic colours, the results obtained being as good as, and in many cases better than, those obtained with antimony. For this purpose it is unnecessary to purify the titanium salts from iron (Barnes, *J. Soc. Chem. Ind.* 1899, 15).

Titanium tannate washed free from sulphate and chlorides, and dissolved in warm aqueous oxalic or tartaric acid, is an excellent dye for cotton, the shade varying with the sp.gr. of the solution. The solution of titanium tannate can also be employed as a further fixing and modifying bath after dyeing, the colours becoming faster and more yellow after such treatment. It also serves as an excellent fixing agent for the Janus colours which have been dyed substantively. Very good colours are also obtained with methylene blue, rhodamine, and aniline black (Barnes, *l.c.*; Kearns and Barnes, *Eng. Pat.* 8589; *J. Soc. Chem. Ind.* 1899, 491; Erban, *Chem. Zeit.* 1906, 30, 145).

A solution containing a titanium salt gives, with tannic acid, an orange precipitate; with gallic and pyrogalllic acids, orange or brownish-yellow solutions; and with salicylic acid a pale-yellow coloration: a yellow to deep orange colour is also produced by hydrogen peroxide; these colours are imparted to wool when the latter is steeped in the hot solutions (Barnes, *J. Soc. Chem. Ind.* 1896, 420; 1897, 238; *Eng. Pat.* 5712).

The oxalate, tartrate, titanium sodium oxalate, titanium tanno-oxalate, titanium sodium sulphate, and titanous chloride can be used with good results in dyeing and mordanting silk. The titanium mordants are also useful in the chrome developing colours, and in the after treatment of silk previously dyed with anthracene yellow or brown or alizarin colours. For this purpose titanium potassium oxalate or titanium sodium sulphate are best used (Hunt, *J. Soc. Dyers and Col.* 1919, 35, 58).
J. Soc. Dyers and Col. 1919, 35, 58).

Titanium salts unite with the tannin matter of leather to form on the fibre a yellowish-brown titanium tannate, which is very fast to light and to the action of soap. On account of its cheapness, potassium titanium oxalate is the most applicable. It is exceedingly soluble in hot water and can be applied to tanned leather either in the dye-bath or with a brush. The mode of application and the previous and subsequent treatment of the leather depend on the quality of the latter, whilst the shade of colour obtained, which varies from bright yellow to a reddish-brown, depends on the nature of the tannage and on the amount of titanium salt used. The basic colours especially give much fuller and richer shades with titanium than without (Lamb, J. Soc. Chem. Ind. 1901, 1111; U.S. Pat. 722857, 1903; Dreher, J. Soc. Chem. Ind. 1902, 771; 1903, 294; 1904, 71; Eng. Pats. 9556, 1901; 27597, 1902; Stiasny, J. Soc. Chem. Ind. 1902, 1329; Erben, *l.c.*).

According to Barnes (*l.c.*) titanium tannate can also be used effectively as a pigment in water-colour drawings, the colour depending upon the conditions of preparation of the pigment and varying from brick-red to almost pure yellow. Titanium salts are also said to be employed in the manufacture of artificial teeth and in colouring porcelain (Ladoff, *l.c.*; Barnes, J. Soc. Chem. Ind. 1896, 421).

See A. H. A. Robinson on Titanium, Dept. of Mines, Canada.

The titration of triphenylmethane and azo dyes with N/20 titanous chloride solution is a satisfactory method for determining the strength of commercial dyes of these classes, and has been applied to the routine analysis of about 30 members of the former and over 100 of the latter class, giving results that could be relied upon to about 0.5 p.c. The concentration of sodium tartrate and of alcohol in the solution to be titrated and the temperature of titration can be varied within wide limits without materially affecting the results obtained. In the case of the azo dyes difficulty was encountered in the intense colour of the reduced solution, which masked the end-point of the titration. It was found that this colour depends to a large extent on the nature of the solvent, and that by a judicious choice of solvents a direct titration is possible. Details are given of a direct titration method and a black titration method for use with azo dyes. In the latter method the reduction products of the dye frequently serve as an indicator, but if not a 0.1 p.c. solution of reduced methylene blue may be added. Water, alcohol, acetic acid, and mixtures of these were used as solvents. The analysis of basic brown dye-stuffs was possible by the indirect method if the titanous chloride was added at room temperature. In the analysis of chrysoidines the temperature had to be kept below 70°C. to avoid decomposition and consequent low results (W. S. Calcott and F. L. English, Ind. Eng. Chem. 1923, 15, 1042-1044; J. Soc. Chem. Ind. 1923, 42, 1122A).

TITANIUM GREEN. Titanium ferrocyanide, prepared by adding potassium ferrocyanide to a solution of hydrated titanous oxide in hydrochloric acid, has been suggested as a substitute for Schweinfurth green and other arsenical

pigments (Elsner, Dingl. poly. J. 905, 130; Gentele, *ibid.* 140, 238).

TIZA. A local South American name for ulexite (*q.v.*).

T.N.T. Trinitrotoluene *v.* **EXPLOSIVES.**

T.N.X. Trinitroxylene.

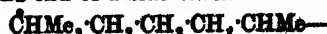
TOAD'S EYE. Native oxide of tin *v.* Tin salts and oxides, art. TIN.

TOAD VENOMS. Toads have long been known to be poisonous, and in the eighteenth century toadskins were employed as a remedy against dropsy. This application now only survives in China. A scientific basis for this therapy has been supplied by the isolation of the following crystalline active principles having a powerful digitalis-like action on the heart.

Bufotalin $C_{25}H_{38}O_8 \cdot C_2H_5O$, m.p. 148°, from alcohol, $2C_{25}H_{38}O_8 \cdot C_2H_5O$, m.p. 154°, from ethyl acetate. In each case the solvent of crystallisation is slowly lost in a high vacuum at 150°. On careful heating bufotalin sublimes at 225°-230°, $[\alpha]_D = +5.4^\circ$. This substance was first obtained in an impure form from the skin of the common European toad by Faust (Arch. exp. Path. Pharm. 1902, 47, 278), and was subsequently obtained pure by Wieland and Weil (Ber. 1913, 46, 3315; see particularly Wieland, Sitzber. bayer. Akad. Wiss. 1920, 329; Abstr. Chem. Soc. 1922, i. 199). Each toad skin yields about 10 mg. of bufotalin (and also 3 mg. of suberic acid). Of the six oxygen atoms, two are present as a lactone group, two as an acetyl group, and two are hydroxylic. Of the latter, one is capable of acetylation (which yields **acetyl bufotalin** $C_{28}H_{38}O_7$, m.p. 254°), the other can be oxidised to a ketone group (present in **bufatolone** $C_{25}H_{34}O_8$, m.p. 261). **Tetrahydrobufotalin** $C_{25}H_{40}O_8$, m.p. 204°-205°, and **bufotalan** $C_{24}H_{38}O_8$, m.p. 198°-199°, have also been prepared, the latter by the removal of one molecule of acetic acid and of water by the action of concentrated hydrochloric acid on bufotalin.

Bufotalin is not present as such in the skin of the toad, but is a product of the decomposition of the actual poison bufotoxin $C_{44}H_{62}O_{11}N_4$, m.p. 204°-205°, hydrolysed by dilute acids to bufotalein $C_{24}H_{38}O_8$ and suberylarginine (Wieland and Alles, Ber. 1922, 55, 1789). Bufotalein differs from bufotalan (above) by having four double bonds, and being yellow.

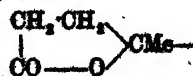
The carbon skeleton of bufotalin, apart from the acetyl group, consists of 24 carbon atoms, with four rings, and the same arrangement is believed to be present in the bile acids. Moreover, cholic acid has been shown by Windaus and Neukirchen (Ber. 1919, 52 [B], 1915) to differ from cholesterol by having an isopropyl group at the end of a side chain



which in cholic acid is represented by



In bufotalin this side chain is probably further oxidised to a γ -lactone



Bufotalidin is a second crystalline toxic substance from the European toad, $C_{25}H_{38}O_7$. With alcohol of crystallisation it melts at 178°.

and after heating in a high vacuum at 228°-230°; it is probably oxybufotalin.

Bufagin $C_{12}H_{22}O_4$, m.p. 217°-218°, $[\alpha]_D = +11^\circ$, occurs in the secretion of the parotid gland of the large Central-American toad *Bufo* *agua* (together with nearly 7 p.c. of adrenaline), and was isolated by Abel and Macht (J. Pharmacol. expt. Ther. 1912, 3, 319). According to Shimizu (*ibid.* 1916, 8, 347) it is also present in the Chinese drug 'senso.'

Bufo *agua* is used for the preparation of an arrow poison by South American Indians.

Wieland considers that the formula for bufagin may require alteration to $C_{27}H_{38}O_8$, which is that of the methyl ether of bufotalin. The above toad venoms are pharmacologically similar to digitalis and strophanthus (*q.v.*). Digitoxigenin is, according to Cloetta (Arch. exp. Path. Pharm. 1920, 88, 113), $C_{24}H_{38}O_8$, and strophanthidin (=cymarigenin, *see art.* STROPHANTHUS), has 23 or possibly 24 carbon atoms. All these heart poisons from animal and vegetable sources seem to be related to cholesterol and the bile acids. G. B.

TOBACCO. The botanical order of the *Solanaceae* includes many well-known plants which are extensively cultivated because certain portions of them are of great utility to the human race. The tuber of the potato and the fruit of the tomato are food substances of great value and of almost universal consumption. Other genera of the order, however, afford instances of cultivation simply for the production of foliage; the dried leaves of the thorn-apple (*Datura Stramonium* [Linn.]) are sometimes smoked as a remedy for asthma. The most important plants of this class, however, belong to the genus *Nicotiana*, and their dried leaves are known as tobacco. The etymology of the word 'tobacco' is somewhat obscure; the geographical origin assigned to it by tracing it either from Tobago, an island in the West Indies, or from Tabasco, an island in the Gulf of Mexico, is probably incorrect. When the Spaniards first visited San Domingo they found that the natives used a peculiar contrivance for inhaling the smoke of burning tobacco leaves. This instrument was called a 'tabaco,' and was shaped like a Y with the arms so close together that they could be inserted up the nostrils, and it is highly probable that the word tobacco thus originated.

Upwards of 40 species of the genus *Nicotiana* have been described, but many of them are simply modifications resulting from the influence of soil and climate on the chief species. *Nicotiana Tabacum* (Linn.), the most important member of the genus, is a fine plant, indigenous to America, where it grows from 6 to 9 ft. high. The stem is slightly viscous, and the leaves, which are oblong or lanceolate in shape, are attached alternately, and surround the stem in the form of a spiral (of which the ninth leaf overhangs the first, the tenth the second, and so on). The distance between the leaves is usually about 2 ins. Characteristic soft downy glandular hairs cover the stem and the under surface of the leaves, and these are of great service in the identification of tobacco by the microscope. The flowers have funnel-shaped corollas, about 2 ins. long, of a rose or pinkish colour, and are produced in large terminal clusters: the seed

pods have two valves, and the seeds are very small and numerous. Modifications in the type have resulted in the production of several varieties of this species, differing chiefly in the size of their leaves. The two principal groups now recognised are *Nicotiana Tabacum*, var. *macrophylla*, or 'Maryland tobacco,' comprising stalked and stalkless forms, and *Nicotiana Tabacum*, var. *angustifolia*, or 'Virginia tobacco.' The finest growths of Cuba, Manila, and Turkey (including Latakia), are now attributed to a form of the stalked Maryland tobacco. Under the name of Shiraz tobacco, *N. persica*, a very fine variety, is cultivated in Persia; but the plant is probably a form of *N. Tabacum*, obtained by cultivation of seed derived from a Brazilian variety. Of the remaining species, *Nicotiana rustica* (Linn.) is the most important. It is of hardier constitution and dwarfer habit than the preceding species, and the flowers are also of a lighter colour. It is cultivated largely in Germany, Hungary, and in the East Indies, and includes the common Hungarian and Turkish varieties.

The use of tobacco for smoking purposes is supposed to have originated among the North American Indians. When America was first discovered, and afterwards when fresh portions of the continent were explored, the practice was found to be prevalent among all the native tribes, and its introduction into Europe very soon followed. The plant was first cultivated in Spain early in the sixteenth century, and was introduced into France and Italy about the year 1560. It attained considerable fame as a medicinal herb, and was at first regarded with universal favour. Sir John Hawkins is said to have brought plants home in 1565, but Sir Walter Raleigh, who learned the uses of the plant from Mr. Ralph Lane, Governor of Virginia, probably first introduced its cultivation. The habit of smoking soon became general, but this use of the plant met with a considerable amount of opposition, not only in England, but also throughout Europe. Nearly the whole of the early literature on the subject was written in an antagonistic strain. Kings' counterblasts, Popes' anathemas, Sultans' decrees and even violent punishments failed to check the growing habit, and plantations sprang up, not only in the New England States, but also all over the United Kingdom. In the year 1604 the tax on the imported article was raised from 2d. per lb. to 6s. 10d. per lb., and English planters were forbidden to produce more than one hundredweight of the leaf. Shortly afterwards the pre-emption of tobacco was made a royal monopoly, and the King enjoined the plucking up of all tobacco found growing in England and Ireland. In the years 1652, 1660, and 1663, Acts were passed prohibiting the cultivation of tobacco in England and Ireland, and these Acts were extended to Scotland in the year 1782. The prohibition as regards Ireland was removed in the year 1779, but was subsequently reimposed in the year 1831. Notwithstanding these measures, the cultivation of tobacco in England did not really cease until the year 1782, when some planters in the vale of York were imprisoned and fined the sum of £30,000. The restrictive legislation as regards Ireland was repealed in 1907, and for Great Britain in 1910.

Culture.—The tobacco plant, though essentially tropical, can, with suitable modifications in the cultural details, be grown successfully in temperate climates. It is cultivated for commercial purposes in the United States, Cuba, Mexico, Brazil, Paraguay, the Dutch Indies and North Borneo, Australia, India, China, Burmah, the Philippines, Persia, the Transvaal, Rhodesia, Nyasaland, the Levant, Greece, Hungary, Germany, Russia, France, and Holland, and is grown on a small scale in the United Kingdom. In Spain and Egypt its cultivation is prohibited. Cigar leaf is grown in Cuba, the East Indies, North and South America, Rhodesia, and Germany; tobacco for pipe smoking in the United States, the Levant, Germany, the Transvaal, Nyasaland, Australia, China, Java, tobacco for cigarettes in the United States, the Levant, Greece, Persia, and other countries. In the United States, several types of leaf are grown, of which the principal are the Seed Leaf and Florida varieties of Cuba and Sumatra tobacco for cigars; White Burley; the Heavy Shipping or dark tobacco of Kentucky, Virginia, and Maryland; the Yellow tobacco of Carolina and Virginia; and the Perique of Louisiana. A spangled type of yellow tobacco is grown also in Ohio. Seed Leaf requires a strong, highly-manured soil, which will promote a rapid growth, so that the plants may be harvested when expansion of the leaves ceases, and the process of granulation and secretion of the gummy substances begins. White Burley flourishes in a highly fertile disintegrated limestone. Heavy Shipping tobacco thrives best on ferruginous clayey soils. Yellow tobaccos need a sandy porous, sterile soil, to which just sufficient fertilizers (superphosphate, potash, and nitrogenous) have been added to promote summer growth; in the autumn the plant's declining vitality causes the leaves to turn more and more yellow until the tint desired is reached, which is afterwards fixed in the curing process. Perique is grown on low-lying lands, black with humus, in the swampy districts of Louisiana. Climate has a great influence on the flavour, but the texture of the leaf depends largely on the nature of the soil in which the plant grows. The northern varieties, for example, planted in the Southern States gradually change in character; the plants ripen earlier and the leaves assume a lighter colour, diminish in size, and increase in thickness and sweetness. * Special attention must be paid to the fertilizers used to ensure that the proportions of ammonia, potash and phosphoric acid most suitable for the type of leaf are employed. Too much ammonia darkens the colour of the leaf and increases its nicotine-content, while too little ammonia retards the growth. Alkaline materials encourage the growth of certain fungoid diseases, especially root-rot, and lime is therefore much less used than was formerly the case.

The seed is sown in February, March, or April, in seed beds, composed of a light friable soil prepared some time beforehand, and a brush heap is burned on the ground prior to sowing to destroy harboured insects. The young plants are raised either in hot beds, or in cold frames protected by plant-matting, according to the locality. In the three months from April to June, when the plants are about 8 ins. high,

they are transplanted into well ploughed soil, thrown up in ridges; and if the weather is dry, they are watered in. A space of from 1½ to 3 ft. is allowed between each plant in the rows, which are made from 3 to 4 ft. apart. The constant removal of suckers from the plants ('suckering'), frequent harrowing of the soil, and destruction of weeds and insect pests are necessary. In Turkey and other Eastern countries, where small leaves are desired, and the buds and flowers are also used, 'topping' is not practised, but the larger growths of the United States, &c., usually require this treatment when the first bloom begins to show. Ten to a dozen leaves in the case of Heavy Shipping tobacco, and 16 to 18 leaves in the other varieties, are allowed to remain on the stem, and the increase in leaf surface may be as much as 50 p.c., when compared with leaves of normal size. Seed Leaf requires from 2 to 3 weeks after this operation to ripen, yellow leaf and Burley take a month, and Heavy Shipping tobacco 2 or 3 weeks longer. An abnormal amount of organic matter accumulates in the cells of ripe tobacco leaf, owing to the 'topping' and 'suckering' of the plant. The continuous accumulation of nicotine, oxidising enzymes and acids which takes place in the cells finally causes the chlorophyll granules to acquire a yellowish colour. The change from the normal deep green tint of the leaf is very noticeable to the experienced eye, and indicates that the time for harvesting has arrived. Another sign of ripeness is that the leaf becomes brittle, and snaps when bent between the fingers on account of the great increase in its starch contents. The constituents of the cells having fulfilled their functions are at this stage going back to the stem to be transferred thence to the upper leaves, to be used for other purposes in the economy of the plant. Compared with the young leaf, the ripe leaf has a density half as high again, and contains about 2½ times as much matter soluble in boiling water. The curing of tobacco is a skilful operation, involving much more than the simple drying of the leaf. Its object is to promote by favourable conditions the important changes in composition which are brought about by enzyme action on the surplus food material stored in the ripened leaf. Until this is accomplished, it is necessary that the life of the leaf, which may persist for several days after harvesting, should be preserved. Any actions which tend to kill the leaf prematurely are to be avoided, e.g. breaking or bruising the leaf, freezing or very rapid drying. The methods of curing are fully described in Farmer's Bulletin, No. 573 of the U.S. Department of Agriculture, 1916. White Burley and Seed Leaf are air cured in houses that can be ventilated at will: this operation requires from 6 to 8 weeks. An alternating change from the moist to the dry condition of the leaves takes place according to atmospheric conditions as the curing proceeds. Yellow leaf is cured by artificial heat, distributed by flues in air-tight barns. The temperature is maintained at 80° to 90°F. for 16 to 36 hours for the leaf to acquire the proper colour, the heat is then raised by 5° to 10° at a time, about every 2 hours, to 115° to 120°F., and maintained at this point until the leaf is properly cured. The curing of the stalks is then effected by raising the temperature hourly by 5° to 10°

to about 180° to 175° F. The whole operation takes about three days. Heavy Shipping tobacco is hung on scaffolds or in barns for some days to become yellow, and the curing is completed by open log-fires, kindled directly under the tobacco and gradually increased in size. In India, Ceylon, and other Eastern countries, sun-curing is sufficient. Where resort to artificial heat is necessary, it is essential that the increase of heat should be at first very gradual, as the object is not so much to dry the leaf as to fix as far as possible its qualities as regards colour, strength, elasticity and flavour. A high initial temperature causes the leaf to dry rapidly and retain its green colour, whereas by slow drying the tint produced will vary from shades of yellow to brown. The proper fixing of the colour of the leaf is of great financial importance to the curer. The leaves, except those of the yellow varieties which are harvested as they ripen, are not usually removed from the stems prior to curing. Perique tobacco undergoes a special process of curing. After the leaves in the drying-houses have acquired a brown tint they are twisted into rolls containing about 30 leaves; these rolls are packed into boxes holding about 50 lbs. and heavy pressure is applied; the rolls are then slightly opened out and exposed to the air to aerate the exuded juices and, when these are re-absorbed, again subjected to pressure. This operation is repeated daily for about 10 days, and at longer intervals for some 3 months, with the result that the tobacco acquires a glossy black colour, and a rich characteristic spirituous odour. In Florida, cigar leaf is now grown from Cuba and Sumatra seed, but success has been achieved only by making considerable changes in the ordinary methods of cultivation. The plants are placed closer together, about 14 ins. apart; the Cuban varieties are topped high, but the Sumatra kinds are allowed to bloom. Each plant yields from 18 to 30 suitable leaves which are primed off as they ripen. The discovery that plants shaded by trees were far superior to those grown in the open fields, led to the adoption of artificial shading, which has also been tried with success in Cuba, Porto Rico, and Connecticut.

Preparation for the market involves the grading, fermentation, and ageing of the tobacco, and is usually managed by the packers and not by the farmers. There are three methods of fermentation; the sweating in bulk, the natural sweat after packing in cases, and the forced sweat in case; but the first is generally used, as it can be more easily controlled. The natural sweat of Seed Leaf is conducted in large wooden cases, each holding about 300 lbs. of leaf; a space of about half an inch is allowed between the boards, through which the air enters and the moisture escapes. In the autumn the leaves are pressed tightly into the boxes, which are then stored in the warehouse in tiers until the sweat occurring in the following summer is finished. The temperature is maintained fairly uniform, and the loss of weight during the process amounts to from 10 to 14 p.c. White Burley and Heavy Shipping tobacco are allowed to sweat in bulk for a short time before being primed, or forced into hogheads by pressure; the hogheads are large enough to hold from 1000 to 1000 lbs. of tobacco leaf.

Yellow tobaccos are also bulked down for a month or two to fix the colour, and are afterwards packed loosely. Cuba, Sumatra, and other cigar tobaccos are carefully graded according to colour, &c., and are fermented in large bulks varying from 3000 lbs., for the light varieties to 15,000 lbs. for the dark varieties of leaf. The fermentation is allowed to proceed for from 6 to 8 days, and the heaps are then re-made, the outside portions being placed in the centre. The operations are conducted in rooms heated by steam pipes to about 165° F., but if the temperature of the heaps is allowed to rise much above 140° F. the enzymes present are liable to undergo oxidation with consequent deterioration in the quality of the tobacco.

Home-grown tobacco. In the year 1886, owing to the agricultural depression in this country, efforts were made to remove the restrictions then existing on the home cultivation of tobacco, and permission was obtained to try experimental growings in several selected localities. These experiments were repeated in the following year, and were sufficiently satisfactory to justify the opinion that tobacco could be grown successfully as a farm crop in the British Isles. Experiments under the auspices of the Department of Agriculture in Dublin were started in Ireland in the year 1900. In the year 1904, the cultivation was commenced on a commercial scale, and in the year 1907 the statutory restrictions were repealed. The Department continues to furnish all possible assistance to the tobacco growers, and annual reports on the progress of the experiments are published in its journal. A total area of about 200 statute acres was devoted to the cultivation of tobacco in the year 1914, as compared with 20 acres in the year 1904. The crop of 1914 yielded about 160,000 lbs. of marketable tobacco. During the war the area under tobacco cultivation was greatly reduced, but in 1922 about 35,000 lbs. of tobacco were raised from 50 acres planted by 46 growers. Cultivation has been tried successfully in the following counties: King's County, Louth, Meath, Kilkenny, Wexford, Tipperary, and Limerick. The experimental tests which have been carried on for several years gave promise that satisfactory roll and plug pipe-tobaccos could be produced from such hybrid varieties of leaf as 'Copper King,' 'Blue Pryor,' and 'Kentucky Black,' also 'Irish Gold' for cigarette tobacco. These varieties were found, however, to suffer from root-rot, a condition which does not obtain in the Italian hybrids 'Skiky,' and 'Turkish,' which have since been tried for pipe and cigarette use respectively. The influence of the cool, moist climate favours the production of large thin leaves which are somewhat deficient in gum, resins and aroma; but these defects have to some extent been overcome by prolonging the ripening season, during which the leaf gains in body. Irish leaf is for the most part used for blending with unfermented dark American tobacco of the Western type, and recent experiments have been directed chiefly to the raising of small crops of heavy dark varieties by working farmers. The Irish climate, however, favours the production of tobacco such as is grown in northern countries, all of which is fermented. The crop of 1922 has been treated thus with satisfactory results. The quantities

for success are deep cultivation, a fine soil, and fields protected from cold winds by high hedges or other means. As regards manures, the initial growth is found to be more rapid when farmyard manure is supplemented by artificial manures. The largest yield is obtained on uplands, when manures containing a large proportion of phosphates are used; potash is more effective for moorlands. Nitrogen and phosphates have a tendency to produce a coarse leaf; with potash a smooth leaf is obtained, and the burning qualities are improved, but the growth is somewhat retarded. In consequence of the minute size of the seed, about 300,000 to the ounce, the plant is forced to rely unusually early on external nourishment. The seeds are sown in glass-covered hot-beds some time between the middle of March and the middle of April, and the plants are transplanted at the latest by June 1st. The usual cultural details are followed: insect pests, on the whole, are not so troublesome as they are abroad, but the cool, moist climate greatly increases the tendency to produce suckers. 'Topping' of all the varieties, except Turkish, is usually practised. Ripening is hastened by the 'topping' and 'suckering' operations, but the usual indications, change of colour, curling of the edges of the leaf, &c., are less manifest under Irish climatic conditions. Harvesting lasts from about the end of July to mid-October, according to whether the leaves are primed off as they ripen, or whether the whole plant is harvested with the leaves still attached to the stem. The practice of allowing the plants to wilt in the open air on scaffolds which are capable of being protected from heavy rains, has been found very valuable. Air-curing, supplemented by suitable artificial heat at critical periods, has proved to be the best method for most classes of tobacco. The subsequent preparation of the leaf for the market involves the usual operations of grading or sorting, fermentation in bulk, and ageing, after the tobacco is packed. A statute acre of land yields on the average about 1000 lbs. of tobacco at a cost of from £20 to £60.

The enactments against the growth of tobacco in Scotland and England were repealed by the Finance Act of the year 1909-1910, and from 1911 to 1913 a rebate of one-third of the duty was allowed on home-grown tobacco. Grants have since been made by the Development Commissioners and the Board of Agriculture with the object of promoting experimental work on the culture of tobacco which has been undertaken in 27 counties in the United Kingdom under the auspices of the British Tobacco Growers Society. Thirty-three acres were planted in the year 1913, in addition to 80 acres cultivated by private growers. In the year 1915 duty was charged upon nearly 33,000 lbs. of tobacco grown in England, and upon 2000 lbs. grown in Scotland; but no tobacco has been grown in Scotland since 1916. The Ministry of Agriculture have also undertaken experiments on the growth and after-treatment of tobacco on government-owned land in Norfolk. In 1923 about 14,000 lbs. of leaf were obtained from 18 acres under cultivation in Hampshire. Since 1918, however, there has been a marked decrease in the areas under tobacco cultivation in the United Kingdom, Northern Ireland, and the

Irish Free State. Growers contended that the rebate of one-sixth from the duty allowed by law in 1919 in the case of home-grown tobacco was not sufficient to allow of tobacco being grown at a profit. A Government Committee appointed by the Treasury to inquire into this question reported in 1923, Cmd. 1983, that though a limited number of agriculturists might derive some benefit from some measure of assistance to the industry of tobacco growing in this country, they came to the conclusion that the nature and extent of that benefit were not such that the committee could recommend any further expenditure of public funds over and above the help already given by Imperial Preference. The principal grounds on which the committee's conclusions were based are as follows:—

(1) Even allowing for the improvements which might be effected in British grown tobacco as the outcome of further experience, they could not anticipate that anything more than a low-grade article would be grown generally in Great Britain.

(2) There is accordingly no prospect of tobacco being grown on a large scale so as to compete successfully with foreign tobacco, except under a preference such as the industry now enjoys; and the amount of such a preference will always be liable to alteration (apart from the automatic decrease which a reduction of duty would bring about).

(3) Competing overseas products would always have the advantage of more suitable climates and of cheaper labour, and it cannot be assumed that Great Britain will have a monopoly of improvement.

(4) The crop is not suitable for smallholders, owing to the heavy capital expenditure required, the uncertainty of the quality and amount of the yield, and the interval which must elapse before a return on the outlay can be expected.

(5) Except on a limited area of land, the crop does not offer such a prospect of effecting a general improvement in the system of agriculture nor so remunerative a substitution for existing crops, as would justify some considerable outlay in bringing about its establishment.

Provision is made for remission of duty on such home-grown tobacco as is used for the preparation of tobacco extract for insecticidal purposes. An approved denaturant must, however, be added to the extract before it is allowed to pass out of revenue control.

Composition.—The tobacco plant contains a large number of substances common to the vegetable kingdom, chief among which are cellulose, starch, albuminoids, saccharine matters, resins, chlorophyll, and many organic acids. On the character and proportion of these organic substances depend largely the uses to which the several varieties of tobacco are put. Freshly-cut green leaves contain from 80 to 90 p.c. of moisture: the normal percentage in the leaf when ready for the market is from 12 to 14 p.c., but in the finer grades of cigar and other leaf 20 p.c. is not uncommonly found. The amount of nicotine, the characteristic constituent of tobacco, varies from about 1 to 10 p.c.: thick-leaved varieties contain more than those with thin leaves, and the top leaves of a plant are richer in nicotine than those at the base of the

stem. Schlessing has shown that the amount present in the leaves increases as growth proceeds: from leaves of the same kind collected on May 25, August 27, and September 25, he obtained 0.79, 2.27, and 4.32 p.c. of nicotine respectively. Dark, heavy tobaccos contain considerably more nicotine than the light coloured varieties. The use of large quantities of nitrogenous manures favours the production of nicotine in the plant. Java leaf contains from 1 to 2 p.c., Havannah, Maryland, Manila, and Turkish from 2 to 4 p.c., Virginia and Kentucky up to 7 p.c., while some heavy French varieties contain as much as 10 p.c. of nicotine. The organic acids present in tobacco are chiefly malic, citric, oxalic, and pectic; acetic acid is sometimes found in fermented leaves. Some proportion of these acids exists in combination as acid salts and gives an acid reaction to the cell-sap. The malates, owing to their hygroscopic properties, are said by Behrens to exercise a considerable influence on the 'life' of the leaf by preserving its elasticity and softness. The changes in the colour of the leaf which occur during the curing process are concomitant with considerable changes in the chemical composition, brought about partly by the etiolation of the chlorophyll granules, and partly by the subsequent oxidation of the sap contents of the dead cells. The acidity of the leaf, and the proportions of soluble albuminoids, and of starch also markedly diminish. Further changes of a complex character occur in the sweating process. The nicotine which exists in the leaf in combination with various organic acids is partially liberated, and part of it and of the amino bodies and albuminoids also, are eliminated. The nitric acid and ammonia-content should be little affected, but excessive fermentation favours the production of ammonium salts. Experiments by Dr. Loew of the United States Department of Agriculture, supplemented by those of Oosthuizen and Shedd, have proved that various soluble ferments or enzymes exist in the tobacco plant during its growth, and their researches have thrown light on the considerable influence enzymes exercise on the changes which occur during the ripening, curing, and fermentation stages. Invertase, diastase, emulsin and reductases have been identified in the tobacco seed, and in the leaf, not only during all stages of its growth, but also after the completion of the curing process. Oxidases have been found to be present in the growing leaf, but after the 'topping' operation they gradually diminish in quantity until maturity is reached, and almost entirely vanish during the 'curing' process. Starch is converted into sugar early in the curing stage by the action of diastase, but may disappear at a later stage, probably through the action of the oxidases present. Proteolytic ferments accomplish a considerable reduction in the amount of 'fat' or protein in the leaf, and reductases exercise a reducing influence on the nitrates and nicotine content of the leaf. Considerable loss of weight occurs during the curing and fermentation periods, amounting to as much as 15 p.c. in the later stage alone, of which about a quarter is solid matter. The retardation of enzyme action by unfavourable conditions in the curing and fermentation processes adversely affects the

flavour and aroma of the tobacco. Many attempts have been made to isolate and identify the bodies which impart the aroma to tobacco, but they have so far proved unsuccessful. At one-time the source of the aroma was believed to be the so-called tobacco-camphor, or nicotianin, a crystalline volatile substance obtained by the steam distillation of fermented tobacco; but experiments have shown that it is not always associated with nicotine in tobacco leaf, as was supposed. The theory of Suchsland, that the distinctive aromas which characterise the different types of tobacco are due to the action of specific bacteria during the sweating process, has not been substantiated by other observers. The formation of the aromatic substances is believed to be due largely to the influence of enzyme action, whereby elimination or breaking down occurs, especially in the nicotine, amino-bodies and other nitrogenous constituents of the leaf, during the fermentation stage. It is well known that a high nicotine content in a cigar is often associated with a poor aroma, and that if the leaf has a high protein content the quality of the aroma is especially liable to be deteriorated by imperfect curing. The deficiency in aroma which is characteristic of bright yellow leaf is no doubt due to the destruction of the enzymes which occurs in consequence of the high temperatures required during the curing stage of this class of tobacco. The aromatic matters of tobacco are soluble in water, and more or less so in alcohol, and are readily dissipated by heat. The odour developed in smoking a cigar may be due partly to the mere volatilisation of the aromatic products of the sweating process and partly to the destruction of certain constituents. Nicotine, ammonia, carbon monoxide, pyridine, trimethylamine, butyric acid, and traces of nicotianin, hydrogen cyanide, formaldehyde, and hydrogen sulphide, in addition to water and carbon dioxide, have been found in tobacco smoke. Kissling recovered from the smoke of two different samples of burning tobacco, each containing originally 3.75 p.c. of nicotine, 27.8 and 52.0 p.c. of the nicotine, while the quantity in the unconsumed portions of the tobacco increased to 4.5 and 5.9 p.c. respectively.

Armstrong and Evans (Brit. Med. J. 1922, (1), 992) found that the amount of carbon monoxide varied with the rate of smoking. Cigarettes smoked normally yield a smoke containing 0.6 to 0.8 p.c. carbon monoxide, pipe-tobaccos from 0.7 to 1.14 p.c., and cigars from 6 to 8 p.c. As regards cigars the results are little affected by make or quality, closeness of packing and rate of smoking being the determining factors.

The table on p. 82 gives analyses of certain kinds of tobacco serves to show the wide differences in the composition of various typical varieties. It is compiled from the results of analysis of many kinds of tobacco, which were made in the Inland Revenue Laboratory under the direction of Dr. James Bell.

The amount of ash found in tobacco varies greatly, and when calculated on the dry leaf ranges from about 10 p.c. to as much as 25 p.c., or even more. The lowest amount is found in the light varieties used for making cigarettes, and the greatest amount in leaf intended for making pipe-tobacco. The ash of tobacco invariably

PERCENTAGE COMPOSITION OF TOBACCO DRIED AT 100°C.

Constituents	Manila	Virginia Ripe	Virginia Bright	Turkey	Havana	Latakia	Kentucky	German	Java	China
Nicotine	3.00	3.86	2.20	0.90	3.98	1.17	4.59	3.22	3.30	2.50
Malic acid (anhydride)	10.72	9.06	4.17	4.90	12.11	9.07	11.57	12.04	6.04	7.46
Citric " "	3.94	3.09	1.00	1.90	2.05	2.40	3.40	2.89	3.30	1.58
Oxalic " "	3.72	1.58	1.72	1.38	1.53	1.98	2.03	2.51	3.38	3.91
Acetic " "	0.36	0.80	0.35	0.14	0.42	0.36	0.43	0.34	0.22	0.31
Tannic " "	0.30	1.34	6.32	3.39	1.13	2.33	1.48	0.68	0.51	3.13
Pectic " "	10.63	7.72	7.51	9.62	11.36	6.25	8.22	10.23	10.13	7.48
Nitric " "	0.43	0.43	0.14	0.05	1.32	0.76	1.88	0.37	0.23	—
Cellulose	11.73	10.38	12.64	9.72	15.76	10.00	12.48	14.48	11.82	7.98
Starch	—	—	1.73	6.28	—	0.69	—	—	—	1.54
Saccharine matter	—	—	14.59	12.07	—	1.46	—	—	—	12.93
Ammonia	0.30	0.05	0.03	0.05	0.49	0.10	0.19	0.32	0.23	0.04
Insoluble albuminoids	11.27	14.29	4.88	5.30	9.75	7.25	8.10	6.62	9.53	4.49
Resins and chlorophyll	7.51	5.21	3.41	7.90	5.15	6.62	1.99	2.13	6.45	6.02
Fatty substances	2.04	1.07	2.27	0.49	1.03	1.12	2.28	0.89	0.81	0.25
Soluble extractive matter rich in Nitrogen	8.34	16.24	13.47	13.24	7.74	18.97	13.90	8.10	10.39	14.35
Indefinite insoluble matter	9.45	12.93	12.41	9.71	8.68	14.94	13.10	12.56	15.20	12.61
Mineral matter	16.26	11.95	11.36	12.96	17.50	14.53	14.36	21.72	18.46	13.42

contains potash, lime, magnesia, iron-oxide, alumina, soda; carbonic, silicic, sulphuric and phosphoric acids, and chlorine. The potash, which exists in the tobacco mainly in combination with the organic acids, may be present to the extent of fully 30 p.c. of the total amount of the ash. The amount of lime present is generally lower than that of potash: magnesia and silica rank next, while the amounts of soda, alumina and iron oxide are relatively small. Lithia and manganous oxide are occasionally present in very small quantities. The combined chlorine varies from a mere trace to as much as 15 p.c. of the total amount of the ash (*cf.* Roberts, Analyst, 1918, 254).

The following table shows the percentage composition of the ash of the several kinds of tobacco enumerated in the preceding table.

The leaves of tobacco contain more magnesia and silicic acid, and less alkali, phosphoric acid and chlorine than the stalks. The nitrates are confined almost entirely to the stalks and stems of the young plant, and decrease in amount as the plant comes to maturity: analysis of cigar-stalks from Missouri and Connecticut showed from 0.5 to 0.75 p.c. of nitrates, as against 0.15 p.c. found in cigarette leaf. Home-grown tobacco as a rule contains a considerably higher percentage of ash than is present in similar varieties grown abroad: this circumstance is probably accounted for by the use of manures either in excessive quantities or of unsuitable character, especially when large quantities of combined chlorine are present.

Good burning qualities in tobacco are associated with a high percentage of ash, rich in

PERCENTAGE COMPOSITION OF ASH.

Constituents	Manila	Virginia Ripe	Virginia Bright	Turkey	Havana	Latakia	Kentucky	German	Java	China
Percentage of ash on dry tobacco (excluding sand)	21.40	14.96	12.32	12.92	21.40	18.18	17.98	25.88	18.80	14.76
Potash	16.25	34.16	22.19	14.51	11.83	19.57	16.78	—	14.06	14.44
Potassium chloride	6.45	2.53	7.01	19.29	12.68	4.06	2.41	24.98	19.61	3.73
Soda	0.54	0.86	1.46	0.54	0.81	0.55	0.66	—	0.67	0.41
Sodium chloride	—	—	—	—	—	—	—	0.60	—	—
Lime	33.26	18.90	21.70	22.54	33.06	34.69	29.51	35.65	22.30	31.09
Calcium chloride	—	—	—	—	—	—	—	5.89	—	—
Alumina	0.22	0.29	0.89	0.76	0.76	0.68	0.19	0.42	1.79	0.97
Iron sesquioxide	0.18	0.40	2.44	0.43	0.45	0.55	0.82	0.23	0.84	1.19
Magnesia	7.22	6.74	12.44	9.21	5.20	5.53	6.78	6.45	8.62	12.70
Silica	1.59	1.55	0.57	2.06	1.07	2.03	4.94	0.86	6.16	3.28
Phosphoric anhydride	3.92	3.23	4.72	6.39	4.17	3.62	3.66	2.19	6.67	5.11
Sulphuric " "	4.47	4.32	8.29	5.29	4.34	3.67	5.07	3.47	7.94	4.63
Carbonic " "	25.90	27.02	18.29	19.07	25.34	25.05	29.58	19.25	11.54	22.24
Percentage of sand on dry tobacco	0.60	0.95	1.28	1.30	1.80	0.92	5.26	0.94	1.72	2.18

lime and potash salts: chlorides, except in the presence of much potash and lime, have a decidedly retarding effect on the combustion, but silicates, phosphates and sulphates have a beneficial effect. Albuminoids hinder, but cellulose promotes the good burning qualities of tobacco; while nicotine appears to be an unimportant factor. The comparative burning qualities, estimated by the time of glowing of the kindled leaf, vary from about four seconds in yellow varieties to as much as 175 seconds in Pennsylvania cigar-leaf.

Tobacco is analysed as regards organic and inorganic constituents by the usual methods described in text-books dealing with agricultural and quantitative chemical analysis. Special processes applicable to tobacco are described in the report on the culture and curing of tobacco in connection with the 10th United States Census of 1880. The percentage of moisture is liable to be under-estimated if the drying-oven is not maintained at a temperature of 100° . The ash should be re-carbonated by the addition of strong solution of ammonium carbonate, and subsequently dried before ascertaining the weight. A convenient method for the estimation of nicotine in tobacco is that of Kissling, which is as follows: Take 20 grms. of tobacco, finely powdered and dried at a temperature not exceeding 60° , grind it up in a mortar with 100 c.c. of alcoholic solution of soda (6 grms. of NaOH dissolved in 40 c.c. of water and then made up to 100 c.c. with absolute alcohol). Transfer the mass to a Soxhlet extraction apparatus and extract for 3 hours with sulphuric ether. Remove as much of the ether as possible by careful distillation, mix the residue with 50 c.c. of a 4 p.c. solution of soda, and distil in a current of steam. The flask containing the nicotine extract should be connected with the condensing apparatus by means of a tube having a safety bulb, and the distillation conducted rapidly and in such a manner that when 200 c.c. of the distillate have been collected not more than 15 c.c. of liquid remain in the distilling flask. Titrate the distillate with decinormal H_2SO_4 , using lacmoid or litmus paper as an indicator. By using a series of test papers and noting the burette-reading against each, the exact point of neutralisation can readily be ascertained when the papers are dry.

The method of Bertrand and Javillier, based on the precipitation of the nicotine as the silicotungstate, may advantageously be employed when the nicotine distillate also contains ammonia. A gravimetric adaptation of their process has been described by R. Spallino (*Gazz. chim. ital.* 1913, 43, 482-486). Five grms. of tobacco are placed in a Kjeldahl flask with 20 c.c. of water and 2 c.c. of 10 p.c. soda solution, and the mixture steam-distilled to a bulk of 500 c.c. Do 100 c.c. of the distillate are added 10 c.c. of dilute HCl, and 10 c.c. of a 12 p.c. solution of pure potassium silicotungstate, and the mixture well stirred and allowed to stand for 2 hours. The precipitate is filtered through a tared Gooch crucible, washed with water acidulated with HCl, and ignited at a red heat. The residue has the composition $12WO_3 \cdot SiO_2$, and its weight multiplied by the factor 0.1136 gives the quantity of nicotine in one gram of the tobacco.

The method just described for the determination

of nicotine in tobacco smoke. Popp and Contzen (*Chem. Zeit.* 1922, 46, 1001) found that the total nicotine in eight kinds of cigar and pipe tobacco varied from 0.31 p.c. to 2.21 p.c. The smoke from these tobaccos contained from 0.30 p.c. to 1.05 p.c. of nicotine. See also Analyst, 1923, 33. According to H. Rhode (*Zeitsch. Untersuch. Nahr. Genussm.* 1923, 45, 112-115), the five brands of tobacco examined contained from 0.68 to 2.37 p.c. of nicotine calculated on the dry substance. When the samples were smoked in a pipe, attached to an aspirator with an intermittent action, from 15.4 to 28.8 p.c. of the total quantity of nicotine was found in the smoke. The amount of the alkaloid present in the smoke was not proportional to that in the tobacco itself (Analyst, 1923, 48, 568, 334).

Various methods of estimating nicotine in tobacco and tobacco extracts have been critically examined by Rasmussen (*Zeitsch. anal. Chem.* 1916, 55, 81; Analyst, 1916, 208), who found that the polarimetric method of Koenig as well as the silicotungstic method of Bertrand and Javillier, and the method of Kissling above described, gave accurate results; whilst Keller's method and that of Toth were less accurate, and those of Ulex, Degrazia, and Thoms were untrustworthy. This investigation has been carried further by Shedd in the Journal of Agricultural Research (Washington D.C.) 1923, 961-970. In the recovery of nicotine by the distillation method he used solid sodium hydroxide and found that, unless the bulk in the distilling flask was maintained at from 15 to 25 c.c., extreme difficulty was experienced in distilling off all the nicotine, especially when derived from tobacco. On the other hand, when 2 grams of soda were added to liberate the nicotine, higher results were obtained from the distillate by precipitation than when less quantities of alkali were used. He attributes the difference to the presence of some other volatile substance, produced by the action of the strong alkali on the small bulk in the distilling flask, which is precipitated by silicotungstic acid. For these reasons he suggests that instead of using the distillation method, the ether extract of the nicotine obtained by the Soxhlet extraction, after careful reduction in bulk, should be extracted in a separator with cold dilute hydrochloric acid (1:4) from 4 to 6 times. The extracts are bulked and an aliquot part, representing about 0.25 gram of tobacco extract, or from 1 to 2 grams of tobacco, is taken and diluted to 400-500 c.c. with water. Sufficient dilute hydrochloric acid—at least 3 p.c. is required—is added to show an acid reaction with methyl orange before precipitation. For this purpose he uses a 12 p.c. solution of silicotungstic acid having the specific formula $SiO_2 \cdot 4H_2O \cdot 12WO_3 \cdot 22H_2O$. The factor for converting the weight of the ignited residue to nicotine is 0.114. The details of the method are as follows: Five grams of finely powdered dry tobacco, or 1 gram of tobacco extract (about 40 p.c. grade), is moistened with 25 c.c. of alcoholic sodium hydroxide solution (6 grams of sodium hydroxide in 40 c.c. of water and 80 c.c. of 90 p.c. alcohol). The extracts 5 c.c. of soda solution is used and the mixture made into a moist paste with calcium carbonate. The sample is extracted for 2 hours with ether in a Soxhlet extractor, and the

taken that the temperature of the cooling jacket does not rise above 20°C. and that the volume of solvent in the extraction flask is never less than 25 c.c. After extraction, the excess of ether is removed, but the volume remaining must be sufficient to keep the whole of the extracted matter in solution. The ether extract is transferred to a separating funnel, the flask being rinsed with ether and finally with hydrochloric acid (1 : 4), and shaken with from 4 to 6 10-c.c. portions of hydrochloric acid (1 : 4). The formation of emulsions can be avoided by adding 1 c.c. of alcohol. The washings are filtered through glass wool into a 100 c.c. graduated flask. When tested portions of the washings no longer give a turbidity with silico-tungstic acid reagent, the whole volume is made up to 100 c.c., an aliquot portion equivalent to 1 to 2 grams of tobacco is diluted to 400–500 c.c., and sufficient hydrochloric acid (1 : 4) added to ensure that at least 3 c.c. of it is present in 100 c.c. of the solution; 1 c.c. of silicotungstic acid solution is then stirred in for every 0.01 gram of nicotine supposed to be present. After stirring for 3 to 5 mins. the precipitate appears crystalline and settles readily. The solution is allowed to remain for 18 to 24 hours and filtered, preferably through a Hirsch or Buchner funnel. The precipitate is washed with hydrochloric acid (1 : 1000), dried, and transferred—with the paper to a platinum crucible. After heating until all carbon is removed the crucible is finally ignited for not more than 10 mins. over a Teclu or Meker burner. The weight of the residue $\times 0.114$ gives the weight of nicotine in the aliquot portion taken. The silicotungstic acid reagent is a 12 p.c. solution of the acid $4\text{H}_2\text{O}_3\text{SiO}_3 \cdot 12\text{WO}_3 \cdot 22\text{H}_2\text{O}$. The other silicotungstic acids do not give a suitable crystalline precipitate with nicotine (O. M. Shedd, J. Agric. Res. 1923, 24, 961–970; J. Soc. Chem. Ind. 1923, 42, 1150A).

Manufacture.—In several European countries, among which may be mentioned France, Spain, Italy, Austria-Hungary, and Turkey, the manufacture of tobacco is a State monopoly. In Canada, the United States, Germany, Holland, and other European countries the manufacture is in private hands. In the United Kingdom, tobacco is subjected to a heavy import duty, but a rebate of one-fourth is allowed on tobacco grown in the British Empire. Certain legal restrictions are imposed, which, however, chiefly affect the manufacturers of the commoner kinds of tobacco. The only substance allowed by law to be used in the manufacture of tobacco is water. The use of olive oil is permitted in spinning and making up roll tobacco, and essential oils are allowed for flavouring purposes. The finished article must not contain more than 32 p.c. of moisture, and if it is roll tobacco, not more than 4 p.c. of olive oil. The leaves of plants other than tobacco may not be employed, nor any preservative except acetic acid. Essential oils for flavouring purposes may be added to snuff, and the addition is allowed of the carbonates, chlorides and sulphates of sodium and potassium, ammonium carbonate, and of 1 p.c. of lime in the form of lime-water. The snuff, when dried, however, must not contain more than 26 p.c. of alkaline salts nor more than 13 p.c. of the oxides of lime and magnesia, inclusive of the amounts naturally

present in tobacco. More latitude is allowed in the manufacture of tobacco in bonded factories: the addition of foreign leaves is not permitted, but any suitable sweetening or flavouring matter may be used. Sugar, honey, liquorice, glycerin, gum, salt, and logwood are the ingredients most commonly used for this purpose in the manufacture of this kind of tobacco, which is known as Cake- or Cut-Cavendish, and is manufactured chiefly for exportation. If intended for home consumption, this tobacco is required to be enclosed in a specially designed Customs' wrapper to distinguish it from the ordinary article, and it is subjected to a higher rate of duty. The sale of cigarettes containing sweetening matter is not permitted.

Tobacco leaf is imported into this country either entire or with that portion of the mid-rib removed which cannot be used in manufacturing, in which case it is called 'strips', and assessed at a slightly higher rate of duty. Apart from fluctuations due to war-time conditions, the proportion of 'strip' tobacco imported is steadily declining, having fallen from 39 p.c. in the year 1907 to 30 p.c. in the year 1925. Over 85 p.c. of the raw material comes from America, and about 6 p.c. from other foreign sources, chiefly the Levant, Dutch Indies, China, and Japan. Empire-grown tobacco secured preferential tariff treatment in 1919, and in 1925 the rebate of duty allowed was increased from one-sixth to one-fourth. About 8 p.c. is now imported, chiefly from India, Nyassaland, Rhodesia, Canada, and North Borneo. The principal kinds of foreign tobacco used are Virginia, Kentucky, Western, Burley, Ohio, Perique, Havannah, Japan, Java, China, Sumatra, Borneo, Turkish, and Latakia. The more tender varieties, such as Turkish, are packed carefully in bales leaf upon leaf, but hogsheds are the usual packages employed: the leaves are packed either in layers or in bunches of ten to a dozen leaves, bound round with another leaf and known as 'hands.' Price, colour, texture, burning qualities, aroma, and body or drinking power, that is, ability to absorb and retain moisture without becoming too wet, are all factors which influence manufacturers in selecting tobacco.

Imported leaf, although apparently dry, usually contains from 10 to 20 p.c. of moisture, but 14 p.c. may be regarded as a fair average. There are two rates of duty on imported leaf tobacco depending on the amount of moisture present. The duty on leaf containing less than 10 p.c. of moisture is levied at a rate substantially higher than on leaf containing 10 p.c. or more of moisture. The manufacturer of the cheaper kinds of tobacco endeavours therefore to secure leaf containing moisture as little in excess of 10 p.c. as possible, and so to obtain a larger profit from the greater amount of water he can add in the process of manufacture. In cigarette, cigar, and other varieties of leaf requiring careful handling, a higher initial percentage of moisture is desirable, and these varieties of leaf sometimes contain as much as 20 p.c. of moisture.

The principal kinds of manufactured tobacco are cut, twist or roll, and cake tobacco; cigars, cigarettes, and snuff. Many kinds of leaf are blended for manufacturing cut tobacco, and in the commoner kinds a considerable quantity of

TOBACCO.

leaf other than American is employed. These 'substitutes' were adopted at the time of the civil war in the United States of North America, which caused a temporary shortage in the supplies of Virginia leaf tobacco. Many of these 'substitutes' have the distinct advantage of being able to retain a large quantity of moisture without appearing to be unduly moist. Other blends are made entirely from Empire-grown tobacco.

The first process in manufacturing tobacco is the 'liquoring' stage: the old crude method of employing a watering-pot has now been superseded by the use of steam appliances which ensure a more even distribution of the moisture. When 'strips' are not employed, the mid-rib of the leaf which absorbs more moisture than the lamina is then removed—this operation is called 'stripping.' A mechanically actuated knife is employed to cut the tobacco into shreds: 'shags' and such like tobaccos undergo the further process of 'panning,' which consists in thoroughly mixing up the cut tobacco on copper trays heated to a suitable temperature; the tobacco is then set aside to cool on racks. The moisture in the common kinds averages about 30 p.c., but the better kinds of smoking mixtures contain from 15 to 25 p.c. The distinctive flavours of these tobaccos are due either to the presence of Latakia, Perique, &c., in the blend of leaves used or to the addition of essential oils such as oils of cassia, geranium, cloves, bergamot, and winter-green. Acetic acid is employed as a preservative. For 'twist' tobacco the darker varieties of American leaf, such as Kentucky, Western, Clarksville, &c., are chiefly employed, but a small quantity of Empire-grown leaf is now used in this class of tobacco. 'Twist' tobacco is made either by hand or on a spinning-wheel: the damp strips or 'fillers' are formed into ropes, the thickness of which depends on the denomination of 'twist' intended to be manufactured, and these ropes are enclosed in a covering wrapper of leaf. The tobacco, at this stage, is known as 'brown twist,' for which a considerable demand exists, chiefly in the North of England. If the tobacco is intended for 'black twist' the rope of tobacco is made up into 'rolls,' consisting of several concentric layers superimposed one on the other. The rolls, after being enclosed in oiled cloths, and tightly bound up with rope, are then baked in steam-heated hydraulic presses until the tobacco assumes a rich black colour, and develops its full aroma; they are then removed to a cold press until cool and fully matured. In order to prevent the coils from sticking to one another in the rolls, olive oil is applied to the tobacco during the 'spinning' and 'rolling' or 'making up' processes, but the amount of oil used is regulated so as to ensure that the finished tobacco does not contain more than 4 p.c. of oil. Acetic acid and essential oils are also employed. Special names are given to different forms of 'twist,' e.g. the terms Ladies' twist, Aloa twist, Liverpool roll, Pigtail and Bogie, have reference to the thickness of the rope; Negrohead indicates a plaited variety; Nailrod is in the form of sticks, and Target is a thick twist coiled up in a single layer. 'Cake' tobacco is prepared either by pressing 'spun' tobacco or by flattening the damp strips under pressure

and then adding an outer covering of leaf. 'Flakes' and 'Cut Cavendish' are obtained by cutting these cakes.

The leaf employed for the manufacture of high-class cigars has to meet many requirements, and blends of different varieties are therefore employed. The component parts of a cigar are the 'filler,' the 'bunch wrapper,' and the 'outer wrapper.' The 'filler' consists of fragments or cuttings of leaf, or even cut tobacco. The 'bunch wrapper' is shaped like a balloon gore, and cut from a tobacco strip of fairly good quality. The outer wrapper is a long rectangular strip of leaf cut from a tough leaf with small veins, of a light and uniform colour and should not possess a pronounced flavour, as it comes in contact with the lips and tongue in smoking; the filler must, however, possess a good aroma, emit an agreeable odour on burning, and have good burning qualities. The finest leaf for cigars comes from Cuba, but Sumatra, North Borneo, Java, &c., supply a considerable quantity of the leaf used for cigar-making in this country. The leaves are moistened with water, opened out carefully, deprived of the midrib, smoothed out and sorted; the perfect leaves are cut in halves and are used as wrappers. The 'filler' is placed on the 'bunch wrapper,' near one end, and the bunch wrapper is then carefully wound round the filler. Over the 'bunch wrapper' the cigar-maker then winds spirally the 'outer wrapper,' commencing at the open end and finishing off at the pointed, or mouth, end. Uniformity in the commoner kinds is secured by the practice of pressing the cigars in moulds before applying the outer wrapper. The cigars are then gauged and cut to the proper length, sorted according to size and colour, dried and packed. Great dexterity is necessary in making cigars, especially in manipulating and keeping the cigars to shape, size, and weight, as well as in evenly packing. The moisture in the finished cigar is reduced to about 10 to 15 p.c. by storage in a drying-room.

The manufacture of cigarettes was introduced into this country by a Greek in the year 1860, and originally Turkish varieties of tobacco only were employed, but 'Virginian' blends are now made in very large quantities from American and other varieties of bright leaf. As the character and the aroma of a cigarette depend on the suitable blending of the various kinds of tobacco employed, this branch of the tobacco industry has become highly specialised. The tobacco used for cigarettes is comparatively dry, the moisture added is just sufficient to permit of the leaf being satisfactorily cut by the machines. The finer varieties of cigarettes are invariably made by hand, either by rolling up the tobacco in the paper, or by filling it into paper tubes closed at one end. In the latter method, charging cylinders slightly smaller in diameter are used, and the tobacco is transferred therefrom to the tubes by means of a small pipe; the closed ends of the paper tubes are subsequently cut off. A great impetus has been given to the production of cigarettes by the employment of cigarette-making machines, which can easily turn out over 60,000 cigarettes per hour. Machines for arranging and packing the cigarettes in cartons are also employed, a single machine being able to deal with at least

380,000 cigarettes per day. The moisture in cigarettes varies according to the time they are stored in the drying-room, and usually ranges from 12 to 18 p.c.; if the tobacco is made too dry it is liable to be shaken out of the wrapper; on the other hand, if the tobacco is left too damp, the cigarette will not burn well. Mouthpieces are often fitted to cigarettes made from Turkish tobacco, on account of its superior burning quality. Cigarettes vary considerably in weight; an ounce may contain from 12 to 40 cigarettes, but 20 to 30 is about the average. Sweetening matter is not allowed to be used in making cigarettes, but the paper wrappers of the 'pectoral' kinds sometimes contain a small quantity of saccharin. Alcoholic solutions of essential oils may be added by manufacturers to the tobacco used in perfumed cigarettes.

Snuff is sold in two forms, dry and moist, the former is made from the stalk or midrib of the leaf, the latter contains a proportion of the lamina. The difference in the quality is dependent on the flavour, the pungency, and the scent. The dry varieties—the Welsh, Scotch, High Toast, and Irish kinds—are, as a rule, more finely ground than the moist varieties. The moisture ranges from about 20 p.c. in Scotch snuffs, to as little as 5 p.c. in Irish snuff. 'Rappees' include such well-known varieties as Latakia, Macuba, and Prince's mixture, and contain from 30 to 50 p.c. of moisture. The tobacco stalks used for snuff-making are cut into small pieces, moistened with alkaline water or sometimes with lime-water, and allowed to ferment, the fermentation period frequently lasting for several months. The material, in the case of Scotch snuff, is then ground to the required degree of fineness, dried down, flavoured, and sifted. The stalks for Irish and Welsh snuff, before being ground, are gently roasted, by which means the characteristic odour of these varieties is produced. For moist snuffs the material is ground wet in a special kind of mortar, and is then allowed to ferment until the required depth of colour is produced. Certain kinds of alkaline salts are mixed with the snuff-flour to increase its pungency, but, as already mentioned, the quantity and the kinds which may be employed are defined by statute. Essential oils, ground orris-root and ground Tonquin beans are used for flavouring purposes. Adulteration of snuff is now rarely practised, but such substances as the oxides of iron, red lead, lead chromates, &c., have been used as colouring materials, and chalk, magnesia, borax, sand, and excessive quantities of alkaline salts have been employed to increase the weight.

Prior to the passing of the Pure Tobacco Act of the year 1842, the adulteration of tobacco with sugar, treacle, honey, gum, &c., and such foreign vegetable matters as rhubarb, coltsfoot, &c., was very general; but in consequence of the heavy penalties imposed by that Act and the vigilance of the Revenue Authorities these practices have almost ceased. The enactments relating to the amounts of moisture and oil in tobacco are also strictly enforced. Such substances as malt combining, moss-litter, &c., are occasionally offered as substitutes for tobacco, but the offenders rarely escape detection and punishment. Manufactured tobacco frequently contains considerable quantities of sand, and

manufacturers are sometimes suspected of using it as an adulterant. The sand, however, usually comes into their possession still retaining a proportion of the sand which was deposited upon it from the soil by the action of the wind and rain during growth. A portion of this sand only is detached from the leaf during the manufacturing operations, which accounts for the presence of sand in the finished article.

In the manufacture of tobacco, a considerable quantity of waste material is produced, siftings, sweepings, &c., and in addition the quantity of stalks obtained by stripping the midrib from the imported leaf is far in excess of that required for conversion into commercial snuff. Repayment of the duty, called 'drawback,' is made by the Crown Authorities on this refuse of tobacco when it is exported or deposited in an approved warehouse to be abandoned to the Crown, or in a bonded factory to be utilised in the manufacture of nicotine or the preparation of 'sheep-dip,' hop-powder, insecticides, &c. Denaturing materials are required to be added to the ground tobacco before it is allowed to be sold, in order to prevent such tobacco being used as a substitute for the duty-paid article. Anthracene oil, bone oil, ground moss-litter, and sulphur are some of the substances used for this purpose.

Statistics.—The amount of tobacco leaf imported into the United Kingdom and the consumption of manufactured tobacco have steadily increased. The imports in the year 1851 amounted to about 28,000,000 lbs. and the consumption was just over 1 lb. per head of the population; in the year 1925, the amount imported was over 152,000,000 lbs. and the consumption was slightly in excess of 3 lbs. per head of the population. The manufacture of tobacco is now one of the most important of the minor industries, and according to the returns made in connection with the Census of Production for the year 1907, the number of persons then employed in tobacco factories was 37,456. The net value of the raw material was £27,988,000 and, including 11,816,000 lbs. of manufactured tobacco exported, the output amounted to 108,292,000 lbs., representing a money value of £23,799,000. The weight of the different kinds was as follows: of cut and roll tobacco, 69,880,000 lbs.; of cigarettes, 29,904,000 lbs.; of cigars, 3,696,000 lbs.; of sweetened cavendish, 3,136,000 lbs.; and of snuff, 1,568,000 lbs. The degree of the popularity of the principal kinds of tobacco, as ascertained from these figures, is pipe tobacco 67·5 p.c., cigarettes 29·0 p.c., and cigars 3·5 p.c. respectively. Cigarettes have, however, materially gained in favour in recent years, and at the present time their proportion may be estimated at 60 p.c.

Tobacco occupies an important position as a source of revenue in the fiscal systems of most civilised countries. In the tariff of the United Kingdom the rate of duty has been more than doubled since the year 1914, and the net amount of duty paid into the Exchequer in the financial year 1924-25 was nearly fifty-two million pounds sterling.

TOBACCO-SEED OIL. Tobacco can yield on pressing, or by extraction with petroleum-ethylene, about 20 to 35 p.c. of a greenish-yellow, mild, and odourless oil, sp. gr. 0·865 at 15° solidifying at -22° which contains some when

exposed to the air. Acid value, 9.5; saponif. value, 196.4; and iodine value, 131.6.

According to Paris (Bot. tec. 1920, 17, 101), tobacco seed contains: water, 9.17 p.c.; crude protein, 21.37 p.c.; fat, 37.68 p.c.; amides and sugar, 6.05 p.c.; pentosans, 2.9 p.c.; cellulose, 7.15 p.c.; and ash, 3.84 p.c. The ash contains 80_2 , 1.97 p.c.; P_2O_5 , 22.12 p.c.; Na_2O , 3.48 p.c.; K_2O , 28.5 p.c.; CaO , 9.54 p.c.; MgO , 14.63 p.c.

A sample of oil from Kentucky seed had d_{20}^{20} 0.9408; temp. of solidification, 12°; acid number, 4; saponif. number, 196; iodine number, 132.8; ether number, 192. The oil consisted of about 52.4 p.c. of olein, 22.1 p.c. of linolein, and 23.9 p.c. of palmitin. Nicotine is not present in the seed except when germinating. The dry, fat-free seed contained 6.5 p.c. of total nitrogen; 3.76 p.c. of protein nitrogen; 2.39 p.c. of nuclein nitrogen, and 0.35 p.c. of non-protein nitrogen. Arginine is present.

TODDALIA ACULEATA (Pers.). This Indian plant, belonging to the *Rutaceae*, is a rambling shrub found in the sub-tropical Himalayas, in the Khasia mountains, and throughout the Western Peninsula and Ceylon.

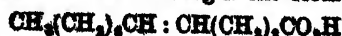
The root bark is or was used in Madras as a yellow dyestuff, and it is also highly spoken of by various writers as one of the most valuable Indian medical products, possessing tonic, stimulant, and antipyretic properties. It was introduced into European medicine in 1771, and at one time enjoyed some celebrity under the name of 'Lopez Root,' but it has long since fallen into disuse.

According to Brooks (Philippine Journal of Science, 1910, v. 442), the plant is common in the Philippines, but so far as is known is not used as a dye by the natives.

The colouring matter it contains is berberine (Perkin and Hummel, Chem. Soc. Trans. 67, 413).

A. G. P.

TÔHAKU OIL. An unsaturated acid $C_{11}H_{18}O_2$, light yellow oil, was isolated from Tôhaku oil obtained from *Lindera obtusiloba*, B.L., and purified through the methyl ester, b.p. 123°-125°C., its properties being as follows: iodine value 126.33, neutral value 282.26, m.p. 1.0°-1.5°C., sp.gr. at 15°/4° 0.9246, n_D^{20} 1.44922, n_D^{15} 1.45113, molecular refraction 57.71; 100 parts of water dissolve 0.027 part of the acid at 17°C. By Hazura's oxidation method, the oil yielded a hydroxy acid, $C_{11}H_{18}O_3(OH)_2$, fine needles, m.p. 102°C., which is easily soluble in hot water, alcohol, and ether, but sparingly soluble in cold water and ether. When the original acid was ozonised and decomposed with hot water, succinic and α -caprylic acids and α -caprylaldehyde were isolated. Y. Iwamoto therefore assigns the formula



and proposes the name *linderic acid* for the fatty acid (Y. Iwamoto, Kôgyô-Kwagaku Zasshi, J. Chem. Ind. Japan, 1925, 26, 708-716; cf. J. 1923, 856.4; J. Soc. Chem. Ind. 1923, 42, 786 A).

TOLAMINE. Syn. for Chloramine T (q.v.).

TOLUENE. *Tolu*, art. BALSAMS.

TOLUENE. A method for the estimation of toluene. The sample is dissolved by heating with $N/1$ hydrochloric acid and the toluene dihydrochloride precipitated by adding 10 times the

volume of saturated sodium chloride solution. The salt is allowed to crystallise for 20-30 mins., is filtered off and washed with saturated sodium chloride solution, dissolved in warm water, and the base liberated with slight excess of ammonia solution, methyl red being used as indicator and a measured volume of standard ammonia being run in. The precipitated toluene is filtered off and washed with water and the excess of ammonia titrated with $N/10$ hydrochloric acid; 1 c.c. of $N/10$ ammonia solution equals 0.0106 gram of toluene. Test analyses carried out on purified toluene gave results varying between 99.52 p.c. and 99.96 p.c. Variations in the concentrations of sodium chloride and hydrochloric acid used are without appreciable effect on the result (S. Palkin, Ind. Eng. Chem. 1923, 15, 1045; J. Soc. Chem. Ind. 1923, 42, 1121 A).

TOLIDENE (*Orthotolidene*) v. DIPHENYL.

TOLITE. A French term for trinitrotoluene. Used as an explosive.

TOLU v. BALSAMS.

TOLOUENE, toluol or methylbenzene, C_6H_5 , or $C_6H_5CH_3$; first discovered by Pelletier and Walther (Ann. Chim. 1838 (2), 67, 278) among the by-products in the manufacture of illuminating gas from the resin of *Pinus maritima*, and named by them retinaphtha. Also obtained by distilling Tolu balsam (Deville, *ibid.* 1841 (3), 3, 168); from dragon's blood (Glenard and Boudault, Compt. rend. 1844, 19, 506); from coal tar (Mansfield, Chem. Soc. Trans. 1847, 1, 244); from wood spirit and wood tar (Cahours, Compt. rend. 1850, 30, 320); from Rangoon tar (De la Rue and Müller, *cf.* Chem. Soc. Trans. 1861, 14, 54); from American petroleum (Young, *ibid.* 1898, 73, 906); from Borneo petroleum (Jones, Chem. Soc. Trans. 1907, 81, 1146f); and from other hydrocarbons (Rittmann, Eng. Pat. 9136 of 1915; J. Ind. Eng. Chem. 1915, 7, 945, 1014, 1019); in the products of distillation of a large number of substances (Ritthausen, J. pr. Chem. 1854, 61, 74; Bunte, J. Gasbeleucht, 1892, 35, 571; and others); and in a number of naturally occurring substances (Poni, Anal. Acad. romane, 23; and others). For sources of toluene, see also Rhéad (J. Soc. Chem. Ind. 1917, 36, 764).

It may also be prepared by the action of sodium on a mixture of bromobenzene and methyl iodide in ethereal solution, thus proving its constitution as methylbenzene (Fittig and Tollens, Ann. 1864, 131, 303); by the action of methyl chloride on benzene in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. 1884, (6) 1, 459; Sifton, Eng. Pat. 8886 and 9437 of 1915; Fr. Pat. 479297), and by other methods (Gardeur, Chem. Zentr. 1896, i. 438; Fromm and Achart, Ber. 1903, 36, 534; Werner and Zilkina, *ibid.* 2116; Mai, *ibid.* 1902, 35, 162; and many others). It is also obtained in a yield of 12 p.c. by treating xylene with 2-4 p.c. of aluminium chloride at the boiling-point of xylene for 2 hours (F. Fischer and Niggemann, Ber. 1916, 49, 1475; Houben, U.S. Pat. 1334033, 1337317), and by cracking solvent naphtha under a variety of conditions (Egloff, J. Ind. Eng. Chem. 1912, 10, 8; Evans, U.S. Pat. 1236087; Synthetic Hydrocarbon Co., Fr. Pat. 479211; and others).

Commercial toluene is mainly obtained from coal tar by rectification of the fraction boiling

between 100°–120° (Couper, *Dingl. poly. J.* 1866, 181, 386; Leuchart, *J. pr. Chem.* 1890, (2) 41, 301; *cf. J. Soc. Chem. Ind.* 1915, 34, 170, 416, 539, 1001; Butler and Popham, *J. Soc. Chem. Ind.* 1918, 37, 220 T).

Toluene may be purified by treatment with sulphuric acid (Friswell, *Chem. News*, 1893, 68, 27), and freed from thiotoluene by treatment with aluminium chloride (St. Denis Co., *Fr. Pat.* 240111 of 1894; D. R. P. 79505 of 1894), whilst analytically pure toluene is obtained by converting the less pure substance into the well crystalline potassium toluene *p*-sulphonate, which is subsequently hydrolysed (Miller, *Chem. Soc. Trans.* 1892, 61, 1025; *see also* Kelbe, *Ber.* 1886, 19, 93; Kraemer and Böttcher, *ibid.* 1887, 20, 601).

Properties.—Toluene is a colourless liquid, b.p. 111°/760 mm., 46·8°/92·0 mm., 38°/56·6 mm., 31·9°/42 mm., 23°/26·58 mm., 14·5°/14·56 mm. (Kahlbaum, *Siedetemp. u. Druck*, 95; *cf.* Neubeck, *Zeitsch. physikal. Chem.* 1887, 1, 656; Young, *Chem. Soc. Trans.* 1898, 73, 906; Linebarger, *Amer. Chem. J.* 1896, 18, 437; m.p. –97° to –99° (Archibald and McIntosh, *J. Amer. Chem. Soc.* 1904, 26, 305; *cf.* Ladenburg and Krügel, *Ber.* 1900, 33, 638; Altschul and Schneider, *Zeitsch. physikal. Chem.* 1895, 16, 25); D_4^{20} 0·8812, $D_4^{12\cdot6}$ 0·87403 or 0·87417 (Orton and Jones, *Chem. Soc. Trans.* 1919, 115, 1067) D 0·8723, D_{25}^{25} 0·8649 or 0·85680 (Linebarger, *l.c.*); D_{50}^{50} 0·8490, D_{100}^{100} 0·8237 (Perkin, *Chem. Soc. Trans.* 1896, 69, 1191); D_4^{100} 0·8708, D_4^{100} 0·77805 (Schiff, *Ann.* 1883, 220, 91); critical temperature 320·8° (Pawlewski, *Ber.* 1883, 16, 2634); critical pressure 41·6 atm. (Altschul, *Zeitsch. physikal. Chem.* 1893, 11, 590); magnetic rotatory power 12·16 at 13·1° (Perkin, *l.c.*; *cf.* Schönrock, *Zeitsch. physikal. Chem.* 1893, 11, 785); vapour pressure at low temperatures (Kahlbaum, *Zeitsch. physikal. Chem.* 1898, 26, 686, 616; Woring, *ibid.* 1900, 34, 257); dielectric constant (Drude, *ibid.* 1897, 23, 309; Abegg, *Ann. Physik.* 60, 56; Landolt and Jahn, *Zeitsch. physikal. Chem.* 1892, 10, 299); refractive index (Landolt and Jahn, *l.c.*); molecular refraction 50·06 (Brühl, *Ber.* 1892, 25, 3075); capillarity constant at the b.p. $\alpha^1 = 4·746$ (Schiff, *Ann.* 1884, 223, 104); molecular heat of combustion 933,762 Cal. (Stohmann, *J. pr. Chem.* 1887, [2], 35, 41; *cf.* Richards and Davis, *J. Amer. Chem. Soc.* 1917, 39, 341; 1920, 42, 1599). For the volatilisation of toluene in steam, *see* Barbaudy (*Compt. rend.* 1923, 176, 1616).

The nature of the products of oxidation of toluene is largely dependent upon the oxidising agent employed, thus, whilst chromic acid and dilute nitric acid yield mainly benzoic acid, potassium persulphate yields a mixture of dibenzyl, and benzaldehyde (Moritz and Wolfenstein, *Ber.* 1899, 32, 432), and manganese dioxide, acetic and sulphuric acids yield *o*- and *p*-tolylphenylmethane, benzaldehyde, benzyl alcohol, benzoic acid, complex hydrocarbons and carboxylic acids (Weiler, *Ber.* 1900, 33, 464).

On oxidation with manganese disulphate at 40°–50°, toluene yields benzaldehyde almost quantitatively, whilst at higher temperatures benzoic acid is formed (B. A. S. F., U.S. Pat. 799,454; D. R. P. 175,295 of 1906); for the

oxidation of toluene by means of lead peroxide, manganese peroxide, chromyl chloride, and persulphates, *see* Law and F. M. Perkin (*Chem. Soc. Trans.* 1907, 91, 260; 1908, 93, 1833), and for the preparation of benzaldehyde by oxidising toluene in presence of various catalysts, *see* Woog (*Compt. rend.* 1907, 145, 124) and Coquillion (*ibid.* 1873, 77, 444). Benzaldehyde and benzoic acid, together with other products, are also obtained by the electrolytic oxidation of toluene in presence of alcohol and dilute sulphuric acid (Renard, *Compt. rend.* 1881, 92, 965; Puls, *Chem. Zeit.* 1901, 25, 263; Merzbacher and Smith, *J. Amer. Chem. Soc.* 1900, 22, 723), the course of the reactions involved during the electrolytic oxidation is detailed by Fichter (*Zeit. elektrochem.* 1913, 19, 781).

100 grams of toluene containing 5 grams of anthraquinone yields, after exposure to sunlight and air for six weeks, 40 grams of benzoic acid, 10 grams of isohydrobenzoin and hydrobenzoin, 0·2 gram of benzaldehyde, and 0·1 gram of dibenzyl (Eckert, *Eng. Pat.* 182487, 1922).

When the vapour of toluene is passed through a red-hot tube, benzene, naphthalene, anthracene, phenanthrene, dibenzyl (Berthelot, *Bull. Soc. chim.* 1867, 7, 218; Graebe, *Ber.* 1874, 7, 48), styrene, diphenyl, &c. (Ferkö, *Ber.* 1887, 20, 662) are formed; but when a mixture of the vapours of toluene and benzene is heated in this manner, a highly complex mixture of hydrocarbons is formed (Carnelley, *Chem. Soc. Trans.* 1880, 37, 702; *cf.* Barbier, *Ann. Chim.* 1876, [5] 7, 472). When electric sparks are passed through toluene, a gas containing acetylene (23–24 p.c.) and hydrogen (76–77 p.c.) is formed (Destrem, *Bull. Soc. chim.* 1884, 42, 267; *Compt. rend.* 1884, 99, 138), whilst distillation over red-hot lead oxide (PbO) yields stilbene, diphenyl, anthracene, phenanthrene, &c. (Lorenz, *Ber.* 1874, 7, 1098; Vincent, *Bull. Soc. chim.* 1890 (3), 4, 7; *Compt. rend.* 1889, 110, 907).

When air charged with toluene vapour is passed over finely divided platinum or manganese dioxide, the temperature rises until the metals become incandescent and the toluene is completely oxidised to carbon dioxide and water. In the presence of iron, nickel, or copper oxide, at temperatures between 150°–300°, it is converted into benzaldehyde, but with carbon at 370°, benzoic acid is formed (Woog, *Compt. rend.* 1907, 145, 124; *cf.* Coquillion, *ibid.* 1873, 77, 444).

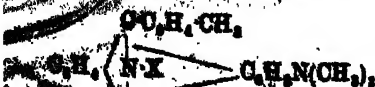
When toluene is boiled in the presence of aluminium chloride, a complex mixture of hydrocarbons, including ethyltoluene, ditolyl (Friedel and Crafts, *Compt. rend.* 1885, 100, 692), benzene, *m*- and a little *p*-xylene (Anschütz, *Ann.* 1886, 235, 178; Anschütz and Immendorff, *Ber.* 1885, 18, 657) are formed; whilst with acetylene tetrabromide, methylene chloride or chloroform in the presence of aluminium chloride, 1:6- and 2:7-dimethylantracene, m.p. 240° and 244·5° respectively, together with a little 3-methylantracene, di-*m*- and di-*p*-tolylmethane, benzene, *m*- and *p*-xylene, and other homologues are produced (Friedel and Crafts, *Ann. Chim.* 1887, [6] 11, 266; Levauz, *Compt. rend.* 1904, 139, 976; 1905, 140, 44, 141, 204, 266; 1906, 142, 687; 1908, 146, 135, 245; 1911, 153, 1400). With ethylidene chloride and aluminium chloride, on the other hand, naphthalene

(a) *p*-ditolylethane and 3-tetramethylantracene hydride, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \langle \frac{\text{CH}(\text{CH}_3)}{\text{CH}(\text{CH}_3)} \rangle \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ are said to be formed (Anschütz, Ann. 1886, 235, 313; Anschütz and Romig, Ber. 1885, 18, 662). When treated with sulphur dichloride in the presence of aluminium chloride, toluene yields ditoluylene disulphide (cf. Jacobsen and Ney, Ber. 1889, 22, 904), whilst with sulphur monochloride the reaction is of a complicated nature (Böeseken and Koning, Rec. trav. chim. 1911, 30, 116). When pyrosulphuryl chloride reacts with toluene at 60° , it yields toluene *p*-sulphonic acid, toluene *p*-sulphonyl chloride, a mixture of dichlorotoluenes and 4-chloro-3 : 4'-ditolyl sulphone (m.p. 136°), which is also formed by the interaction of *o*-chlorotoluene and toluene *p*-sulphonyl chloride dissolved in light petroleum in presence of aluminium chloride at 55° . A vigorous reaction ensues when toluene is added to a mixture of pyrosulphuryl chloride and aluminium chloride at -5° to 0° with the formation of toluene *p*-sulphonic acid, *o*- and *p*-chlorotoluene, *p*:*p*-ditolylsulphone, and a substance, needles, m.p. 215° - 217° , containing chlorine but no sulphur (Steinkopf and Buchheim, Ber. 1921, 54, 2963). With isobutyl bromide and aluminium chloride, toluene yields tertiary butyltoluene, tertiary butylbenzene, ditertiary butylxylene, ditertiary butylbenzene, and ditertiary butyltoluene (Baur, Ber. 1894, 27, 1606; cf. Konowalow, J. Russ. Phys. Chem. Soc. 1898, 30, 1036; Verley, Bull. Soc. chim. 1898, (3) 19, 67). On boiling with ferric chloride a mixture of chlorotoluenes is formed, but no benzyl chloride (Thomas, Compt. rend. 1898, 126, 1213), and on heating with phosphonium iodide at 350° , a hydrocarbon, C_7H_{10} , is formed, whilst with concentrated hydriodic acid at 280° , toluene yields hexahydrotoluene, dimethylpentamethylene, and methylpentamethylene (Markownikoff and Karpowitsch, Ber. 1897, 30, 1216). On treating pure toluene with ozone, ozotoluene, $\text{C}_7\text{H}_8\text{O}_3$, an amorphous explosive compound, which is decomposed by water into benzoic acid, formic acid, and carbon dioxide, is formed. By the prolonged interaction of nitrogen peroxide and toluene, *o*-nitrotoluene, dinitro-*o*-cresol, oxalic acid, benzoic acid, and a dihydroxybenzoic acid are produced (Leeds, Ber. 1881, 14, 482).

Nitrogen tetroxide at room temperature oxidises toluene to oxalic and benzoic acids, phenols, and benzaldehyde (Schaarschmidt and Smolla, Ber. 1924, 57, 32).

Nitrosyl chloride reacts readily with toluene in sunlight to give crystals of benzaldoxime hydrochloride (Lynn and Arkley, J. Amer. Chem. Soc. 1923, 45, 1045).

Like benzene and dimethylaniline, toluene reacts with tetramethyl-diaminodiphenyl-hydroxyanthranol, forming a colourless additive compound which yields highly coloured salts and reacts with one molecule of phenylhydrazine or hydroxylamine, eliminating two molecules of water and forming the compound



where $\text{X} = \text{OH}$ or $\text{C}_6\text{H}_4\text{NH}$ (Haller and Guyot, Compt. rend. 1903, 137, 606). Toluene reacts with ethyldiazoacetate at 118° , forming ethyl 4-methylnorcaradiene carboxylate, b.p. 122° - $126^\circ/15$ mm. (Buchner and Feldmann, Ber. 1903, 36, 3509). It also condenses with benzaldehyde in presence of concentrated sulphuric acid forming di-*p*-tolylphenylmethane (Kliegl, Ber. 1905, 38, 84), and with diphenic anhydride forming fluorene derivatives (Pick, Monatsch. 1904, 25, 979).

Commercial toluene should give only a pale-brown coloration with concentrated sulphuric acid, but pure toluene should give no coloration with this reagent, and should not decolorise a N/10 solution of bromine. When shaken with nitric acid (sp.gr. 1.44), the acid should be coloured red, but should not become viscid or greenish. On distilling crude toluene at least 90 p.c. should boil below 120° ; and a 'pure toluene' of commerce should distil between 110° - 113° , and the greater part between 111° - 112° (Schultz, Chem. des. Steinkohlentheers). Unless coal-tar toluene has been purified by shaking with concentrated sulphuric acid, it always contains 2- and 3-methylthiophene (thiotoluene). For estimation of toluene in gases, see Davis, Davis and MacGregor (J. Ind. Eng. Chem. 1918, 10, 712). For the estimation of impurities in toluene, and the estimation of toluene in commercial mixtures, petroleum, &c., see Colman (J. Gas Lighting, 1915, 129, 196, 314); Wilson and erts (*ibid.* 1916, 134, 225); Harker (J. Roy. Soc. New South Wales, 1916, 50, 99); James (J. Soc. Chem. Ind. 1916, 35, 236); Edwards (*ibid.* 1916, 35, 587); Spielman and Jones (*ibid.* 1917, 36, 489); Thole (*ibid.* 1919, 38, 39 T); Colman and Yeoman (*ibid.* 1919, 38, 82 T); Lewis (*ibid.* 1920, 39, 50 T); Colman (*ibid.* 1920, 39, 50 T); Northall-Laurie (Analyst, 1915, 40, 384); Evans (*ibid.* 1920, 45, 54); Egloff (Met. and Chem. Eng. 1917, 16, 259); Orton and Jones (Chem. Soc. Trans. 1919, 115, 1055); Lumsden (*ibid.* 1366); Tausz and Stube (Zeitsch. angew. Chem. 1919, 32, 175).

Toluene is employed in the manufacture of nitrotoluene, toluidine, benzyl chloride, benzal chloride, benzotrichloride, benzaldehyde, benzoic acid, and cinnamic acid. It is also used in the manufacture of dyestuffs, explosives, synthetic drugs and perfumes. Formerly toluene formed an essential ingredient of the benzene employed as the starting-point in the manufacture of magenta, but now it is usual to start with pure benzene and pure toluene. •

HALOGEN DERIVATIVES OF TOLUENE.

In the chlorination or bromination of toluene, substitution may take place either in the nucleus or in the side chain. In contrast with the more qualitative nature of the observations relating to the process of chlorination, quantitative measurements, indicating the rôle played by the various factors in the side-chain or nuclear substitution, have been obtained in the case of the bromination of toluene. Temperature, catalysts, and the photo-chemical action of light are the conditions which play a prominent part in these reactions. A comprehensive account of the chlorination and bromination of toluene from

the point of view of 'halogen carriers' and the electrochemistry of light has been given by Bancroft (J. Phys. Chem. 1908, 12, 417). When chlorine or bromine acts upon toluene, side-chain substitution takes place in the sunlight at 0° and at higher temperatures (Schramm, Ber. 1884, 17, 2292; *ibid.* 1885, 18, 350, 606, 1272; *ibid.* 1886, 19, 212; Bull. Acad. Sci. Cracow, 1898, 61), in diffused daylight and in the dark, a mixture of *o*- and *p*-chloro- and bromo-derivatives is formed. According to Schramm, the most active rays are the yellow and green. Gaseous toluene and chlorine vapour on subjection to the action of ultra-violet rays yield benzyl chloride, benzal chloride, and benzotrichloride (Gibbs and Geiger, U.S. Pat. 1246739 of 1917).

Cannizzaro (Compt. rend. 1855, 41, 517) found that side-chain substitution also takes place in the dark at the boiling-point of toluene.

In the absence of a catalyst the chlorination of toluene at 100° yields benzyl chloride almost exclusively, but in the presence of lead chloride, however, the product is a mixture of *o*- and *p*-chlorotoluenes containing about 62 p.c. of the *o*-isomeride (Wahl, Normand and Vermeylen, Compt. rend. 1922, 174, 946; Book and Eggert, Zeitsch. Elektrochem. 1923, 29, 521).

According to Haussermann and Beck (Ber. 1892, 25, 2445) side-chain substitution is greatly facilitated in the case of nitrotoluene by the presence of sulphur, whence it appears that sulphur behaves differently from the usual 'halogen carriers.'

Selenium accelerates substitution by chlorine in the nucleus (Silberrad, Chem. Soc. Trans. 1925, 127, 2449).

On the other hand, nuclear substitution is effected in the presence of such 'carriers' as ferrio chloride, molybdenum pentachloride, antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple.

The work of Holleman, Polak, van der Laan and Euwe (Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 512; Rec. trav. chim. 1908, 27, 435), and of Bruner and co-workers (Zeitsch. physikal. Chem. 1902, 41, 513; Bull. Acad. Sci. Cracow, 1907, 691; 1909, 221, 285, 322; 1910, 516, 560; Zeitsch. Elektrochem. 1910, 16, 204) has shown that the relative proportion of bromine which enters the side-chain is not only increased by light, but in the dark it is increased by rise of temperature and by dilution of the reacting bromine, the influence of light being greater than that of heat in inducing substitution in the side-chain (Cohen, Dawson, Blockey and Woodmansey, Chem. Soc. Trans. 1910, 97, 1623; Cohen and Dutt, *ibid.* 1914, 105, 504; see also Cohen and Dakin, *ibid.* 1906, 89, 1455).

The influence of the nature of the medium on the distribution of bromine between the side-chain and the nucleus has also been investigated, and it has been found that the influence of such solvents as carbon disulphide, carbon tetrachloride, benzene, chloroform, acetic acid, benzonitrile, and nitrobenzene is 'not only observable in the dark, but also manifests itself in the process of photobromination. The effect of nitrobenzene, and, to a lesser extent, of acetic acid and benzonitrile, is greatly to diminish the

proportion of side-chain substitution, whilst in the case of dilution with carbon tetrachloride the distribution is the same as in the case of pure toluene. The most noteworthy contribution is the work of Cohen, Dawson, Blockey and Woodmansey (*l.c.*), who showed that at the boiling-point of toluene moist chlorine in the dark produces nuclear substitution to the extent of nearly 90 p.c., whereas, in the light, dry chlorine increases side-chain substitution, yielding on the average about 94 p.c. of benzyl chloride. It thus appears to be established that side-chain substitution is favoured by light, rise of temperature and the absence of moisture, and that the effect of moisture is opposed to that of light.

Various hypotheses have been proposed to account for these phenomena. Bruner supposes that side-chain substitution is due to molecular halogen, whilst nuclear substitution is effected by atomic or ionic bromine, resulting from the dissociation of the bromine molecules. According to this hypothesis, the action of 'carriers,' such as iodine, consists in forming compounds with bromine, which undergo dissociation with the production of bromine atoms or ions in much greater concentration than that which is obtained in the case of pure solutions of bromine; hydrogen perbromide is supposed to be a dissociating compound of this nature.

Bruner's theory that nuclear substitution is due to ionic bromine is shared by Bancroft (*l.c.*), who further assumes that nuclear substitution only occurs when negative bromine ions are present in excess of the corresponding positive ions, a condition which would be attained by the combination of molecular bromine with the positive bromine ions, thus: $\text{Br}_2 = \text{Br}^+ + \text{Br}^-$;

$\text{Br}_2 + \text{Br}^+ \rightarrow \text{Br}_3^+$. On the other hand, Bancroft maintains that side-chain substitution is effected under conditions which tend to produce a preponderance of positive bromine ions.

Holleman (*l.c.*), however, assumes that side-chain substitution is due to molecular bromine and that nuclear substitution is induced by a perbromide, HBr_3 .

According to Cohen (*l.c.*), the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears, on the whole, to be the more acceptable, for the facts are difficult to reconcile with the ionic theory of nuclear substitution, and it must be confessed that nothing definite is known about the mechanism of the process. An explanation of these and similar phenomena on the basis of the electronic theory of valency has been put forward by Fry (The Electronic Conception of Valency, and the Theory of Benzene, by H. S. Fry, Longmans, Green and Co., 1921).

Fichter and Glantzstein (Ber. 1918, 49, 2473) have observed that at least three atoms of chlorine are introduced into the benzene nucleus before the methyl group is attacked when toluene is electrochemically chlorinated in the dark. This is taken as evidence in support of Bruner's hypothesis that atomic chlorine attacks the ring and molecular chlorine the aliphatic side-chain, and the fact that the electrochemical chlorination is an almost impossible process in the aliphatic series confirms this.

FLUORO DERIVATIVES OF TOLUENE.

ω-Difluoro-toluene $C_6H_5CHF_2$. By treating *ω*-difluoro-*ω*-chlorotoluene with sodium amalgam in alcoholic solution. Liquid, b.p. 133°5'. Decomposed by warm concentrated sulphuric acid or water at 200°, yielding hydrogen fluoride and benzaldehyde (Swarts, Bull. Acad. roy. Belg. 1900, 414).

ω-Trifluoro-toluene.—Together with *ω*-difluorochlorotoluene and *ω*-dichlorofluorotoluene by treating benzotrichloride with antimony fluoride. Colourless liquid, b.p. 103°5', D_{14}^{20} 1.19632, n_D^{20} 1.41707. Very resistant to the action of water, alkalis, arylamines, phenol and copper (Swarts, Bull. Acad. roy. Belg. 1920, 389, 399).

p-Fluoro-toluene.—By heating *p*-fluorotoluene sulphonic acid (prepared from *p*-toluidine *m*-sulphonic acid) with concentrated hydrochloric acid (Paterno and Oliveri, Gazz. chim. ital. 1883, 13, 535); by treating *p*-toluenediazopiperidine (obtained by treating a cold aqueous solution of *p*-toluenediazonium chloride with piperidine) with concentrated hydrofluoric acid (Wallach, Ann. 1886, 235, 261; cf. Holleman, Rec. trav. chim. 1906 (2), 25, 330); by warming an aqueous solution of *p*-toluenediazonium chloride with hydrofluoric acid (Valentiner and Schwarz, Eng. Pat. 9827 of 1897; U.S. Pat. 656229; Fr. Pat. 266155; D. R. P. 96153 of 1896).

Liquid, with odour of bitter almonds, b.p. 116°–117°, sp.gr. 0.992 at 25° (Wallach). Oxidised by chromic acid mixture at 160° to *p*-fluorobenzoic acid. On nitration it yields a very small proportion of two fluoronitrotoluenes, m.p. 27°, b.p. 138°–139°/83 mm., and b.p. 134°–135°/83 mm., respectively, the chief product being 3-nitro-*p*-cresol (Slothouwer, Chem. Weekblad, 1914, 11, 956).

CHLORO DERIVATIVES.

As previously mentioned chlorotoluenes are usually prepared by means of chlorine in the presence of a carrier, but there are other methods of producing these compounds, thus the electrolytic chlorination of toluene has been studied by Cohen, Dawson and Crossland (Chem. Soc. Trans. 1905, 87, 1034); Brunner and co-workers, Bull. Acad. Sci. Cracow, 1907, 691; 1909, 221, 265, 322; Fichter and Glantzstein (Ber. 1916, 49, 2473). Datta and Fernandes (J. Amer. Chem. Soc. 1914, 36, 1007) found that toluene could be chlorinated by means of a mixture of nitric and hydrochloric acids, whilst advantage is often taken of the ease with which derivatives of toluene, such as the sulphonic acids, are chlorinated and subsequently hydrolysed (B. A. S. F., D. R. P. 294635 of 1914; Ges. für Chem. Ind. in Basel, D. R. P. 133000 of 1901; Green and Herbert, Eng. Pat. 170056 of 1920). Amino-derivatives of toluene are readily chlorinated in the nucleus by means of sodium chlorate and acetic and hydrochloric acids (Reverdin and Répéaux, Ber. 1900, 33, 2503), and this reaction together with the Sandmeyer reaction readily leads to the production of higher chlorinated toluenes. The use of bleaching powder as a chlorinating agent in the case of amino-derivatives—a reaction employed by Claus and Beilstein (Ann. 1892, 374, 296), and studied in detail by Gattermann and Orton (Chem. Soc.

Trans. 1900, 77, 790, &c.)—is often of advantage for the preparation of chloro-derivatives of toluene, for by this method better yields are sometimes obtained than by the ordinary methods.

Toluene on chlorination in the presence of the aluminium-mercury couple yields 65 p.c. *o*-chloro-toluene and 35 p.c. *p*-chloro-toluene (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1111). For the rapid analysis of chlorinated toluenes, see Lubs and Clark (J. Amer. Chem. Soc. 1918, 40, 1449).

Prior to the exhaustive examination of the products of the nuclear chlorination of toluene by Cohen and his collaborators, the work carried out by various observers on the formation of dichloro-toluenes was both conflicting and unsatisfactory. Beilstein and Geitner (Ann. 1866, 139, 331), Beilstein and Kuhlberg (*ibid.* 1869, 150, 313; 152, 234) in their first papers described only one monochlorotoluene. Hübner and Majert (Ber. 1873, 6, 790) found two chloro-derivatives, and identified them as *o*- and *p*-compounds. Aronheim and Dietrich (Ber. 1875, 8, 1401), using molybdenum pentachloride, gave proof of the existence of two dichloro-derivatives, by conversion into the barium salts of the dichlorobenzoic acids, thus agreeing substantially with Beilstein and Kuhlberg. R. Schultz (Ann. 1877, 187, 260) repeated the work of the previous investigators, and by the fractional crystallisation of the barium salts of the chlorobenzoic acids, obtained on oxidation of the crude product of chlorination, gave evidence of the existence of three dichloro-toluenes. A more thorough investigation by Seelig (Ann. 1887, 237, 129) of the action of chlorine on toluene in the presence of ferric chloride or molybdenum chloride, showed the presence of a 2:4- and 2:3-dichloro-derivative, with no mention of either the 3:4- or 2:6-isomerides. According to Seelig the 2:3- and 2:4-dichlorotoluenes may be separated by means of their calcium sulphonates, and the 2:3-dichlorotoluene gives a dinitro-compound, m.p. 121°, and the 2:4-dichloro-toluene a dinitro-derivative, m.p. 101°–102°. Wynne (Chem. Soc. Trans. 1892, 61, 1051) regards the evidence in support of the 2:3-formula as inconclusive, and considers the 2:5-formula more probable. Armstrong (*ibid.* 1892, 61, 1035), after a study of the bromination of toluene carried out by Miller (*ibid.* 1892, 61, 1023), also favours the 2:5-formula. Miller (*loc.*) states that by brominating *o*-bromotoluene, 2:5-dibromotoluene is formed as the chief product and 2:4-dibromotoluene as the subsidiary product, whilst from *p*-bromotoluene he obtained 3:4-dibromotoluene as the chief, and the 2:4-isomeride as the subsidiary product. Contrary evidence, however, is afforded by the work of Willgerodt and Sahnmann (J. pr. Chem. 1889, (3) 39, 465), who showed that by brominating *o*-chlorotoluene the 2:4- and 2:6-compounds are formed, whilst by chlorinating *p*-bromotoluene, the 2:4- and 3:4-derivatives are produced, no 2:5-derivative being observed. Claus and Stavenhagen (Ann. 1892, 269, 236) have found that by chlorinating *o*-chlorotoluene two dichlorotoluenes are formed, which, on oxidation, give 2:4- and 2:6-dichlorobenzoic acids, from which it would appear that 2:5-dichlorotoluene is one of the direct products.

of chlorination. The combined results of all these observers afford evidence of the existence of four dichlorotoluenes formed by chlorinating toluene in the presence of molybdenum or ferric chloride, viz. 2:3-, 2:4-, 3:4-, 2:6-, with the possibility of a fifth, 2:5-dichlorotoluene. The cause of these conflicting results is the impossibility of separating the liquid dichloro-derivatives into the constituents by fractional distillation as their boiling-points lie too close together, and the isolation of solid derivatives is a matter of difficulty. Cohen and Dakin (Chem. Soc. Trans. 1901, 79, 1111), by using the aluminium-mercury couple as the 'carrier,' established the presence of 2:3-, 2:4-, 2:6-, 3:4-, and the probable existence of 2:5-dichlorotoluene, but could find no trace of the 3:5-isomeride. *o*-Chlorotoluene on chlorination yields 2:3-, 2:6-, 2:4-, and probably the 2:5-dichlorotoluene, whilst *m*-chlorotoluene yields 3:4- and 2:5-dichlorotoluene, and *p*-chlorotoluene yields the 2:4- and 3:4-isomerides. With regard to the trichlorotoluenes, though some of the various isomerides have been obtained by the direct chlorination of toluene in the presence of various 'carriers,' it is preferable to obtain them by chlorinating the dichlorotoluenes. Thus, 2:4:5- and 2:3:4-trichlorotoluene have been obtained by Limpricht (Ann. 1866, 139, 326), Aronheim and Dietrich (Ber. 1875, 8, 1401), and Seelig (Ann. 1887, 237, 231), by chlorinating toluene and *o*- or *p*-chlorotoluene in presence of iodine, molybdenum pentachloride, or ferric chloride, whilst the former is also obtained, together with 2:3:4-trichlorotoluene and probably a small amount of the 2:4:6-isomeride, by chlorinating 2:4-dichlorotoluene in presence of the aluminium-mercury couple, and, together with 2:3:6-trichlorotoluene, by chlorinating 2:5-dichlorotoluene in a similar manner (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1340, 1342). 2:3:4-Trichlorotoluene is accompanied by a tetrachlorotoluene when 2:3-dichlorotoluene is chlorinated in presence of the couple (Cohen and Dakin, *ibid.* 1339). 3:4-Dichlorotoluene, on the other hand, yields 2:4:5-trichlorotoluene almost exclusively in a similar manner, whilst 2:3:5-trichlorotoluene and 2:3:6-trichlorotoluene are obtained almost exclusively from 3:5- and 2:6-dichlorotoluene, respectively.

By chlorinating toluene Limpricht (Ann. 1886, 139, 327) obtained a tetrachlorotoluene, m.p. 96°, b.p. 276.5°, whilst Beilstein and Kuhlberg (Ann. 1869, 150, 286), repeating Limpricht's work which they carried out in the first stage with iodine and subsequently with antimony pentachloride, obtained a product, fine needles, m.p. 91°-92°, b.p. 271°. Pieper (Ann. 1867, 142, 305) prepared a liquid tetrachlorotoluene (b.p. 280°-290°) by heating the additive compound, $C_7H_4Cl_4$, with alcoholic potash at 110°. This product is impure or more probably a totally different compound, and the substance prepared by Beilstein and Kuhlberg would be either 2:3:4:6- or 2:3:5:6-tetrachlorotoluene, m.p. 91°-92° and 93°-94° respectively, or a mixture of the two, since both compounds are formed on chlorination (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1279). 2:3:4:6-Tetrachlorotoluene is also produced by the further chlorination of 2:4:6-trichlorotoluene in presence of the aluminium-mercury

couple, whilst 2:3:5:6-tetrachlorotoluene is produced by the chlorination of 2:3:6- and 2:3:5-trichlorotoluene under similar conditions. On the other hand, there is no evidence of the production of 2:3:4:5-tetrachlorotoluene by the further chlorination of 2:4:5-trichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1279; 1906, 89, 1453). Beilstein and Kuhlberg (Ann. 1869, 150, 298) by chlorinating toluene initially in the presence of iodine and finally with phosphorus pentachloride obtained pentachlorotoluene.

Benzyl chloride, ω -chlorotoluene, $C_6H_5CH_2Cl$; by passing hydrogen chloride into benzyl alcohol (Cannizzaro, Ann. 1853, 88, 130; 1855, 96, 246; Deville, Ann. Chim. 1841, [3] 3, 178); by the action of chlorine on boiling toluene (Cannizzaro, Ann. Chim. 1855, [3] 45, 468; Beilstein and Geitner, Ann. 1866, 139, 337; Wahl, Normand and Vermeylen, Compt. rend. 1922, 174, 946); by the action of chlorine on toluene in sunlight (Schramm, Ber. 1885, 18, 608); from equimolecular proportions of methylene chloride and benzene in carbon disulphide solution in presence of zinc dust or zinc chloride and hydrochloric acid (Grasse-Cristaldi and Maselli, Gazz. chim. ital. 1898, 28, 498); from benzylamine and nitrosyl chloride in ethereal solution at -15° to -20° (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431); in small quantities together with other products by the action of *aqua regia* on benzylamine (Solonina, *l.c.* 822).

Benzyl chloride is manufactured by passing chlorine into toluene contained in acid-proof earthenware vessels and heated to boiling by means of a lead steam-spiral. The operation is interrupted when the toluene shows the theoretical increase in weight (37.5 p.c.). The vapours are condensed in a reflux worm, and the escaping hydrogen chloride passed into water. The product is shaken with dilute alkali and then rectified, by which means it is freed from unchanged toluene and higher chlorinated products. The addition of a small quantity of phosphorus trichloride and the action of sunlight increases the velocity of chlorination. Very good yields are also said to be obtained by allowing sulphuryl chloride to act on an excess of toluene in the dark at a temperature a little below 130° (Wohl, D. R. P. 139552 of 1901). Further, a mixture of toluene and bleaching powder is treated with sulphur dioxide, and the resulting benzyl chloride separated by distillation (Conant, U.S. Pat. 1233986 of 1917; J. Soc. Chem. Ind. 1917, 36, 1002).

M.p. -48° (Haase, Ber. 1893, 26, 1063), or -43.2° (Schneider, Zeitsch. physikal. Chem. 1897, 22, 233); b.p. 175°-176.2°/760.3 mm. (Schiff, Ann. 1883, 220, 99; cf. Ber. 1889, 19, 543); b.p. 63°/8-16 mm.; 73.9°/17 mm.; 78.2°/22-14 mm.; 81.8°/26-74 mm.; 89.9°/40 mm.; 98.8°/62 mm.; 106.2°/92 mm.; 179°/760 mm. (Kahlbaum, Siedetemp. u. Druck, 84); 64°-64.2°/12 mm. (Anschütz and Burns, Ber. 1887, 20, 1390); D_4^{20} 1.1135; D_{16}^{15} 1.1040; D_{25}^{25} 1.0967 (Perkin, Chem. Soc. Trans. 1896, 89, 1243); D_4^{175} 0.94535 (Schiff, *l.c.*); absorption spectrum (Spring, Rec. trav. chim. 1897, 16, 1); magnetic rotatory power 14.01 at 15.3° (Perkin, *l.c.*); dielectric

constant (Jahn and *Zeitsch. physikal. Chem.* 1894, 13, 387).

Insoluble in water, but by heating with water to 100°–110°, or by boiling with water under a reflux for 24 hours, it is converted into benzyl alcohol (Vandeveldt, *Bull. Acad. roy. Belg.* 1897, [3] 34, 894; Niederist, *Ann.* 1879, 196, 353); the same transformation is still more readily effected by boiling benzyl chloride with the calculated quantity of potassium carbonate dissolved in about 8 to 10 parts of water (Meunier, *Bull. Soc. chim.* 1882, [2] 38, 159; Busch and Weiss, *Ber.* 1900, 33, 2702). When boiled with hydrazine hydrate in aqueous alcoholic solution, it yields *α*-dibenzyl-hydrazine (Busch and Weiss, *l.c.*), dibenzyl and stilbene (Rothenburg, *Ber.* 1893, 26, 867). On oxidation it yields first benzaldehyde and then benzoic acid, and on heating with water at 200° and distilling the product, anthracene and benzyl-toluene, amongst other substances, are formed (Dorp, *Ber.* 1872, 5, 1070; Zincke, *Ber.* 1874, 7, 276; Limpricht, *Ann.* 1866, 139, 308). When treated with aluminium chloride in carbon disulphide solution, an insoluble hydrocarbon ($C_{11}H_{10}$) is obtained (Friedel and Crafts, *Bull. Soc. chim.* 1885, 43, 53). Aluminium chloride or zinc dust acts upon a mixture of benzyl chloride and benzene yielding diphenylmethane and a product which on distillation yields anthracene and toluene (Zincke, *Ann.* 1871, 159, 374; Friedel and Crafts, *Ann. Chim.* 1884, (6) 1, 478; *cf.* Perkin and Hodgkinson, *Chem. Soc. Trans.* 1880, 37, 726; Hirst and Cohen, *ibid.* 1895, 67, 827; Radziewanowski, *Ber.* 1894, 27, 3236; 1895, 28, 1136). With a large amount of benzene in presence of aluminium chloride, anthracene is the main product (Schramm, *Ber.* 1893, 26, 1706). On boiling with zinc dust a vigorous reaction occurs with evolution of hydrogen chloride, and the product, on distillation, yields toluene, anthracene, phenyl-tolyl-methane and a substance $C_{11}H_{10}$ (?) (Prost, *Bull. Soc. chim.* 1886, [2] 46, 248). Phenyl acetate and benzyl chloride in the presence of aluminium chloride yield acetic anhydride, toluene, anthracene and an oil, b.p. 310°–320° (Perkin and Hodgkinson, *l.c.*). By heating benzyl chloride with aromatic hydrocarbons and zinc dust, the benzyl group enters the hydrocarbon nucleus, thus with benzene, benzylbenzene is formed, and with toluene, *p*-benzyltoluene, a little *o*-benzyltoluene, anthracene, and a hydrocarbon $C_{11}H_{10}$ are formed (Zincke, *Ann.* 1872, 161, 93; *Ber.* 1873, 6, 137). When heated with sodium or copper, benzyl chloride is converted into dibenzyl (Cannizzaro and Rossi, *Ann.* 1862, 121, 250; Fittig and Stelling, *Ann.* 1866, 137, 258; Comey, *Ber.* 1890, 23, 1115; Onufrowicz, *Ber.* 1884, 17, 838). When benzyl chloride is boiled with an aqueous solution of lead nitrate benzaldehyde is obtained. The latter is also formed, together with benzoic acid and anthracene, by heating benzyl chloride with potassium nitrite and a little water at 150° (Brunner, *Ber.* 1876, 9, 1745). Fuming nitric acid yields nitrobenzyl chloride, whilst alcoholic ammonia yields a mixture of benzylamine, dibenzylamine and tribenzylamine (Cannizzaro, *Ann.* 1865, 134, 128; *ibid.* Suppl. 4, 24, 80; Dhonmès, *Compt. rend.* 1901, 123, 636). When treated with chromyl chloride in carbon disulphide solution benzyl chloride yields a brown pre-

cipitate, $C_6H_5CH_2Cl \cdot CrO_2Cl_2$, which is converted slowly by moist air into benzaldehyde. The compound when heated to 170° loses hydrogen chloride, forming a compound, $C_6H_5CHCl \cdot CrO_2Cl_2$, which also yields benzaldehyde with moist air (Etard, *Ann. Chim.* 1881, [5] 22, 235). With aniline, benzyl chloride forms benzylaniline, and with methylaniline it gives the hydrochloride of benzylmethylaniline, from which the free base, b.p. 305°–306°, may be obtained by treatment with sodium hydroxide. The corresponding ethyl compound, b.p. 286°/710 mm., $D_{18}^{20} 1.034$, is obtained in a similar manner. Both these substances and their sulphonic acids are used as intermediates in the preparation of dyes. When treated with a metallic salicylate at 130°–140° benzyl chloride yields *benzyl salicylate*, an odourless, colourless liquid, b.p. 208°/26 mm., which is said to be useful for external application in medicine (Eng. Pat. 25735 of 1899). When subjected to an electric current, hydrochloric acid is evolved and stilbene is formed (Loeb, *Zeitsch. Elektrochem.* 1903, 9, 903).

Benzyl chloride is used in the preparation of benzaldehyde and benzoic acid, and also for introducing the benzyl group into basic colouring matters, prior to sulphonation, in the preparation of acid colouring matters.

Commercial benzyl chloride generally contains moisture, benzal chloride and benzo-trichloride, chlorotoluenes, and even unchanged toluene. It should show the correct boiling-point and specific gravity. In order to determine the chlorine present in the side-chain, a weighed quantity of the substance is boiled for some minutes with a hot saturated alcoholic solution of silver nitrate under a reflux; the silver chloride, which will represent only the chlorine from the side-chain, is then collected and weighed (Schulze, *Ber.* 1884, 17, 1675). Benzo-trichloride may be detected by the green colouring matter (Malachite Green) which is formed when the substance is heated with dimethylaniline and zinc chloride (Döbner).

m-Chlorobenzyl chloride; by chlorinating *m*-chlorotoluene at its boiling-point until the increase in weight amounts to about one-half of that required by theory. B.p. 213°–214°/740 mm. (Kenner and Witham, *Chem. Soc. Trans.* 1921, 119, 1460).

p-Chlorobenzyl chloride; by chlorinating benzyl chloride in presence of iodine, or more conveniently, by chlorinating *p*-chlorotoluene at its boiling-point (Beilstein, Kuhlberg and Neuhof, *Ann.* 1868, 146, 320; Jackson and Field, *Amer. Chem. J.* 1880–1, 2, 85; *P. Amer. A.* 14, 54; *Ber.* 1878, 11, 904); by chlorinating toluene first in the cold and finally at the boiling-point (Walther and Wetzlich, *J. pr. Chem.* 1900, [2] 61, 187; *cf.* van Raalte, *Rec. trav. chim.* 1899, 18, 387). Needles or prisms, m.p. 29°, b.p. 213°–214° (Jackson and Field; *cf.* Beilstein, Geitner and Kuhlberg, *Zeit. f. Chem.* 1868, 2, 66, 307, 653; Beilstein, Kuhlberg and Neuhof, *Ann.* 1868, 147, 339). On boiling with water it yields *p*-chlorobenzyl alcohol (Jackson and Field), whilst with lead nitrate it yields *p*-chlorobenzaldehyde (Beilstein and Kuhlberg, *Ann.* 1868, 146, 320; 1868, 147, 352), and with oxidising agents *p*-chlorobenzoic acid. By the action of potassium cyanide on a boiling alcoholic solution at 120°–130°, it yields *p*-chlorobenzyl acetonitrile (Neuhof, *l.c.*), and on treatment

potassium iodide, *p*-chlorobenzyl iodide, needles, m.p. 64°.

Dichlorobenzyl chloride, b.p. 241°; by chlorinating benzyl chloride in presence of iodine (Beilstein and Kuhlberg).

Trichlorobenzyl chloride; by chlorinating hot trichlorotoluene. Oil, b.p. 273°, D_{20}^{25} 1.547 (Beilstein and Kuhlberg, Ann. 1869, 150, 286).

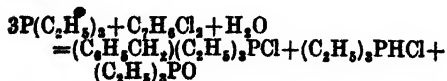
Tetrachlorobenzyl chloride; by chlorinating tetrachlorotoluene at high temperatures. Oil, p.b. 290°, D_{20}^{25} 1.634 (Beilstein and Kuhlberg, Ann. 1869, 15 0, 298). Further chlorination gives hexachlorobenzene and carbon tetrachloride.

Pentachlorobenzyl chloride; by chlorinating benzyl chloride in presence of antimony pentachloride; also by chlorinating boiling pentachlorotoluene (Beilstein and Kuhlberg; cf. Deville, Ann. 1841, 44, 304).

Benzylidene chloride, *benzal chloride*, *o*-dichlorotoluene, $C_6H_4CHCl_2$; by the action of phosphorus pentachloride (Cahours, Ann. Chim. 1848, (3) 23, 329; Ann. 1849, 70, 39; Suppl. 2, 253, 306), succinyl chloride (Rembold, Ann. 1866, 138, 189), or phosgene (Kempf, Zeit. f. Chem. 1871, 7, 79), on benzaldehyde; by chlorinating toluene at the boiling-point (Beilstein, Ann. 1860, 116, 336; Beilstein and Kuhlberg, Ann. 1868, 146, 322; Lauth and Grimaux, Bull. Soc. chim. 1860, 2, 347; cf. Limpricht, Ann. 1866, 139, 318); in nearly theoretical yield from toluene with 2 mols. of phosphorus pentachloride at 170°–200° (Colson and Gautier, Ann. Chim. 1887, (6) 11, 21). It is manufactured by chlorinating boiling toluene in direct sunlight.

Colourless, powerfully refractive liquid, b.p. 212°–214° (Hübner and Bente, Ber. 1873, 6, 804), or 203.5°/756.2 mm. (Schiff, Ber. 1886, 19, 563), m.p. –16.1° (Zeitsch. physikal. Chem. 1897, 22, 234; cf. Altschul, *ibid.* 1895, 16, 24); D_{20}^{25} 1.2699; D_{20}^{25} 1.2122; D_{20}^{25} 1.1877; D_{20}^{25} 1.0407 (Schiff, *l.c.*), D_{14}^{25} 1.2557.

Water at 140°–160°, or sulphuric acid at 50° (Oppenheim, Ber. 1869, 2, 213), alkalis and silver oxalate (Golowsinsky, Ann. 1859, 111, 252), convert benzylidene chloride into benzaldehyde. When treated with sodium it yields stilbene, and with copper powder at 100° stilbene dichloride, $C_6H_4CHCl_2CHCl_2C_6H_5$, and the corresponding tetrachloride are produced (Onufrowicz, Ber. 1884, 17, 833). Ammonia yields hydrobenzamide ($C_6H_5NH_2$, cf. Böttger, Ber. 1878, 11, 840). The reaction with triethylphosphine in presence of alcohol at 120°–130° proceeds thus:



whilst phosphonium iodide yields tribenzylphosphine (Hofmann, Ann. Suppl. 1, 323).

When treated with anhydrous alkali acetates for 10–20 hours at 180°–200° cinnamic acid is formed (B. A. S. F., Eng. Pat. 3330 of 1880; Fr. Pat. 138275; D. R. PP. 17467 of 1890, and 18232 of 1881). For the behaviour of benzylidene chloride with acid esters or alcohols in presence of metals or metallic salts, see E. Jacobsen, Eng. Pat. 2878 of 1880; Fr. Pat. 137419; D. R. PP. 11494 of 1879, and 13127 of 1880.

It forms *p*-nitrobenzylidene chloride

(Hübner and Bente, Ber. 1873, 6, 803; cf. Beilstein, Ann. 1868, 146, 333); red-hot soda lime forms benzene (Limpricht, Bull. Soc. chim. 1866, (2) 6, 467); and zinc ethyl diluted with benzene forms $C_{11}H_{10}$, diethylphenylmethane, and $C_{12}H_{10}$ (Dafert, Monatsch. 1884, 4, 618).

Benzylidene chloride is employed in the manufacture of benzaldehyde, benzoic acid and cinnamic acid. The commercial product is always impure. It may be tested by its boiling-point, and by determining the percentage of chlorine.

o-Chlorobenzylidene chloride; from salicylaldehyde and phosphorus pentachloride (Henry, Ber. 1869, 2, 135); by passing a current of chlorine through a mixture of dry *o*-chlorotoluene and phosphorus pentachloride at 150°–180° in bright daylight (Erdmann, Ann. 1893, 272, 151; Vanino, Präparative Chemie, 1923, vol. ii. p. 410); by passing chlorine over *o*-toluenesulphonyl chloride at 150°–200° (Gilliard, Monnet and Cartier, Eng. Pat. 29717 of 1896; U.S. Pat. 606470; Fr. Pat. 268607; D. R. P. 98433 of 1896); by chlorinating benzylidene chloride in presence of iodine (Beilstein and Kuhlberg, *l.c.*). Oil, b.p. 227°–230° [H], or 228.5° (Gill, Ber. 1893, 26, 650); D_{20}^{25} 1.4 [H], D_{14}^{25} 1.399 [G]. It is decomposed by water at 170°, yielding *o*-chlorobenzaldehyde and hydrogen chloride, and with chromic acid yielding *o*-chlorobenzoic acid, whilst with silver in methyl alcoholic solution it yields *o*:*o*-dichloro-stilbene dichloride, and on distillation with dry oxalic acid *o*-chloro-benzaldehyde is formed (Anschütz, Ann. 1884, 226, 19).

p-Chlorobenzylidene chloride; by chlorinating benzylidene chloride in presence of iodine (Beilstein and Kuhlberg, *l.c.*); together with *p*-chlorobenzotrichloride by passing chlorine over toluene *o*-sulphonyl chloride (Gilliard, Monnet and Cartier, *l.c.*). Hübner and Bente (Ber. 1873, 6, 804) obtained a chlorobenzylidene chloride, b.p. 255°–260°, which on oxidation yielded impure *p*-chlorobenzoic acid. *p*-Chlorobenzylidene chloride is a liquid, b.p. 234°.

(β) 2:4-Dichlorobenzylidene chloride; by passing chlorine into 2:4-dichlorotoluene heated at 230°. Liquid, b.p. about 260°. On treatment with sulphuric acid it yields the corresponding dichlorobenzaldehyde (Seelig, Ann. 1887, 237, 167).

2:5-Dichlorobenzylidene chloride; by careful addition of chlorosulphonic acid to a chloroform solution of 2:5-dichlorobenzaldehyde. Cubic crystals, m.p. 42° (Gnehm and Schuele, Ann. 1898, 299, 358).

3:4-Dichlorobenzylidene chloride; by chlorinating boiling 3:4-dichlorotoluene. Oil, b.p. 257°, D_{20}^{25} 1.518 (Beilstein and Kuhlberg). When heated with water at 220°, 3:4-dichlorobenzaldehyde is formed.

2:3:4-Trichlorobenzylidene chloride; by chlorinating 2:3:4-trichlorotoluene near the boiling-point. It melts at 84°, boils at 275°–285°, and yields 2:3:4-trichlorobenzaldehyde with fuming sulphuric acid (Seelig).

2:4:5-Trichlorobenzylidene chloride; by chlorinating 2:4:5-trichlorotoluene at the boiling-point. Liquid, solidifying to crystalline needles at 0°. It boils at 280°–281°, and has D_{20}^{25} 1.607. Decomposed by water at 250°, or by sulphuric acid, yielding hydrochloric acid and

2:4:5-trichlorobenzaldehyde (Beilstein and Kuhlberg, Ann. 1869, 150, 298).

Tetrachlorobenzylidene chloride; by chlorinating boiling tetrachlorotoluene. Liquid, b.p. 305°–306°, D_{20}^{25} 1.704. With water at 280° it yields tetrachlorobenzaldehyde (Beilstein and Kuhlberg; cf. Cassella & Co., Eng. Pat. 16317 of 1914).

Pentachlorobenzylidene chloride; by chlorinating benzylidene chloride in presence of iodine and subsequently in presence of antimony pentachloride. Long flat plates, m.p. 109°, b.p. 334° (Beilstein and Kuhlberg), m.p. 119.5° (Zincke, Ber. 1893, 26, 318). It is not affected by water at 300°.

Benzotrichloride, phenyl-chloroform; from benzoyl chloride and phosphorus pentachloride (Schischkoff and Rösing, Compt. rend. 1858, 46, 367; Limpricht, Ann. 1865, 134, 55; 1865, 135, 80; Bull. Soc. chim. 1866, (2) 6, 468; Wöhler and Liebig, Ann. 1832, 3, 265); by exhaustive chlorination of heated toluene (Limpricht, Ann. 1865, 135, 80; 1866, 139, 323); by chlorinating toluene (Naquet, Compt. rend. 1862, 55, 407; 1863, 56, 482), or benzylidene chloride (Cahours, *ibid.* 1863, 56, 703); manufactured by chlorinating boiling toluene in direct sunlight until the weight of the product no longer increases. Colourless, powerfully refractive liquid, m.p. –22.5° (Haase, Ber. 1893, 26, 1053) or –21.2° (Schneider, Zeitsch. physikal. Chem. 1897, 22, 234); setting-point –17° (Altschul, *ibid.* 1895, 16, 24); b.p. 213°–214° (Beilstein and Kuhlberg); D_{15}^{20} 1.380 [L]. With water at 150° or with water in presence of iron or iron salts at 90°–95° (Schultze, D. R. P. 82927 of 1894) it yields benzoic and hydrochloric acids; with alcohol, ethyl benzoate and hydrochloric acid; with sodium benzoate, ethyl orthobenzoate $C_6H_5C(OC_2H_5)_2$; with ammonia, benzoic acid, benzamide and benzonitrile; with aniline, benzenyldiphenylamide; with dimethylaniline and zinc chloride, Malachite Green; with methyldiphenylamine or diamylaniline, similar green colouring matters; with aniline hydrochloride, nitrobenzene and iron filings at 180° for 3–4 hours, diamino-triphenylcarbinol $(NH_2C_6H_4)_3C \cdot OH(C_6H_5)$ (Doebner, Ber. 1882, 15, 232); with phenol, dihydroxy-triphenylcarbinol (Doebner, Ann. 1883, 217, 226); with copper powder, toluene tetrachloride $C_{11}H_9Cl_4$, α - and β -tolane di-chloride $C_{11}H_7Cl_2$ (Hanhart, Ber. 1882, 15, 899; cf. Onufrowicz, Ber. 1884, 17, 825); with zinc ethyl in presence of benzene, diethylphenylmethane $C_6H_5CH(C_2H_5)_2$ (Lippmann and Loughaine, Zeitsch. f. Chem. 1867, (2) 3, 674); with fuming nitric acid, *m*-nitro-benzoic acid (Beilstein and Kuhlberg, Ann. 1868, 146, 333). By treating benzotrichloride with chlorine in sunlight, the compound $C_{11}Cl_{11}$, m.p. 152°–153°, is obtained, which on treatment with zinc and sulphuric acid yields the compound $C_{11}HCl_{11}$, m.p. 102° (Smith, Jahresbericht, 1877, 420; Ber. 1880, 13, 33). For the behaviour of benzotrichloride with metals, metallic chlorides and other salts, see E. Jacobsen (Eng. Pat. 2878 of 1890; Tr. Pat. 137419; D. R. P. 11494 of 1879, and 13127 of 1890); and for its use in the preparation of rhodamine dyes, see B. A. S. F. (D. R. P. 36018 of 1889).

Commercial benzotrichloride is tested by

examining its boiling-point. It generally contains compounds chlorinated in the nucleus.

o-Chlorobenzotrichloride; from salicylaldehyde and phosphorus pentachloride (Kolbe and Lautemann, Ann. 1860, 116, 195), m.p. 30°, b.p. 260°, D_{15}^{20} 1.51 (in liquid state). With water at 150° it yields hydrochloric acid and *o*-chlorobenzoic acid, and with copper powder in presence of benzene it yields α - and β -*o*-dichlorotoluene dichloride (Fox, Ber. 1893, 26, 653).

m-Chlorobenzotrichloride; from *m*-sulphobenzoic acid and phosphorus pentachloride (Carius and Kämmerer, Ann. 1864, 131, 158); from *m*-hydroxy-benzoic acid and 3 mols. of phosphorus pentachloride at 180° (Anschütz and Moore, Ann. 1887, 239, 342). Liquid, b.p. 247°–250° (A. and M.).

p-Chlorobenzotrichloride; by chlorinating benzotrichloride in presence of iodine (Beilstein and Kuhlberg, l.c.); by heating *p*-oxybenzide

$C_6H_5 \begin{matrix} \diagup O \\ | \\ \diagdown CO \end{matrix}$ with phosphorus pentachloride at

290°–300° (Klepl, J. pr. Chem. 1883, (2) 28, 204); in small quantities by heating 1 mol. of *p*-hydroxybenzoic acid with 3 mols. of phosphorus pentachloride at 180° (Anschütz and Moore, l.c. 347); in small quantities, together with benzotrichloride, from benzoyl chloride and phosphorus pentachloride in a similar manner (Limpricht, Ann. 1865, 134, 57; 1866, 139, 326); from toluene *p*-sulphonyl chloride by the action of chlorine at 150°–200° (Gilliard, Monnet and Cartier, D. R. P. 98433 of 1896). Liquid, b.p. 245° or 255°, D_{15}^{20} 1.495 (Limpricht). With water at 200° or warm concentrated sulphuric acid it is decomposed, yielding *p*-chlorobenzoic acid.

Dichlorobenzotrichloride; by chlorinating boiling dichlorotoluene. Liquid, b.p. 273°, D_{15}^{20} 1.587 (Beilstein and Kuhlberg, Ann. 1869, 150, 298). From the work of Aronheim and Dietrich (Ber. 1875, 8, 1401), as well as that of Schultz (Ann. 1877, 187, 260), it appears that by the chlorination of dichlorotoluene three isomerides are formed, since crude dichlorotoluene is itself a mixture of 3 isomerides.

2:4:5-Trichlorobenzotrichloride; by passing chlorine into boiling trichlorotoluene. Very fine needles, m.p. 82°, b.p. 307°–308°. Decomposed by water at 250°, yielding 2:4:5-trichlorobenzoic acid (Beilstein and Kuhlberg, Ann. 1869, 156, 305).

Tetrachlorobenzotrichloride; by chlorinating boiling tetrachlorotoluene. Needles, m.p. 104°, b.p. 316°. Decomposed by prolonged action of water at 270° into tetrachlorobenzoic acid (Beilstein and Kuhlberg, l.c., 306).

Dichlorotoluene hexachloride $Cl_6 \cdot C_6H_2Cl_2 \cdot CH_3$; by treating toluene with an excess of chlorine and allowing the mixture to stand (Pieper, Ann. 1867, 142, 304). Large prisms, m.p. 150°, partially decomposed by water at 200°. When treated with alcoholic potash at 100° it is said to yield a *tetrachlorotoluene*, b.p. 280°–290° (but this is either impure or possibly a totally different substance), and dichlorobenzoic acid.

ω-Difluoro-*ω*-chlorotoluene $C_6H_4 \cdot CF_2 \cdot CH_2$; together with trifluorotoluene from benzotrichloride and antimony fluoride. Colourless liquid of strongly irritant odour, b.p. 142°–170 mm., D_{15}^{20} 1.2645. With water it yields

acid; and with sodium amalgam, *o*-difluoro toluene; with fuming nitric acid and phosphoric oxide below 0° it yields a *nitro-derivative*, colourless liquid, b.p. 230°, D_{15}^{20} 1.4638, and some *m*-nitrobenzoic acid (Swarts, Bull. Acad. roy. Belg. 1900, 414).

o-Dichloro-*o*-fluorotoluene; by the action of antimony fluoride on benzotrichloride at low temperatures. Colourless liquid of piercing odour, b.p. 178°–180°, D_{15}^{20} 1.3138, n_D^{20} 1.5180; *nitro-derivative*, colourless liquid, b.p. 280° (Swarts, *l.c.*). Fluorine derivatives of toluene have been described by Holleman (Rec. trav. chim. 1906, (2) 25, 330).

o-Chlorotoluene; by chlorinating toluene in presence of iodine (Hübner and Majert, Ber. 1873, 6, 790), or better, in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 152); in a yield of 65 p.c. by chlorination in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1119); from *o*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, Ann. 1870, 156, 79; Erdmann, *ibid.* 1893, 272, 145; Sandmeyer, Ber. 1884, 17, 2651; Gasiorowski and Wajss, Ber. 1885, 18, 1939; Vanino, Präparative Chemie, 1923, vol. ii. p. 406; Wynne, Chem. Soc. Trans. 1892, 61, 1072); by chlorination of toluene *p*-sulphonic acid, or its chloride or amide in sulphuric acid solution, followed by the removal of the sulphonic group by heating in a current of steam (B. A. S. F., D. R. P. 294638 of 1914); by hydrolysis of *o*-chlorotoluene *p*-sulphonic acid by boiling with 80 p.c. sulphuric acid (Ges. für Chem. Ind. in Basel, D. R. P. 133000 of 1901); readily by hydrolysis of 6-chlorotoluene *o*-sulphonic acid (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920). M.p. –34° (Haase, Ber. 1893, 26, 1053); b.p. 159.5°/759.5 mm., n_D^{20} 1.4977 (Wibaut, Rec. trav. chim. 1913, (2) 32, 244); D_{15}^{20} 1.0973, D_{15}^{25} 1.0877, D_{25}^{20} 1.0801 (Perkin, Chem. Soc. Trans. 1896, 69, 1243), D_{25}^{20} 1.08073 (Seubert, Ber. 1889, 22, 2520). For specific gravity and boiling-point under diminished pressure, see Feitler (Zeitsch. physikal. Chem. 1889, 4, 73); molecular refractive power and dispersion coefficient (Seubert, *l.c.*); magnetic rotatory power at 15.4°, 13.72° (Perkin, *l.c.*).

On treatment with chromyl chloride and subsequent treatment of the product with water, *o*-chlorotoluene yields *o*-chlorobenzaldehyde (Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 804); the latter product is also obtained in a yield of 66 p.c. by the gradual addition of cerium oxide to a suspension of *o*-chlorotoluene in 60–65 p.c. sulphuric acid at 50°, the temperature being raised gradually to 90° (M. L. B., D. R. P. 174238 of 1903). It is reduced by hydriodic acid and phosphorus to toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 41, 322), whilst on oxidation with potassium permanganate it yields *o*-chlorobenzoic acid, m.p. 134°–135° (Wroblewski, Zeit. f. Chem. 1869, (2) 5, 460; Cohen and Dakin, *l.c.* 1120). *o*-Chlorotoluene exists in two modifications (von Ostrowskij, Zeitach. physikal. Chem. 1906, 57, 341).

m-Chlorotoluene; from *m*-toluidine or 3-chloro-*p*-toluidine (Wroblewski, Ann. 1873, 168, 199; Vanino, Präparative Chemie, 1923, vol. ii. p. 406); by the diazo-reaction; from 5-chloro-*o*-

toluidine and 3-chloro-*p*-toluidine by treating the corresponding hydrazines with copper sulphate solution (Wynne, Chem. Soc. Trans. 1892, 61, 1047, 1059); from the dibromide of dihydro-*m*-chlorotoluene by boiling with quinoline (Klages and Knoevenagel, Ber. 1894, 27, 3022). M.p. –47.8°; b.p. 162.2°/756.52 mm.; $D_{162.2}^{20}$ 0.92723 (Haase, Ber. 1893, 26, 1053); D_{162}^{20} 1.07218 (Seubert, Ber. 1889, 22, 2520); molecular refractive power and dispersion coefficient (Seubert, *l.c.*); specific gravity and boiling point under diminished pressure (Feitler, Zeitsch. physikal. Chem. 1889, 4, 76). On nitration it yields a mixture of *o*- and *p*-nitro-chlorotoluenes (Reverdin and Crépiaux, Ber. 1900, 33, 2505). On heating with dilute nitric acid in a sealed tube at 130°–140° it yields 3-chlorobenzoic acid, needles, m.p. 152° (Wynne, *l.c.*).

p-Chlorotoluene; by chlorinating toluene in presence of iodine (Beilstein and Geitner, Ann. 1866, 139, 334; Bull. Soc. chim. 1869, (2) 1, 251), or molybdenum pentachloride (Aronheim and Dietrich, Ber. 1875, 8, 1402), in a yield of 35 p.c. by using the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1119); from *p*-toluidine by the diazo-reaction (Gasiorowski and Wajss, Ber. 1885, 18, 1939; Hübner and Majert, Ber. 1873, 6, 794; Sandmeyer, Ber. 1884, 17, 2651; Vanino, *l.c.*); by hydrolysis of *p*-chlorotoluene *o*-sulphonic acid (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920). M.p. 7.4° (Seubert); b.p. 162.3°/756.4 mm.; $D_{162.3}^{20}$ 1.0847, D_{15}^{20} 1.0749, D_{25}^{20} 1.0672 (Perkin, Chem. Soc. Trans. 1896, 69, 1243), $D_{162.3}^{20}$ 1.06974 (Seubert, Ber. 1889, 22, 2519), $D_{162.3}^{20}$ 0.92360 (cf. Feitler, Zeitsch. physikal. Chem. 1889, 4, 78); magnetic rotatory power at 15.2°, 13.25° (Perkin, *l.c.*). It is oxidised by chromic acid mixture or by potassium permanganate (Cohen and Dakin, *l.c.* 1120) to *p*-chlorobenzoic acid, m.p. 236°; and when treated with hydriodic acid and phosphorus it is converted into toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322).

(a) 2:3-Dichlorotoluene; by chlorination of *o*-chlorotoluene in presence of the aluminium-mercury couple; from 2-chloro-3-toluidine by the diazo-reaction (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1128); *o*-chlorotoluene sulphonic acid (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151); by chlorination of toluene or *o*-chlorotoluene in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 157, 168); from crude dichlorotoluene by treatment with fuming sulphuric acid at high temperatures, then neutralising the product with lime, the calcium sulphate of 2:3-dichlorotoluene being less soluble than that of the accompanying 2:4-dichlorotoluene. The calcium salt is then converted into the sodium salt, and the sulphonic group removed by steam distillation at 180° in presence of sulphuric acid (Seelig). Doubt has been cast upon the orientation of Seelig's product by Wynne (Chem. Soc. Trans. 1892, 61, 1051) and by Armstrong (*ibid.* 1892, 61, 1035).

Liquid, b.p. 204°–206°/755 mm. (Cohen and Dakin, *l.c.* 1128) or 207°–208°/760 mm. (Wynne and Greeves, *l.c.*). On oxidation with nitric acid in a sealed tube at 140° for some hours it yields

2:3-dichlorobenzoic acid, m.p. 163° (Cohen and Dakin, *l.c.*), or 164° (Wynne and Greeves, *l.c.*), or 166° (Seelig, *l.c.*). It yields a *nitro-derivative*, m.p. 50.5°–51.5°; a *dinitro-derivative*, m.p. 71°–72°; a *sulphonamide*, m.p. 221°–222° (Cohen and Dakin, *l.c.*); a *sulphonyl chloride*, needles, m.p. 45° (Wynne and Greeves, *l.c.*). Wynne and Greeves state that 2:3-dichlorotoluene on sulphonation yields two isomeric sulphonic acids, the one whose amide and chloride are described above being accompanied by 2:3-dichlorotoluene 5-sulphonic acid (*chloride*, prisms, m.p. 85°, *amide*, m.p. 183°), but this was not confirmed by Cohen and Dakin.

(β) 2:4-Dichlorotoluene; by chlorination of toluene or *p*-chlorotoluene (Seelig, Ann. 1887, 237, 182), in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1116); from 2:4-toluylenediamine (Erdmann, Ber. 1891, 24, 2769; Vanino, *l.c.*) or *o*-chloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 314); by treating 2:4-dibromo-*o*-toluenediazonium chloride with hydrogen chloride in alcoholic solution (Hantzsch, Ber. 1897, 30, 2334); from 2:4-dinitro-*o*-toluidine; from *o*-chlorotoluenesulphonic acid (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151). M.p. 26.5° (Hantzsch, *l.c.*), b.p. 194°/735 mm. (Lellmann and Klotz); b.p. 199°–200°/760 mm. (Wynne and Greeves, *l.c.*), D₂₀²⁰ 1.24597 (L. and K.). - It yields a *mononitro-compound*, m.p. 54°–55°, and a *dinitro-compound*, prisms, m.p. 103°–104° (Cohen and Dakin, *l.c.* 1129) on nitration; 2:4-dichlorotoluene 5-sulphonic acid (*chloride*, m.p. 71°, *amide* m.p. 177°) on sulphonation (Wynne and Greeves, *l.c.*); and 2:4-dichlorobenzoic acid, m.p. 159°–160°, b.p. 198°–200°, on oxidation (Cohen and Dakin, *l.c.*).

2:5-Dichlorotoluene; from 5-chloro-*o*-toluidine by the diazo-reaction (Lellmann and Klotz, Ann. 1885, 231, 318; Wynne, Chem. Soc. Trans. 1892, 61, 1049); by chlorination of *o*- and *m*-chlorotoluene in presence of the aluminium-mercury couple (Cohen and Dakin, *l.c.*); by chlorination of aceto-*o*-toluidide followed by hydrolysis and replacement of the amino-group by chlorine (Lellmann and Klotz, *l.c.*); by the action of sodium hypochlorite on aceto-*o*-toluidide followed by conversion of the nitrogen chloride into 5-chloroaceto-*o*-toluidide, hydrolysis and replacement of the amino-group by chlorine (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790; Cohen and Dakin, *l.c.* 1130); by hydrolysis of 2:5-dichlorotoluene *p*-sulphonic acid which is prepared by chlorinating toluene *p*-sulphonic acid or its soluble salts (B. D. C. Green and Clibbens, Eng. Pat. 169025 of 1920; cf. Wynne, *l.c.*). Liquid, b.p. 200°/770 mm. (Wynne, *l.c.*), 194°/745 mm. (Lellmann and Klotz), 198°–199°/760 mm., which lies in a freezing mixture to crystals, m.p. 5° (Cohen and Dakin, *l.c.*).

On nitration it yields a *mononitro-derivative*, m.p. 50°–51°, and a *dinitro-derivative*, m.p. 100°–11°, and on oxidation with dilute nitric acid at 10°–140° for 10 hours it yields 2:5-dichlorobenzoic acid, m.p. 152° (Wynne, *l.c.*; Cohen and Dakin, *l.c.*).

2:6-Dichlorotoluene; by chlorination of *o*-toluene in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1117); from 6-nitro-*o*-toluidine

or 6-nitro-*p*-toluidine (Cohen and Dakin, *ibid.* 1131); readily by distilling an aqueous solution of the sodium salt of 2:6-dichlorotoluene *p*-sulphonic acid with superheated steam at 250° (Davies, Chem. Soc. Trans. 1920, 119, 873). Liquid, b.p. 197°–199°/757 mm. (Davies), yielding on nitration a *mononitro-derivative*, m.p. 53°, and a *dinitro-derivative*, m.p. 121°–122° (Cohen and Dakin, *ibid.* 1132; Davies, *l.c.*); and, on oxidation with dilute nitric acid in a sealed tube, 2:6-dichlorobenzoic acid, colourless needles, m.p. 139°–140° (Cohen and Dakin, *l.c.*; Wynne and Greeves, *l.c.*; cf. Claus and Stavenhagen, Ann. 1892, 269, 224.)

3:4-Dichlorotoluene; from 3-chloro-*p*-cresol and phosphorus pentachloride (Schall and Dralle, Ber. 1884, 17, 2535); by chlorination of toluene, *o*- and *m*-chlorotoluene (Beilstein and Geitner, Ann. 1866, 139, 341; Beilstein and Kuhlberg, Ann. 1869, 150, 313; Aronheim and Dietrich, Ber. 1875, 8, 1401; Neuhof, Zeit. f. Chem. 1886 (2), 2, 653; Schultz, Ann. 1877, 187, 263; Cohen and Dakin, *l.c.*); from 3-nitro-*p*-toluidine (Cohen and Dakin); from 3-chloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 312; Wynne, Chem. Soc. Trans. 1892, 61, 1060; Vanino, *l.c.*); by hydrolysis of 3:4-dichlorotoluene sulphonic acid (Wynne, *ibid.* 1069). Liquid, b.p. 205.5°–206.5°/763.5 mm. (Wynne), 200.5°/741 mm. (L. and K.); D₂₀²⁰ 1.2512 (L. and K.). On nitration it yields 3:4-dichloro-6-nitrotoluene, m.p. 63°–64°, and 3:4-dichloro-2:6-dinitrotoluene, m.p. 91.5°–92.5° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1133; 1902, 81, 1349); and, on oxidation with dilute nitric acid in a sealed tube, 3:4-dichlorobenzoic acid, m.p. 202° (Wynne; Cohen and Dakin).

3:5-Dichlorotoluene (cf. Hantzsch, Ber. 1897, 30, 2334); from 3:5-dichloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 323); from 3:5-dichloro-*o*-toluidine (Wynne and Greeves, Chem. Soc. Trans. 1892, 61, 1060); from 3:5-dichloroaceto-*o*-toluidide (prepared according to the method of Chattaway and Orton, *ibid.* 1896, 69, 850) by hydrolysis with hydrochloric acid in a sealed tube for 8 hours at 160°, followed by elimination of the amino-group (Cohen and Dakin, *ibid.* 1133). M.p. 26°, b.p. 195°/729 mm. (L. and K.), or 201°–202°/atm. (Wynne and Greeves), sublimes at the ordinary temperature. Yields a *nitro-derivative*, needles, m.p. 61°–62°, and a *dinitro-derivative*, needles, m.p. 99°–100°, and on oxidation with dilute nitric acid at 150° it yields 3:5-dichlorobenzoic acid, long needles, m.p. 182°–183° (Cohen and Dakin).

(β) 2:3:4-Trichlorotoluene, together with 2:4:5-trichlorotoluene, by chlorinating either *o*- or *p*-chlorotoluene in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 36, 133; cf. Prentiss, Ann. 1897, 296, 180); together with a tetrachlorotoluene, by chlorinating 2:3-dichlorotoluene in presence of the aluminium-mercury couple; together with 2:4:5-trichlorotoluene and probably a small amount of 2:4:6-trichlorotoluene by 2:4-dichlorotoluene in a similar manner; from 4-nitro-2:3-dichlorotoluene by reduction and diazotisation (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1323, 1329).

Forms a *mononitro-derivative*, white needles, m.p. 60°–61°, a 5:6-*dinitro-derivative*, m.p. 140°–141°, and a *sulphonic acid* which is decomposed by superheated steam at 210°, whilst on oxidation with dilute nitric acid in a sealed tube at 150° it yields 2:3:4-trichlorobenzoic acid, m.p. 186°–187° (Cohen and Dakin; Seelig, *l.c.*, gives m.p. 129°).

2:3:5-*Trichlorotoluene*; almost exclusively by chlorination of 3:5-dichlorotoluene in presence of the aluminium-mercury couple; from 3:5-dichloro-*o*-toluidine (prepared by hydrolysis of the acetyl-derivative obtained by the action of bleaching powder on aceto-*o*-toluidide according to the method of Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 791) by the diazo-reaction, and from 2:5-dichloro-*m*-toluidine. Long needles, m.p. 45°–46°, b.p. 229°–231°/757 mm. Yields a *nitro-derivative*, felted needles, m.p. 58°–59°, a *dinitro-derivative*, flat needles, m.p. 149°–150°, and with 20 p.c. nitric acid in a sealed tube at 140°, it yields 2:3:5-trichlorobenzoic acid, m.p. 162° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

2:3:6-*Trichlorotoluene*; almost exclusively by chlorination of 2:6-dichlorotoluene; together with 2:4:5-trichlorotoluene by chlorination of 2:5-dichlorotoluene in presence of the aluminium-mercury couple; from 2:6-dichloro-*m*-toluidine by the diazo-reaction. On nitration it yields a *mononitro-derivative*, long needles, m.p. 57°–58°, and 2:3:6-trichloro-4:5-*dinitro-toluene*, prisms, m.p. 140°–142°, and on oxidation, 2:3:6-trichlorobenzoic acid, flaky crystals, m.p. 163°–164° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1331, 1343). The chlorination of toluene *p*-sulphonic acid or its soluble salts results in the formation of 2:5-dichloro- and 2:3:6-trichlorotoluene *p*-sulphonic acid. The latter is readily separated on account of the much greater insolubility of its sodium salt, and on hydrolysis a good yield of 2:3:6-trichlorotoluene is claimed (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920).

(a) 2:4:5-*Trichlorotoluene*, together with 2:3:4-trichlorotoluene by chlorinating toluene in presence of iodine (Limpricht, Ann. 1866, 139, 326), $\frac{1}{4}$ –1 p.c. of molybdenum pentachloride (Aronheim and Dietrich, Ber. 1875, 8, 1401) or ferric chloride (Seelig, Ann. 1887, 237, 131), the crude product being shaken with two parts of fuming sulphuric acid for a minute at 60° (whereby only the 2:3:4-isomeride is sulphonated) and precipitated with water and steam distilled; together with 2:3:4-trichlorotoluene and probably a small amount of 2:4:6-trichlorotoluene by chlorinating 2:4-dichlorotoluene in presence of the aluminium-mercury couple; together with 2:3:6-trichlorotoluene by chlorinating 2:5-dichlorotoluene in a similar manner, and as sole product by chlorinating 3:4-dichlorotoluene in a similar manner; from 4:6-dichloro-*m*-toluidine and 4:5-dichloro-*o*-toluidine (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1332, 1343); from 2:5-dichloro-*p*-toluidine and 5-chloro-2:4-toluylenediamine by the diazo-reaction (Morgan and Drew, *ibid.* 1920, 117, 789; 1900, 77, 1209). Long white needles volatile with steam, m.p. 81°–82° (Cohen and Dakin), b.p. 229°–230°/716 mm. On nitration it yields a *mononitro-derivative*, m.p. 91°–92°, 2:4:5-trichloro-3:6-*dinitrotoluene*,

m.p. 226°–227°, and on oxidation 2:4:5-trichlorobenzoic acid, white silky needles, m.p. 162°–164° (Cohen and Dakin; Seelig; Jannasch, Ann. 1887, 142, 301).

2:4:6-*Trichlorotoluene*; see 2:3:4- and 2:4:5-trichlorotoluenes; by chlorinating aceto-*m*-toluidide in glacial acetic acid—hydrochloric acid solution by means of sodium chlorate at 15°–25°, followed by hydrolysis and elimination of the amino-group (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1335); from 6-chloro-2:4-toluylenediamine by the Sandmeyer reaction (Morgan and Drew, *ibid.* 1920, 117, 786). Long white needles, m.p. 33°–34°, yielding on nitration the 3-*nitro-derivative*, m.p. 54° (indefinite), the 3:5-*dinitro-derivative*, m.p. 178°–180°, and on oxidation 2:4:6-trichlorobenzoic acid, m.p. 160°–161° (Cohen and Dakin, *l.c.*).

3:4:5-*Trichlorotoluene*; by hydrolysis of potassium 3:4:5-trichlorotoluene sulphonate (Wynne, Chem. Soc. Trans. 1892, 61, 1070); from 3:5-dichloro-*p*-toluidine or 4:5-dichloro-*m*-toluidine (Cohen and Dakin, *ibid.* 1902, 81, 1336); as a derivative of the products of the action of sulphuryl chloride on aceto-*p*-toluidide (Wynne, *ibid.* 1892, 62, 1042). M.p. 41.5°–45.5°, volatile with steam (Cohen and Dakin). On oxidation with dilute nitric acid it yields the corresponding trichlorobenzoic acid (Wynne; Cohen and Dakin).

2:3:4:5-*Tetrachlorotoluene*; from 2:4:5- or 3:4:5-trichlorotoluene by nitration, reduction and replacement of the amino-group by chlorine. There is no evidence of the formation of this substance by the further chlorination of 2:4:5-trichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1906, 89, 1453); the product, m.p. 86°–88°, previously stated (*ibid.* 1904, 85, 1280) to be 2:3:4:5-tetrachlorotoluene is probably a mixture of tetrachlorotoluene and trichloronitrotoluene (m.p. 81°). 2:3:4:5-Tetrachlorotoluene melts at 97°–98° and forms a *nitro-derivative*, m.p. 159° (Cohen and Dakin, *ibid.* 1906, 89, 1483).

2:3:4:6-*Tetrachlorotoluene*; from 2:4:6-trichloro-aceto-*m*-toluidide by hydrolysis and replacement of the amino-group by chlorine; by further chlorination of 2:4:6-trichlorotoluene in presence of the aluminium-mercury couple. Shining needles, m.p. 91.5°–92°. 5-*Nitro-derivative*, m.p. 131°–134° (not pure), and on further nitration a compound, highly refractive plates, m.p. 153°, is formed (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1280, 1284).

2:3:5:6-*Tetrachlorotoluene*; from 2:3:6-trichlorotoluene by nitration, reduction and replacement of the amino-group by chlorine; by chlorination of 2:3:5- and 2:3:6-trichlorotoluene in presence of the aluminium-mercury couple. White opaque felted needles, m.p. 93°–94°; 4-*nitro-derivative*, small hexagonal plates, m.p. 150°–152° (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1281). The tetrachloro-derivatives obtained by Limpricht (Ann. 1866, 189, 327), Beilstein and Kuhlberg (Ann. 1869, 150, 286), and Pieper (Ann. 1867, 145, 305) are impure. A tetrachlorotoluene has been obtained in 90 p.c. yield, together with less highly halogenated derivatives and traces of pentachlorotoluene, |

| mixture of dry toluene and chloride with stirring; the maximum

were being 50°, whilst, if the temperature be kept at 12°–15°, trichlorotoluene is formed (Casella & Co., Eng. Pat. 16317 of 1914).

Pentachlorotoluene; by chlorinating toluene initially in presence of iodine and finally in presence of phosphorus pentachloride. Long hair-like needles, m.p. 218°, b.p. 301° (Beilstein and Kuhlberg, Ann. 1869, 150, 298).

Bromo derivatives.—A quantitative examination of the influence of light, temperature and bromine 'carriers' on the action of bromine on an excess of toluene has been carried out by Holleman and van der Laan (Proc. K. Akad. Wetensch. Amsterdam, 1906, 8, 512), van der Laan (Chem. Weekblad, 1906, 3, 15), Holleman, Polack, van der Laan and Euwe (Rec. trav. chim. 1908, (2) 27, 435); cf. Andrich and le Blanc (Zeitsch. Wiss. Photochem. 1916, 15, 148) and Swenson (*ibid.* 1921, 20, 206). The investigations of van der Laan have left the question undecided whether *m*-bromotoluene is formed by the bromination of toluene in addition to *o*- and *p*-bromotoluene and benzyl bromide. Holleman (Rec. trav. chim. 1914 (2), 33, 183) concludes, on the evidence of the index of refraction and of the first and second points of solidification of the products of bromination, that *m*-bromotoluene is not produced when bromine acts on a large excess of toluene. Cohen and Dutt (Chem. Soc. Trans. 1914, 105, 504), however, arrive at a contrary conclusion when using the aluminium-mercury couple, although Holleman regards the experimental proof of the presence of *m*-bromotoluene as not sufficiently definite. A further proof of the contention of Cohen and Dutt is given in Chem. Soc. Proc. 1914, 30, 271.

In addition to the ordinary methods for brominating toluene, a mixture of nitric and hydrobromic acids may be used, but it is preferable to use a mixture of bromine and nitric acid (Datta and Chatterjee, J. Amer. Chem. Soc. 1916, 38, 2545).

***o*-Bromotoluene** on further bromination in of the aluminium-mercury couple mainly 2:5-dibromotoluene with smaller quantities of 2:4-dibromotoluene; *m*-bromotoluene similarly yields 2:5-dibromotoluene with 3:4-dibromotoluene, a little 4:5-tribromotoluene and a trace of 3:4-dibromotoluene; whilst *p*-bromotoluene yields 4-dibromotoluene as the main product ether with 3:4-dibromotoluene (Cohen and L., *l.c.*) and 2:4:5-tribromotoluene (Miller, 1892, 61, 1023).

2:3-Dibromotoluene on similar treatment 2:3:6-tribromotoluene as the main act, together with a little of the 2:3:5- whilst the presence of 2:3:4-olene is doubtful; 2:4-dibromotoluene yields a mixture of 2:4:5- and 2:4:6-oluenes; 2:5-dibromotoluene yields 2:4:5-tribromotoluene together with 2:3:5-isomeride; whilst 3:4-dibromotoluene yields mainly 2:4:5-tribromotoluene, with a very small amount of 3:4:5-oluenes, and 3:5-dibromotoluene yields 1:5-tribromotoluene (Cohen and Dutt, Chem. 1914, 105, 501). The bromination in presence of the aluminium-yields mainly 2-chloro-5-bromo- with smaller quantities of

2-chloro-4-bromotoluene; of *m*-chlorotoluene, 3-chloro-6-bromotoluene and smaller quantities of 3-chloro-4-bromotoluene; of *p*-chlorotoluene, mainly 4-chloro-2-bromotoluene together with 4-chloro-3-bromotoluene. The chlorination of *o*-bromotoluene under similar conditions yields mainly 4-chloro-2-bromotoluene together with 6-chloro-2-bromotoluene; of *m*-bromotoluene, mainly 6-chloro-3-bromotoluene together with 4-chloro-3-bromotoluene; and of *p*-bromotoluene, 2-chloro-4-bromotoluene as main product together with 3-chloro-4-bromotoluene (Cohen and Smithells, *ibid.* 1914, 105, 1910).

Benzyl bromide; by saturating benzyl alcohol with hydrogen bromide (Kekulé, Ann. 1866, 137, 190); by the action of bromine on toluene at the boiling-point (Beilstein, Ann. 1867, 143, 369; Jackson and Field, Amer. Chem. J. 1880–1, 2, 11), in sunlight (Schramm, Ber. 1885, 18, 608; cf. Grimaux and Lauth, Bull. Soc. chim. 1867 (2), 7, 108). From benzyl chloride and arsenic tribromide (Brix, Ann. 1884, 225, 163). Liquid, b.p. 198°–199° D_{20}^{22} 1.4380. The vapour has lachrymatory properties.

The zinc-copper couple reacts energetically with benzyl bromide yielding two isomeric benzylenes (C_7H_8)₂ with evolution of hydrogen bromide, whilst if the reaction be carried out in ethereal solution no hydrogen bromide is evolved, and toluene and dibenzyl are formed when the reaction product is treated with water. Similar products are obtained in presence of ethyl alcohol or water (Gladstone and Tribe, Chem. Soc. Trans. 1885, 47, 448).

***o*-Bromobenzyl bromide**; together with the *p*-compound by brominating crude toluene, most of the *p*-compound being removed by pressing the cooled product, the remainder being distilled with steam when the *o*-compound distils first; in a pure condition by brominating *o*-bromotoluene. Crystallises at 0° in very pungent rhombic plates, volatile with steam, m.p. 30°, and on treatment with sodium in ethereal solution it yields phenanthrene, anthracene, dibenzyl and other products (Jackson and others, Amer. Chem. J. 1879, 1, 93; 1880–1, 2, 315; Ber. 1876, 9, 932; 1879, 12, 1965; 1880, 13, 1218).

***m*-Bromobenzyl bromide**; by brominating heated *m*-bromotoluene. Pungent plates or needles, m.p. 41°, slightly volatile with steam, but very volatile with ether vapour; like *o*-bromobenzyl bromide, it is unattacked by chromic acid (Jackson, Ber. 1876, 9, 931; Amer. Chem. J. 1879, 1, 93).

***p*-Bromobenzyl bromide**; by passing bromine vapour into boiling *p*-bromotoluene; by brominating benzyl bromide (Jackson, *l.c.*); by brominating *p*-bromotoluene in the cold and in presence of sunlight (Schramm, Ber. 1884, 17, 2922; 1885, 18, 350). Very pungent needles or large rhombic prisms, m.p. 61°, volatile with steam. When boiled with alcoholic potash it yields *p*-bromobenzyl alcohol and ethyl *p*-bromobenzoate (Elbe, J. pr. Chem. 1886, (2) 24, 241), and with zinc dust *p*-*p*-dibromodibenzyl (Errera, Gazz. chim. ital. 1886, 16, 227; cf. Fittig and Stelling, Ann. 1866, 137, 266).

Benzylidene bromide; from benzyl alcohol and phosphorus pentabromide (Michaelson and Lammann, Bull. Soc. chim. 1865, (2) 2, 251; Curran

and Quedenfeldt, J. pr. Chem. 1898, (2) 58, 389) Liquid, b.p. 156°/23 mm., D_{15}^{20} 1.51, n_D^{20} = 1.541 It is decomposed by cold water forming hydrogen bromide and benzaldehyde, whilst with alcohol it yields ethyl bromide and a liquid, b.p. 50°/11 mm. ($C_6H_5 \cdot CHBrOC_2H_5$), which on treatment with water yields hydrogen bromide and benzaldehyde (Curtius and Quedenfeldt). With sodium at 180° it yields toluene and dibenzyl (Michaelson and Lippmann).

p-Bromobenzyl chloride; by heating *p*-bromobenzyl alcohol with fuming hydrochloric acid at 150° for 3-4 hours. Glistening needles, m.p. 38°-39° (Errera, Gazz. chim. ital. 1888, 18, 239)

o-Bromotoluene; together with *p*-bromotoluene by brominating cold toluene in the dark in daylight or in presence of iodine (Longuinine, Ber. 1871, 4, 514; Dmochowsky, Ber. 1872, 5, 333; Schramm, Ber. 1885, 18, 607; Glinzer and Fittig, Ann. 1865, 133, 47; 1865, 136, 301; Kekulé, Ann. 1866, 137, 192; Cannizzaro Ann. 1867, 141, 198; Beilstein, Ann. 1867, 143, 369; Fittig, Ann. 1868, 147, 39; Hübner and Post, Ann. 1873, 169, 1; Hübner and Jannasch Ann. 1873, 170, 117; Hübner and Wallach Ann. 1870, 154, 293; Zeit. f. Chem. 1869, (2) 5, 22, 138, 499; Rosenstiel and Nikiforoff, *ibid.* 1869, (2) 5, 635; Hübner and Retschy, *ibid.* 1871, (2) 7, 618; Lauth and Grimaux, Bull. Soc. chim. 1866, (2) 5, 347; 1867, (2) 7, 108; Miller, Chem. Soc. Trans. 1892, 61, 1025).

The product is shaken with dilute sodium hydroxide to remove bromine, steam distilled and fractionated. The crude mixture of *o*- and *p*-bromotoluenes is then subjected to the alternate action of a good freezing mixture and weakly fuming sulphuric acid, when an approximate separation is effected (Miller); another method of separation is given by Reymann (Bull. Soc. chim. 1876, (2) 26, 533). A better method of preparing *o*-bromotoluene is to add bromine to a concentrated solution of pure potassium toluene *p*-sulphonate and to heat at 60°-70°. The mixture is then steam distilled, when the *o*-bromosulphonate crystallises from the residual solution on cooling. On hydrolysing the latter, pure *o*-bromotoluene is obtained (Miller). It may also be prepared from *o*-toluidine by the Sandmeyer reaction (Wroblewsky, Ann. 1873, 168, 171) and together with naphthalene by the action of α -bromonaphthalene on toluene in the presence of aluminium chloride (Roux, Bull. Soc. chim. 1886, (2) 45, 520). M.p. -25.9°; b.p. 180.33°/753.91 mm. (Haase, Ber. 1893, 26, 1053; cf. Feitler, Zeitsch. physikal. Chem. 1889, 4, 73); D_{15}^{20} 1.4437, D_{15}^{20} 1.4309 or 1.431, D_{25}^{20} 1.4222 (Perkin, Chem. Soc. Trans. 1896, 69, 1243; Miller, *ibid.* 1892, 61, 1029; Kelbe, Ber. 1886, 19, 93), D_{20}^{20} 1.4222 (Seubert, Ber. 1889, 22, 2520), D_{15}^{20} 1.21861 (Haase, *l.c.*); molecular refractive power and dispersion coefficient (Seubert, *l.c.*); magnetic rotatory power at 16.7° 15.67 (Perkin, *l.c.*).

On treatment with dilute nitric acid (Zincke, Ber. 1874, 7, 1502) or by prolonged heating with potassium ferrocyanide (Noyes, Amer. Chem. J. 1885, 7, 145) it is oxidised to *o*-bromobenzoic acid; and with chromyl chloride in carbon disulphide solution, followed by decomposition of the product with water, it yields *o*-bromobenzaldehyde and *o*-bromobenzylidene chloride

(Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 804). When brominated in presence of iodine (Miller, *ibid.* 1892, 61, 1032) or the aluminium-mercury couple (Cohen and Dutt, *ibid.* 1914, 105, 501) it yields 2:5-dibromotoluene and a small quantity of 2:4-dibromotoluene, and on reduction with hydriodic acid and phosphorus at 250° it yields toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322). The zinc-copper couple has no action (Gladstone and Tribe, Chem. Soc. Trans. 1885, 47, 448). For its conversion into *o*-ditolyl, see Fittig (Ann. 1866, 139, 178) and Carnelley (Jahresbericht, 1877, 384), and for the two modifications of *o*-bromotoluene, see Ostromisslensky (Zeitsch. physikal. Chem. 1906, 57, 341).

For its conversion into *o*-cresol, see Bodroux (Compt. rend. 1903, 136, 158; Bull. Soc. chim. 1904, (3) 31, 34).

m-Bromotoluene; from *m*-toluidine by the diazo-reaction and from *m*-bromo-*p*-toluidine by the elimination of the amino-group (Wroblewsky, Zeit. f. Chem. 1871, (2) 7, 609; Ann. 1873, 168, 155; cf. Grete, *ibid.* 1875, 177, 231; Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 950); from *m*-bromo-*p*-toluidine by nitration, elimination of the amino-group, reduction and replacement of the amino-group by bromine (Wroblewsky, Ann. 1878, 192, 206). M.p. -39.8°; b.p. 183.67°/759.46 mm.; D_{15}^{20} 1.20082 (Haase, Ber. 1893, 26, 1053; Feitler, Zeitsch. physikal. Chem. 1889, 4, 73); D_{15}^{20} 1.40988, D_{25}^{20} 1.4009 (Wroblewsky) (Seubert, Ber. 1889, 22, 2520). Optical behaviour (Seubert) Oxidised by chromic acid to *m*-bromobenzoic acid. When sodium acts on a mixture of *m*-bromotoluene and bromobenzene in ethereal solution at 40°-50° for 5 hours, a mixture of diphenyl, *m*-ditolyl and *m*-phenyltoluene is formed (Perrier, Compt. rend. 1891, 114, 484; Bull. Soc. chim. 1892, (3) 182).

On bromination in presence of the aluminium-mercury couple, *m*-bromotoluene yields 2:5-dibromotoluene, 3:4-dibromotoluene, a little 2:4:5-tribromotoluene and a trace of 3:5-dibromotoluene (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 506), whilst on chlorination under similar conditions yields mainly 4-chloro-2-bromotoluene together with 6-chloro-2-bromotoluene (Cohen and Smithells, *ibid.* 1914, 105, 1910).

p-Bromotoluene; together with *o*-bromotoluene by brominating cold toluene (see under *o*-bromotoluene and Hübner and Post, Ann. 1873, 169, 1; Miller, Chem. Soc. Trans. 1892, 61, 1025; Michaelis and Geuzen, Ann. 1887, 242, 165); together with *o*-bromotoluene-sulphonic acid by brominating potassium toluene *p*-sulphonate (Miller). The products of the latter reaction are steam distilled, and the oily, volatile product, consisting of *p*-bromotoluene, a dibromotoluene and *p*-bromobenzyl bromide, is fractionally distilled. The fraction boiling at about 185° solidifies on cooling and consists of *p*-bromotoluene, which is readily obtained pure by redistillation and crystallisation (Miller).

Rhombic crystals (Hübner and Post) or colourless plates (Miller); m.p. 28.5°; b.p. 85.2° (Hübner and Post) or 183.67°/759.46 mm. (Feitler); D_{15}^{20} 1.3959, D_{25}^{20} 1.3856, D_{15}^{20} 1.3637 (Perkin, Chem. Soc. Trans. 1896, 69,

1243), D_{40}^{20} 1.19306 (Hübner and Post; cf. Feitler, D_{40}^{20} 1.38977 (Seubert, Ber. 1889, 22, 2519; cf. Kekulé, Ann. 1866, 137, 192); magnetic rotatory power at 39° 15.06 (Perkin); optical behaviour (Seubert).

On bromination in presence of the aluminium-mercury couple (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 509) or iodine (Miller, *ibid.* 1892, 61, 1304), it yields 2:4- and a little 3:4-dibromotoluene, and on treatment with chromyl chloride in carbon disulphide, followed by decomposition of the product with water, it yields *p*-bromobenzaldehyde (Etard, Ann. Chim. 1881, (5) 22, 241), whilst on reduction with hydriodic acid at 250° it is converted into toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322). Sodium reacts with a mixture of *p*-bromotoluene and bromobenzene to form *p*-phenyltoluene (Carnelley, Chem. Soc. Trans. 1876, 29, 16; 1880, 37, 706). With sodium it yields 4:4-ditolyl, dibenzyl, 3:4-ditolyl and 4-tolylphenylmethane, etc. (Zincke, Ber. 1871, 4, 396; Longuinine, Ber. 1871, 4, 514; Weiler, Ber. 1899, 32, 1056). The zinc-copper couple has no reaction (Gladstone and Tribe), whilst chromic acid yields *p*-bromobenzoic acid. When chlorinated hot *p*-bromotoluene yields *p*-bromobenzyl chloride (Baeseken, Rec. trav. chim. 1904, 23, 98). It condenses with benzophenone in the presence of sodium to yield *p*-tolylidiphenylmethane (Acree, Amer. Chem. J. 1903, 29, 588).

The magnesium derivative of *p*-bromotoluene on treatment with oxygen yields *p*-cresol (Bodroux, Compt. rend. 1903, 136, 158; Bull. Soc. chim. 1904, (3) 31, 34), whilst it condenses with ethyl-*o*-formate to yield *p*-tolualdehyde (Bodroux, Bull. Soc. chim. 1904, (3) 31, 586; Compt. rend. 1904, 138, 92, 700), with dimethyl sulphate to form *p*-xylene (Werner and Zilkens, Ber. 1903, 36, 2116; Houben, *ibid.* 3083), and with carbonyl sulphide to form *p*-thiotoluic acid and a little tritolyl-carbinol. A similar reaction takes place with the magnesium derivative of *o*-bromotoluene (Weigert, *ibid.* 1007).

2:3-Dibromotoluene; from 5:6-dibromo-*m*-toluidine by elimination of the amino-group (Nevile and Winther, Ber. 1880, 13, 962; 1881, 14, 417; Chem. Soc. Trans. 1880, 37, 429). According to Fittig (Ann., 1868, 147, 39) a *p*-bromotoluene, long needles, m.p. 107° – 108° , obtained by brominating cold toluene without the addition of iodine. The constitution of product is questioned by Nevile and Finther, and Miller (Chem. Soc. Trans. 1892, 61, 1031) regards it as being probably impure 1:4:5-tribromotoluene.

2:3-Dibromotoluene melts at 27.4° – 27.8° and W.) or 30° – 31° (Wynne, Chem. Soc. ns. 1892, 61, 1040). On oxidation with fute nitric acid at 130° , 2:3-dibromobenzoic m.p. 146° – 148° , is formed, whilst on action in carbon tetrachloride solution presence of the aluminium-mercury couple yields mainly 2:3:6-tribromotoluene together with a little of the 2:3:5-tribromotoluene, whilst the presence of the 2:3:4-*iso*-isomeride is doubtful (Cohen and Chem. Soc. Trans. 1914, 105, 616).

2:4-Dibromotoluene; from *p*-bromo-*o*-toluene and 4:5-dibromo-*o*-toluidine by the

dialzo-reaction (Nevile and Winther, *l.c.*); together with a greater proportion of 2:5-dibromotoluene by bromination of *o*-bromotoluene, or together with 3:4-dibromotoluene and 2:4:5-tribromotoluene by brominating *p*-bromotoluene (Miller, Chem. Soc. Trans. 1892, 61, 1023).

Liquid, which does not solidify at -20° , b.p. 152° – $158^\circ/80$ mm. (Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 50). On oxidation with dilute nitric acid it yields 2:4-dibromobenzoic acid, tables, m.p. 168° – 170° (N. and W.), whilst on bromination a mixture of 2:4:5- and 2:4:6-tribromotoluene is formed (Cohen and Dutt, *l.c.*).

2:5-Dibromotoluene; by brominating toluene (Wroblewsky, Zeit. f. Chem. 1870, (2) 6, 239) or *m*-bromotoluene (Wroblewsky, Ann. 1873, 168, 681); from 6-bromo-*m*-toluidine or 5-bromo-*o*-toluidine by the dialzo-reaction (Nevile and Winther, *l.c.*); as the main product, together with 2:4-dibromotoluene, by brominating *o*-bromotoluene (Miller, Chem. Soc. Trans. 1892, 61, 1031; cf. Cohen and Dutt, *ibid.* 1914, 105, 506).

Liquid, which does not solidify at -20° , b.p. 236° , D_{40}^{20} 1.8127 (Wroblewsky). On prolonged boiling with dilute nitric acid it yields 2:5-dibromobenzoic acid, and on bromination in carbon tetrachloride solution in presence of the aluminium-mercury couple, it yields mainly 2:4:5-tribromotoluene together with the 2:3:6-isomeride (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 518).

2:6-Dibromotoluene; from 2:6-dibromo-*m*-toluidine, 2:6-dibromo-*p*-toluidine (Nevile and Winther, *l.c.*; Wroblewsky, *l.c.*), and 6-bromo-*o*-toluidine (Blankama, Chem. Weekblad. 1912, 9, 968) by the dialzo-reaction.

Colourless crystals, m.p. 2° (Blankama), b.p. 246° , D_{40}^{20} 1.812 (Wroblewsky; cf. Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 51). On bromination it yields 2:3:6-tribromotoluene (Cohen and Dutt, *l.c.*).

3:4-Dibromotoluene; from 3-bromo-*p*-toluidine (Nevile and Winther, *l.c.*; Wroblewsky); the product obtained by Jannasch (Ann. 1876, 176, 286) by brominating toluene is stated to be a mixture of isomerides by Miller (Chem. Soc. Trans. 1892, 61, 1605); together with other products by brominating *p*-bromotoluene (Miller, *l.c.*). Liquid, b.p. 160° – $165^\circ/65$ mm. (Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 52), b.p. 238° – 239° , D_{40}^{20} 1.812 (Wroblewsky). On oxidation with dilute nitric acid or chromic acid, 3:4-dibromobenzoic acid, m.p. 232° – 233° (cf. Burghardt, Ber. 1875, 8, 559), is obtained. On further bromination 2:4:5-tribromotoluene, together with a very small quantity of 3:4:5-tribromotoluene, is formed (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 519).

3:5-Dibromotoluene; from 3:5-dibromo-*p*-toluidine or 3:5-dibromo-*o*-toluidine (Wroblewsky, *l.c.*; Nevile and Winther). Long needles, m.p. 39° , b.p. 246° (Nevile and Winther). On oxidation with chromic acid it yields 3:5-dibromobenzoic acid, m.p. 208° – 209° , whilst on further bromination 2:3:5-tribromotoluene is formed (Cohen and Dutt, *l.c.*).

Dibromotoluene, m.p. 106° . The existence of this substance, said to be formed by the bromination of toluene (Fittig, Ann. 1868, 147, 39) is questioned by Nevile and Winther.

2:3:4-Tribromotoluene; from 4:5:6-tribromo-

bromo-*m*-toluidine (Nevile and Winther, *l.c.*); by bromination of 4:5-dibromoaceto-*m*-toluidine, followed by hydrolysis with dilute sulphuric acid and elimination of the amino-group. It melts at 45°–46° and when heated for 6 hours in a sealed tube at 150°–160° with dilute nitric acid it yields 2:3:4-tribromobenzoic acid (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 511).

2:3:5-*Tribromotoluene*; from 3:5-dibromo-*o*-toluidine (N. and W.) or 5:6-dibromo-*m*-toluidine (Cohen and Dutt, *l.c.*) by the diazo-reaction. Long flat needles, m.p. 52°–53°. On oxidation with dilute nitric acid at 135°–140° for 6 hours it yields 2:3:5-tribromobenzoic acid, m.p. 193°–194°.

2:3:6-*Tribromotoluene*; from 2:5:6-tribromo-*m*-toluidine (N. and W.), 2:5:6-tribromo-*p*-toluidine, and 5:6-dibromo-*o*-toluidine (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 514). Flat needles, m.p. 58°–59° (N. and W.). The corresponding tribromobenzoic acid could not be obtained by direct oxidation with dilute nitric acid in a sealed tube (Cohen and Dutt, *l.c.*).

2:4:5-*Tribromotoluene*; from 4:6-dibromo-*m*-toluidine and 4:5-dibromo-*o*-toluidine (Nevile and Winther, *l.c.*; Cohen and Dutt, *l.c.*); from 5-bromo-2:4-toluylenediamine (Morgan and Clayton, *Chem. Soc. Trans.* 1905, 87, 951); by nitration of 3:4-dibromotoluene followed by reduction (Nevile and Winther, *Ber.* 1881, 14, 417); by brominating *p*-bromotoluene (Miller, *Chem. Soc. Trans.* 1892, 61, 1033).

Colourless needles, m.p. 112°–113°. On oxidation with dilute nitric acid in a sealed tube it yields 2:4:5-tribromobenzoic acid, m.p. 195°–196° (Cohen and Dutt, *l.c.*). According to Pfankuch (*J. pr. Chem.* 1873, (2) 6, 108) a *tribromotoluene*, small needles, m.p. 150°, is obtained by heating the potassium salt of tribromophenol with potassium acetate.

2:4:6-*Tribromotoluene*; from 2:4:6-tribromo-*m*-toluidine by the diazo-reaction (Nevile and Winther, *Ber.* 1880, 13, 975; 1881, 14, 417; *Chem. Soc. Trans.* 1880, 37, 446); by brominating *m*-toluidine followed by the elimination of the amino-group (Cohen and Dutt, *l.c.*). M.p. 66° (N. and W.), b.p. 290° (Wroblewsky, *Ann.* 1873, 168, 194). On oxidation it yields 2:4:6-tribromobenzoic acid, m.p. 186°–187° (Cohen and Dutt).

3:4:5-*Tribromotoluene*; from 3:5-dibromo-*p*-toluidine by the diazo-reaction. M.p. 88°–89° (Nevile and Winther, *l.c.*; Cohen and Dutt, *l.c.*). On oxidation it yields 3:4:5-tribromobenzoic acid, m.p. 235° (Cohen and Dutt).

(v)-2:3:4:5-*Tetrabromotoluene*; from 4:5:6-tribromo-*m*-toluidine by the diazo-reaction. Needles, m.p. 111°–111.5° (Nevile and Winther).

(a)-2:3:4:6-*Tetrabromotoluene*; from 2:4:6-tribromo-*m*-toluidine and tetrabromo-*m*-toluidine (m.p. 224°) by the diazo-reaction. M.p. 106.8°–108° (Nevile and Winther).

(s)-2:3:5:6-*Tetrabromotoluene*; from 2:5:6-tribromo-*m*-toluidine by the diazo-reaction. Fine needles, m.p. 116°–117° (Nevile and Winther).

Pentabromotoluene; by careful addition of toluene to pure bromine at 0° in presence of

aluminium bromide (Gustavson, *J. Russ. Phys. Chem. Soc.* 1877, 9, 236; *Bull. Soc. chim.* 1877, (2) 28, 347; *Ber.* 1877, 10, 971); from tetrabromo-*m*-toluidine (m.p. 223°–224°) (Nevile and Winther, *Ber.* 1880, 13, 976; *Chem. Soc. Trans.* 1880, 37, 450); from cycloheptane (Markownikoff, *J. Russ. Chem. Phys. Soc.* 1893, 25, 544) or methylcyclohexane (Kursanoff, *Ber.* 1899, 32, 2973) by the action of bromine in presence of aluminium bromide; from ethyl- and propyl-cymene by means of bromine in presence of aluminium (Klages and Sommer, *Ber.* 1906, 39, 2306; Klages, *Ber.* 1907, 40, 2360).

Long needles which sublime, m.p. 282°–283° (Kursanoff) or 279°–280° (Zelinsky and Generosow, *Ber.* 1896, 29, 732; cf. Jäger, *Z. Kristall*, 1903, 38, 89). It is reduced to toluene by phosphorus and hydriodic acid at 302° (Klages and Liecke, *J. pr. Chem.* 1900, (2) 61, 322).

2-*Chloro-3-bromotoluene*, m.p. 18°, on oxidation yields 2-chloro-3-bromobenzoic acid, m.p. 165°, and on nitration yields a *mononitro-derivative*, m.p. 44°–45°, and a *dinitro-derivative*, m.p. 89°–93° (Cohen and Smithells, *Chem. Soc. Trans.* 1914, 105, 1908).

2-*Chloro-4-bromotoluene*; from 2-nitro-*p*-toluidine (Cohen and Raper, *Chem. Soc. Trans.* 1904, 85, 1266); together with 3-chloro-4-bromotoluene by chlorinating *p*-bromotoluene (Cohen and Smithells, *l.c.* 1910; cf. Willgerodt and Salzmann, *J. pr. Chem.* 1889, (2) 39, 465.) Liquid, b.p. 100°–110°/10 mm., which on oxidation yields 2-chloro-4-bromobenzoic acid, m.p. 166°–167° (Cohen and Raper). Its *nitro-derivative* melts at 65°–66° and its *dinitro-derivative* at 110°–111° (Cohen and Smithells).

2-*Chloro-5-bromotoluene*; from 5-nitro-*o*-toluidine. Liquid, b.p. 127°–129°/45 mm. It yields 2-chloro-5-bromobenzoic acid on oxidation (Cohen and Raper), and on nitration a *mononitro-derivative*, m.p. 68°–69°, and a *dinitro-derivative*, m.p. 109°–110° (Cohen and Smithells).

2-*Chloro-6-bromotoluene*; from 2:6-dinitrotoluene. Liquid, b.p. 118°–120°/40 mm. which yields 2-chloro-6-bromobenzoic acid, m.p. 143°–144°, on oxidation (Cohen and Raper, *l.c.*; Willgerodt and Salzmann) and a *mononitro-derivative*, m.p. 50°–52°, and a *dinitro-derivative*, m.p. 143°–144°, on nitration (Cohen and Smithells).

3-*Chloro-2-bromotoluene*; from 3-nitro-*o*-toluidine (Cohen and Raper, *Chem. Soc. Trans.* 1904, 85, 1266). It melts at 4°–5° (Cohen and Smithells, *ibid.* 1914, 105, 1908) and boils at 103°–105°/25 mm. On oxidation it yields 3-chloro 2-bromobenzoic acid, m.p. 143°–144° (Cohen and Raper), and on nitration a *mono-* and a *dinitro-derivative*, m.p. 58°–59.5° and 81° respectively (Cohen and Smithells).

3-*Chloro-4-bromotoluene*; from *m*-chloro-*p*-toluidine by the diazo-reaction (Cohen and Raper, *l.c.*); by chlorinating *p*-bromotoluene (Willgerodt and Salzmann, *l.c.*). Liquid, b.p. 125°–130°, which on oxidation yields 3-chloro-4-bromobenzoic acid, m.p. 218° (Cohen and Raper), and on nitration yields a *mono-* and a *dinitro-derivative*, melting at 72° and 101°–102° respectively (Cohen and Smithells, *l.c.*).

3-*Chloro-5-bromotoluene*; from aceto-*p*-toluidide by successive bromination and chlorination with hydrochloric acid and sodium chlorate in acetic acid, followed by hydrolysis to 3-chloro-

5-bromo-*p*-toluidine and elimination of the amino-group; by chlorination of aceto-*p*-toluidine and hydrolysis to 3-chloro-*p*-toluidine followed by bromination and elimination of the amino-group. Crystals, m.p. 26°–27°. Its 6-nitro-derivative, colourless needles, melts at 71° and its 2:6(1)-dinitro-derivative at 144°. On oxidation it yields 3-chloro-5-bromobenzoic acid, m.p. 189°–190° (Cohen and Raper; Cohen and Smithells; Cohen and Murray, Chem. Soc. Trans. 1915, 107, 847).

4-Chloro-2-bromotoluene; by chlorinating o-bromotoluene or by brominating *p*-chlorotoluene; from 2-nitro-*p*-toluidine. Liquid, b.p. 112°–114°/12 mm. On oxidation it yields 4-chloro-2-bromobenzoic acid, m.p. 154°–155° (Cohen and Raper, Chem. Soc. Trans. 1904, 85, 1267; cf. Willgerodt and Salzmann, J. pr. Chem. 1889, (2) 39, 465, and Cohen and Dakin, Chem. Soc. Trans. 1899, 75, 895), and on nitration a mononitro- and a dinitro-derivative, melting at 64°–65° and 124°–5° respectively, are formed (Cohen and Smithells, Chem. Soc. Trans. 1914, 105, 1908).

4-Chloro-3-bromotoluene; from *m*-nitro-*p*-toluidine. Liquid, b.p. 120°–125°/28 mm. It yields 4-chloro-3-bromobenzoic acid, m.p. 214°, on oxidation (Cohen and Raper, l.c.), and a mononitro-derivative, m.p. 67°–5°, and a dinitro-derivative, m.p. 127°, on nitration (Cohen and Smithells).

4-Chloro-dibromotoluene; by brominating bromo-*p*-chlorotoluene in presence of the aluminium mercury couple. M.p. 94° (Cohen and Dakin, Chem. Soc. Trans. 1899, 75, 893).

5-Chloro-2-bromotoluene; from 5-chloro-*o*-toluidine. Liquid, b.p. 98°–100°/25 mm. The nitro-derivative melts at 66°–67°, the dinitro-derivative at 117°, and oxidation yields 5-chloro-2-bromobenzoic acid, m.p. 153° (Cohen and Raper; Cohen and Smithells).

The following compounds have been obtained by Willgerodt and Salzmann (J. pr. Chem. 1889, (2) 39, 482): *o*-chloro-dibromotoluene, needles, m.p. 100°, b.p. 275°–280°, by brominating *o*-chlorotoluene; dichloro-*p*-bromotoluene, glistening needles, m.p. 87°, b.p. 240°–245°; trichloro-*p*-bromotoluene, needles, m.p. 55°–60°, b.p. 265°–275°; and tetrachloro-*p*-bromotoluene, needles, m.p. 213°, by chlorinating *p*-bromotoluene.

3:4:6(1)-Trichloro-5-bromotoluene, m.p. 98°–100°, is obtained from 3:4-dichloro-5-bromotoluene by nitration, reduction and replacement of the amino-group by chlorine. Its nitro-derivative melts at 171°–173° (Cohen and Dakin, Chem. Soc. Trans. 1906, 89, 1453).

2(1):3:4-Trichloro-5-bromotoluene, m.p. 92°–94°, is formed by chlorinating 3:4-dichloro-5-bromotoluene. Its nitro-derivative melts at 175°–176° (Cohen and Dakin, l.c.).

2-Chloro-3:4:5:6-tetrabromotoluene melts at 256°–259° (Mouneyrat and Pourcet, Compt. rend. 1899, 129, 607).

o-Iodotoluene; from *o*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, Ann. 1871, 158, 347; Kekulé, Ber. 1874, 7, 1007; Mabery and Robinson, Amer. Chem. J. 1882, 4, 101); together with *p*-iodotoluene by heating a solution of toluene in light petroleum with powdered sulphur iodide and an excess of dilute nitric acid (D 1.34) for several hours at 100°

(Edinger and Goldberg, Ber. 1900, 33, 2875). Oil, b.p. 204° (B. and K.) or 211° (Kekulé), D₂₀ 1.697 (B. and K.).

When oxidised with dilute nitric acid it yields *o*-iodobenzoic acid, m.p. 157°. With chromyl chloride and treatment of the product with water, it yields *o*-iodo-*o*-dichlorotoluene and a little *o*-iodobenzaldehyde (Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 805). When heated with sulphuric acid it yields di- and tri-iodotoluene, together with iodotoluene sulphonic acid (Neumann, Ann. 1887, 241, 62; Ber. 1887, 20, 581), whilst on nitration mainly 5-nitro-2-iodotoluene is formed (Reverdin, Ber. 1897, 30, 3000). On treatment with chlorine in chloroform solution *o*-iodotoluene yields a dichloride, crystals, decomposing about 91° (Willgerodt, Ber. 1893, 26, 360).

m-Iodotoluene; from *m*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, l.c.). Liquid, b.p. 204°, D₂₀ 1.698.

p-Iodotoluene; from *p*-toluidine by the diazo-reaction (Körner, Zeitsch. f. Chem. 1868, (2) 4, 327; Bull. Acad. roy. Belg. 1867, 157); together with *o*-iodotoluene by the iodination of toluene according to the method of Edinger and Goldberg (above). Plates which sublime, m.p. 35°, b.p. 211°–5°. *p*-Iodotoluene is stated to be formed also by the action of iodine on mercury ditolyl, the melting-point being given as 20° (Dreher and Otto, Ann. 1870, 154, 171).

When chlorinated, two forms of the iodo-dichloride are obtained, the α -form separates from chloroform in needles, decomposing at 85°, and the β -form in irregular rhombic crystals, exploding at 110°–118° (Willgerodt, Ber. 1893, 26, 357). With nitric acid (D 1.51) at the ordinary temperature it yields *p*-nitrotoluene, *p*-iodo-*o*-nitrotoluene, and a di-iodo-nitrotoluene (Reverdin, Ber. 1897, 30, 3001), and on heating with sulphuric acid di- and tri-iodotoluene and iodotoluene sulphonic acid are formed (Neumann, Ann. 1887, 241, 58; Ber. 1887, 20, 581). On oxidation it yields *p*-iodobenzoic acid.

2:3-Di-iodotoluene; from 2-iodo-*m*-toluidine by the diazo-reaction. Colourless plates, m.p. 31°–32° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:4-Di-iodotoluene; by heating 1 part of *o*- or *p*-iodotoluene with 1 part of sulphuric acid (D 1.85) at 170°. Oil, b.p. 295°–296°. With dilute nitric acid at 200° it yields 2:4-di-iodobenzoic acid (Neumann, Ann. 1887, 241, 51; Ber. 1887, 20, 581).

2:5-Di-iodotoluene; from 5-iodo-*o*-toluidine by the diazo-reaction. Long colourless plates, m.p. 30°–31° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 498).

2:6-Di-iodotoluene; from 2-iodo-6-amino-toluene by the diazo-reaction. Almost colourless needles, m.p. 40°–42° (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1827).

3:5-Di-iodotoluene; from 3:5-di-iodo-*p*-toluidine by the diazo-reaction. Yellow needles, m.p. 44°–45° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:3:4-Tri-iodo-toluene; from 4:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. It melts at 92° (Wheeler, Brautlecht, Hoffman and Scholes, Amer. Chem. J. 1910, 44, 126, 493).

2:3:5-*Tri-iodotoluene*; from 2:5^o or 5:6-di-iodo-*m*-toluidine by the diazo-reaction. Pale orange plates, m.p. 72°-73° (Wheeler, etc.).

2:3:6-*Tri-iodotoluene*; m.p. 80°-5°, is obtained from 2:6-di-iodo-*m*-toluidine or 3:6-di-iodo-*o*-toluidine by the diazo-reaction (Wheeler, etc.).

2:4:5-*Tri-iodotoluene*; from 4:5-di-iodo-*o*-toluidine, 2:5-di-iodo-*p*-toluidine, and 4:6-di-iodo-*m*-toluidine (Wheeler, etc.); or by heating equal parts of *o*- or *p*-iodotoluene with sulphuric acid (D 1·85) at 170° (Neumann, Ann. 1887, 241, 55). Long brown needles, m.p. 119°-120°, b.p. above 300°.

2:4:6-*Tri-iodotoluene*; from 2:4:6-tri-iodo-*m*-toluidine by the diazo-reaction. Colourless needles, m.p. 105° (Wheeler, etc.).

3:4:5-*Tri-iodotoluene*; from 3:5-di-iodo-*p*-toluidine by the diazo-reaction. Long silky needles, m.p. 122°-123° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:3:4:5-*Tetraiodotoluene*; from 4:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. Straw-coloured needles, m.p. 284°-285° (Wheeler, etc.).

2:3:4:6-*Tetraiodotoluene*; from 2:4:6-tri-iodo-*m*-toluidine by the diazo-reaction. Long needles, m.p. 170° (Wheeler, etc.).

2:3:5:6-*Tetraiodotoluene*; from 2:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. Colourless needles, m.p. 125° (Wheeler, etc.).

Penta-iodotoluene; from 2:4:5:6-tetraiodo-*m*-toluidine by the diazo-reaction. Small dull yellow needles, m.p. 340° (decomp.) (Wheeler, etc.).

Chloro-o-iodotoluene; from chlorinated *o*-toluidine. B.p. 240°, D₄²⁰ 1·702 (Beilstein and Kuhlberg, Ann. 1870, 156, 82).

α-Chlorotoluene does not solidify at -14°, b.p. 242°, D₄²⁰ 1·716 (Wroblewsky, Ann. 1873, 168, 210).

β-Chlorotoluene solidifies at 10°, b.p. 240°, D₄²⁰ 1·770 (Wroblewsky).

2-*Chloro-6-iodotoluene*; from 2-chloro-6-aminotoluene by the diazo-reaction. Colourless liquid, b.p. 132°-133°/25 mm., D₂₀²⁰ 1·844 (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627).

5-*Chloro-4-iodo-3-nitrotoluene*; from 5-chloro-3-nitro-*p*-toluidine. Colourless plates, m.p. 92° (Kenner and Judd, *ibid.* 1920, 117, 776).

m-Bromo-o-iodotoluene; by treating *m*-bromo-*o*-diazo-toluene with hydriodic acid (Wroblewsky). Colourless liquid, b.p. 260°, D₁₅²⁰ 2·139.

2-*Bromo-6-iodotoluene*; from 2-bromo-6-aminotoluene by the diazo-reaction. Colourless liquid, b.p. 135°-140°/15 mm., D₂₀²⁰ 2·044 (Cohen and Miller).

3-*Bromo-4-iodotoluene*; from *m*-bromo-*p*-toluidine by the diazo-reaction. Oil, b.p. 265°, D₂₀²⁰ 2·044. It yields a *mononitro-derivative*, m.p. 118° (Wroblewsky).

3-*Bromo-2-iodotoluene*; from 6-iodo-*m*-toluidine by the diazo-reaction. B.p. 262°-265°, n_D^{20} 1·684 (Holleman, Rec. trav. chim. 1912, 31, 267).

The constitution of the product obtained by Hirtz (Ber. 1896, 29, 1406) by brominating *o*-iodotoluene as 4-(1)-*bromo-2-iodotoluene* is doubtful, as the reaction-product is of a very complicated nature (Holleman, *l.c.*).

3:5-*Dibromo-2-iodotoluene*; from 3:5-di-bromo-*o*-toluidine by the diazo-reaction. Needles, m.p. 68°, b.p. 314° (with slight decomp.).

On chlorinating in chloroform solution it yields a *dichloride*, yellow cubic crystals, m.p. 95° (decomp.) (McCrae, Chem. Soc. Trans. 1898, 73, 691).

3:5-*Dibromo-4-iodotoluene*; from 3:5-di-bromo-*p*-toluidine by replacement of the amino-group by iodine (Wroblewsky, Ann. 1873, 168, 190); from 3-bromo-5-nitro-*p*-toluidine by replacement of the amino-group by iodine and of the nitro-group by bromine (Wroblewsky, Ann. 1878, 192, 209). Long needles, m.p. 86°, b.p. 270°. Its *mononitro-derivative* melts at 69°.

3:5-*Dibromo-2:4-di-iodotoluene*; from nitrated bromiodotoluene by replacing the nitro-group by iodine. Prisms, volatile with steam, m.p. 68°. Its *mononitro-derivative* melts at 129° (Wroblewsky, Ann. 1878, 192, 212).

o-Iodosotoluene; from *o*-iodotoluene dichloride and dilute sodium hydroxide solution (Willgerodt, Ber. 1893, 26, 361) or water and pyridine (Ortoleva, Gazz. chim. ital. 1900, 30, ii. 5). Almost colourless crystals, m.p. 178° (decomp.), acetate m.p. 130°-132° (Ortoleva). 3:5-*Dibromo-2-iodosotoluene*, is obtained from the corresponding dichloride by treatment with soda solution. Yellow amorphous mass decomposing at about 87°. Its acetate forms needles, m.p. 66°-5° (McCrae, *l.c.*).

m-Iodosotoluene; from *m*-iodotoluene dichloride (yellow needles, decomposing at 104°) by the action of water on a solution in pyridine (Ortoleva), or by the action of sodium hydroxide (Willgerodt and Umbach, Ann. 1903, 327, 269). Yellowish-white amorphous powder exploding at 206°-207° (Willgerodt and Umbach) or decomposing at 180°-185° (Ortoleva). The acetate, colourless needles, melts at 148°-149° (Ortoleva; Willgerodt and Umbach), the *difluoride*, small colourless needles, melts at 180°, decomposing at 188°, on rapid heating (Weinland and Stille, Ann. 1903, 328, 132).

p-Iodosotoluene; by treating *p*-iodotoluene dichloride with dilute sodium hydroxide solution, followed by purification of the crude product with chloroform (Willgerodt, Ber. 1893, 26, 359); or in a manner analogous to that of the *o*-isomeride (Ortoleva, *l.c.*). It decomposes at 175°-178°, and on boiling with water yields a mixture of *p*-iodotoluene and *p*-iodoxytoluene (Willgerodt). On adding hydrofluoric acid slowly to a solution of *p*-iodosotoluene in acetic acid, *p*-toluene-iodo-fluoride, small yellow needles, m.p. 112°, decomposing at 115°, is formed (Weinland and Stille, *l.c.*).

o-Iodoxytoluene; by boiling *o*-iodosotoluene with water in presence of air (Willgerodt, Ber. 1893, 26, 361); by oxidising *o*-iodotoluene with Caro's acid (Bamberger and Hill, Ber. 1900, 33, 535). Crystalline mass, exploding at 210°, which when treated with hydrofluoric acid yields *o*-toluene-iodosulphuride, leafy aggregates of granules, commencing to melt at 120° and decomposing at 170°-190° (Weinland and Stille, Ber. 1901, 34, 2631).

m-Iodoxytoluene; by treating an intimate mixture of *m*-tolyl iododichloride and a concentrated solution of bleaching powder with a little hydrochloric acid (Willgerodt and Umbach); by oxidising a pyridine solution of *m*-iodotoluene

with chlorine (Ortoleva, Gazz. chim. ital. 1900, 30, ii. 1). White needles, exploding at 220° (Ortoleva, l.c.; cf. Bamberger and Hill). On warming with aqueous hydrogen peroxide it yields *m*-iodotoluene.

p-Iodoxytoluene; in a similar manner to the *o*- and *m*-isomerides. Silky leaflets, exploding at 228° (Willgerodt, Ber. 1896, 29, 1573; Bamberger and Hill, Ber. 1900, 33, 525; Ortoleva, Gazz. chim. ital. 1900, 30, ii. 8). It forms an iodosulfuride, lustrous needles, decomposing at 206° (Weinland and Stille, l.c.).

NITROSO- AND NITRO-DERIVATIVES.

2-Nitrosotoluene; by oxidation of *o*-tolylhydroxylamine (Bamberger, Ber. 1895, 28, 249); by the action of nitrogen trioxide or peroxide on a cold chloroform solution of mercury-*o*-ditolyl (Kunz, Ber. 1898, 31, 1530). White needles, melting at 72°–72.5° to a green liquid, extremely volatile with steam. On treatment with cold concentrated sulphuric acid it yields 4-nitroso-2:3-ditolylhydroxylamine, glistening yellow needles (+H₂O), decomposing about 130°; the anhydrous product melts at 110°–115° (Bamberger, Büsdorf and Sand, Ber. 1898, 31, 1517). 3-Nitro-2-nitrosotoluene, pale yellow leaflets, m.p. 126°–127° (decomp.), is obtained by oxidising 3-nitro-*o*-toluidine with Caro's acid, and is transformed by nitric acid into 2:3-dinitrotoluene (Meisenheimer and Hesse, Ber. 1919, 52, 1161). Its 5-nitro-derivative, almost colourless crystals, m.p. 143°–144°, is formed by the action of Caro's acid on the corresponding amine, and together with dinitroazoxytoluene by treating 2:5-dinitrotoluene with hydroxylamine followed by acidification. It is readily oxidised to 2:5-dinitrotoluene. When the reduction of 2:5-dinitrotoluene by means of hydroxylamine is effected in highly concentrated solution potassium nitrotoluene-iso-diazotate is precipitated in yellow needles, decomposing at 202° (Meisenheimer and Hesse, l.c.). Its 6-nitro-derivative, obtained by oxidising an aqueous alcoholic solution of 6-nitro-*o*-tolylhydroxylamine with ferric chloride in presence of sodium acetate, forms colourless needles, melting at 117° to a green liquid (Brand and Zöller, Ber. 1907, 40, 3324).

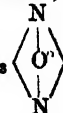
3-Nitrosotoluene is prepared in a similar manner to the *o*-derivative. Small needles, readily volatile with steam, m.p. 53°–53.5° (Bamberger, l.c.). Its 2-nitro-derivative forms yellow leaflets, m.p. 92°–93°, and its 4-nitro-derivative, yellow leaflets, m.p. 141° (Meisenheimer and Hesse, l.c.); its 6-nitro-derivative, m.p. 113°, is obtained by oxidising 6-nitro-*m*-toluidine by means of Caro's acid (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 859).

4-Nitrosotoluene; by oxidation of *p*-tolylhydroxylamine (Bamberger, l.c.; Bamberger and Brady, Ber. 1900, 33, 274); by oxidation of *p*-toluidine by means of potassium permanganate in sulphuric acid solution in presence of form- (Bamberger and Tschirner, Ber. 1898, 31, 1524); together with other products by the action of nitrogen trioxide or peroxide on a cold chloroform solution of mercury-*p*-ditolyl (Kunz, Ber. 1898, 31, 1528). White needles, extremely volatile with steam, m.p. 48.5°. For the action of hydrogen chloride and hydrogen bromide, see Bamberger, Büsdorf and Szalaydi (Ber. 1899,

32, 216). Its 2-nitro-derivative, colourless needles, m.p. 87°, is formed by oxidising 2-nitro-*p*-tolylhydroxylamine (Brand and Zöller); its 3-nitro-derivative is obtained by oxidising *m*-nitro-*p*-toluidine by means of Caro's acid (Bamberger and Hübner, Ber. 1903, 36, 3803), or together with 4-nitro-3-nitroso-toluene and other products by the action of hydroxylamine on 3:4-dinitrotoluene, followed by acidification (Meisenheimer and Hesse), and forms greenish-yellow needles, m.p. 145°–145.5°.

As a result of the work of Green and Rowe (Chem. Soc. Trans. 1912, 101, 2452; 1913, 103, 897), Forster and Fierz (*ibid.* 1907, 91, 1942), and Forster and Barker (*ibid.* 1913, 103, 1918), the compounds originally regarded as '*o*-dinitroso' compounds are shown to be actually iso-oxadiazole oxides, furoxans or furazan oxides, and whereas the above constitution has been proved to be correct for the '*o*-dinitroso' compounds, it appears probable that only the '*p*-dinitroso' compounds have the constitution of 'quinone-dioxime peroxides,' ascribed by Forster and Fierz to the whole class.

Tolu-2: 3-iso-oxadiazole oxide, tolu-furoxan,



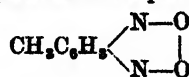
tolufurazon oxide, CH₃C₆H₄, from 3-

nitro-2-diazo-toluene-imide by the action of heat. Leaflets, m.p. 60° (Zincke, J. pr. Chem. 1896, [2] 53, 340; Zincke and Schwarz, Ann. 1899, 307, 28). The corresponding dioxime melts at 140° (decomp.) and the iso-oxadiazole or

furazan, CH₃C₆H₄, at 44° (Zincke, and

Schwarz). The 4(?)*-nitro-derivative* forms brown crystals, m.p. 162°; the 5-nitro-derivative, yellow plates, m.p. 70°; the 4:6(?)*-dinitro-derivative*, yellow needles, m.p. 122°–123° (Zincke and Drost, Ann. 1900, 313, 299).

Tolu-2: 5-quinonedioximeperoxide



by oxidation of 2:5-toluquinonedioxime with alkaline potassium ferriyanide (Nietzki and Guitermann, Ber. 1888, 21, 432; Mehne, *ibid.* 21, 734). Yellow crystals, volatile with steam, m.p. 133° (N. and G.) or 144° with slight detonation (M.). Oxidation with nitric acid yields 2:5-dinitrotoluene, whilst treatment with hydroxylamine regenerates the dioxime. Its 4-chloro-derivative is a lemon-yellow powder, m.p. 163°–165° (Kehrmann, Silva and Keleti, Ber. 1915, 48, 2029).

Tolu-3: 4-iso-oxadiazole oxide, m.p. 96°–97°, is formed by heating the corresponding nitro-diazoimide (Zincke, J. pr. Chem. 1896, [2] 53, 340), or by the oxidation of *m*-nitro-*p*-toluidine or *p*-nitro-*m*-toluidine with alkaline sodium hypochlorite (Green and Rowe). The corresponding dioxime, yellowish-brown needles, melts at 127°–128°, and the iso-oxadiazole or furazan, long white needles, melts at 37° (Zincke and Schwarz, Ann. 1899, 307, 28); the latter compound is also formed by the oxidation of *m*-nitrosoaceto-*p*-toluidide with alkaline sodium hypochlorite (Green and Rowe, Chem. Soc.

Trans. 1917, 111, 612). The 2 (or 6)-*nitro-derivative*, obtained by nitrating the furoxan or the imide of *o*-nitro-*p*-toluidine and heating the product of the latter reaction in a brine-bath, forms pale yellow needles, m.p. 164° (decomp.). This nitro-compound, on nitration in presence of sulphuric acid, yields the 2 : 6-*dinitro-derivative*, silky yellow needles, m.p. 133° (decomp.). Its 5(?)*-nitro-derivative* forms yellowish-leaflets, m.p. 145° (Zincke and Drost, Ann. 1900, 313, 299).

NITRO DERIVATIVES.

When toluene is nitrated with nitric acid (D 1.475), the quantity of *o*-, *m*-, or *p*-mononitro-derivative obtained depends on the temperature, solvent, and other factors (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1908, 11, 248; Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; Bruner and Vorbrodt, Anzeiger Akad. Wiss. Cracow, 1909, 221; cf. Kohn, Monatsh. 1910, 31, 745; Fischer, Zeitsch. Elektrochem. 1910, 16, 161; Bell and Spry, J. Ind. Eng. Chem. 1921, 13, 60; Friswell, J. Soc. Chem. Ind. 1908, 27, 258; van der Arend, Verslagen. K. Akad. Wetensch. Amsterdam, 1908, 208; Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 275; Holdermann, Ber. 1906, 39, 1256). When the nitration is carried out at -30°, 0°, 30°, and 60° with nitric acid (D 1.475) the product contains 41.7 p.c., 40.9 p.c., 39.9 p.c., and 38.5 p.c. respectively, of *p*-nitrotoluene, 55.6 p.c., 56 p.c., 56.9 p.c., and 57.5 p.c. respectively, of *o*-nitrotoluene, and 2.7 p.c., 3.1 p.c., 3.2 p.c., and 4.0 p.c. respectively, of *m*-nitrotoluene (Holleman), thus showing that the percentage of *p*-nitrotoluene decreases with rise of temperature, whilst that of the *o*- and *m*-nitrotoluenes increases, the last being always present only in small quantity. When a mixture of pure nitric acid and acetic anhydride is added to toluene at 30° a violent reaction sets in and the product contains 57.7 p.c. *o*-, 4.4 p.c. *m*-, and 37.3 p.c. *p*-nitrotoluene (Holleman, Vermeulen and De Mooy).

Toluene is readily nitrated in the cold with nitric acid of specific gravity not less than 1.5. In the manufacture of nitrotoluene 1 part of toluene is poured into 1½ parts of nitric acid (D 1.5), the temperature not exceeding 15°. By this means the *o*-derivative is readily formed and is isolated by fractionating the oil which is formed when the nitration mixture, after standing for 10 hours, is poured into water. Commercial nitrotoluene usually contains about 60 p.c. *ortho*-, 2 p.c. *meta*-, and 38 p.c. *para*-nitrotoluene; this mixture has a specific gravity of 1.167, and distils between 220°-240°.

o- and *p*-Nitrotoluene may be separated by treating the crude nitrotoluene with sulphonating agents, whereby the *o*-derivative is sulphonated, and the *p*-isomeride remains unchanged (Lange, Eng. Pat. 1407 of 1890), or by fractional reduction by means of sulphides or hydrosulphides, particularly with Le Blanc soda residues (Clayton Aniline Co., Fr. Pat. 255957; D. R. P. 92991 of 1896). *o*-Nitrotoluene may also be separated from its isomerides by heating with salts of arsenious acid, and the *o*-nitrotoluene, which is unaltered by this treatment, is isolated by treatment with acid, steam distillation, &c. (Loeser, D. R. P. 78002 of 1894; J. pr. Chem.

1894, [2] 50, 567). *o*- and *p*-Nitrotoluenes may also be separated by fractional distillation at a pressure of 20 mm. (Molinari, Atti Congr. Nar. Chim. Ind., 1924, 402; Chem. Soc. Abstr. 1925, 128, i. 380).

For the estimation of nitrotoluenes by means of stannous chloride and titanous chloride, see Colver and Prideaux (J. Soc. Chem. Ind. 1917, 36, 480, 856) and Knecht (*ibid.* 1917, 36, 694).

o-Nitrotoluene; by nitration of toluene (Glenard and Boudault, Compt. rend. 1844, 19, 505; Hofmann and Muspratt, Ann. 1845, 53, 221; Kekulé, Zeit. f. Chem. 1867 [2] 3, 225; Rosenstiehl, Ann. Chim. 1872, [4] 27, 433); by elimination of the amino-group from 2-nitro-*p*-toluidine and nitrated *m*-toluidine (Beilstein and Kuhlberg, Ann. 1870, 155, 1; 1871, 188, 348). When freshly distilled *o*-nitrotoluene is cooled rapidly to -20°, it solidifies sometimes to the labile α -modification, m.p. -10.56°, and sometimes to the stable β -form, m.p. -4.14°. The latter may also be prepared by cooling the liquid to -50° or -60°, when the α -form separates first, but changes rapidly into the β -form. Superheating of the vapours during distillation also favours the formation of the latter modification (Ostromisslensky, Zeitsch. physikal. Chem. 1907, 57, 341; cf. Walker and Spencer, Chem. Soc. Trans. 1904, 85, 1109). According to Knoevenagel (Ber. 1907, 40, 508) the α -form melts at -9.4° and the β -form at -3.6° (cf. Streng, Ber. 1891, 24, 1987, and Schneider, Zeitsch. physikal. Chem. 1896, 19, 157). It is possible to purify *o*-nitrotoluene by cooling the crude product to temperatures between -4° and -10°, and removing the liquid portion by means of the centrifuge when about half has crystallised (M. L. B., D. R. P. 158219 of 1903; Fr. Pat. 350200 of 1904).

Pure *o*-nitrotoluene is a clear liquid, solidifying at -10.56° (see above), b.p. 218° (Spreng, Ber. 1891, 24, 1987) or 225.7° (corr.) (Perkin, Chem. Soc. Trans. 1896, 69, 1250) or 220.4°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 624); D_4^{15} 1.1742, D_{15}^{15} 1.1643, D_{25}^{25} 1.1572 (Perkin), D_{15}^{15} 1.168 (Spreng). Refractive index, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218); absorption spectrum, Spreng (Rec. trav. chim. 1897, 16, 1); magnetic rotatory power, Perkin (*loc.*); dielectric constant, Turner (Zeitsch. physikal. Chem. 1901, 35, 421); n_D^{21} 1.5462, $n_D^{21.5}$ 1.5271 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1).

When oxidised with nitric acid or chromic acid in the cold it yields *o*-nitro-benzaldehyde (Lauth, Bull. Soc. chim. 1904, (3) 31, 133), whilst treatment with potassium permanganate or long boiling with alkaline potassium ferricyanide yields *o*-nitrobenzoic acid. The extent to which manganese dioxide and sulphuric acid oxidise *o*-nitrotoluene depends upon the concentration of the acid. When heated in an autoclave with 2 parts of finely powdered manganese dioxide and 10 parts of sulphuric acid (D 1.36-1.38) at 140°-105° for 2-3 hours at a pressure not exceeding 10 atmospheres, the product is chiefly *o*-nitrobenzaldehyde, whilst with sulphuric acid (D 1.68-1.71) at 135°-145° *o*-nitrobenzoic acid is the main product (B. A. S. F., D. R. P. 179559 of 1899).

The former product is also formed when the oxidation is effected by means of cerium dioxide

and sulphuric acid (60-65 p.c.) at 80°-85° (M. L. B., D. R. P. 174238 of 1903). When oxidised electrolytically *o*-nitrotoluene yields chiefly *o*-nitrobenzyl alcohol (Pierron, Bull. Soc. chim. 1901, [3] 25, 852; Fichter and Bonhöte, Helv. Chim. Acta. 1920, 3, 395). When treated with bromine at 170° *o*-nitrotoluene is converted into 3 : 4-dibromo-2-(or 6)-aminobenzoic acid (Wachendorff, Ann. 1877, 185, 281; Greiff, Ber. 1880, 13, 288), but with bromine in the presence of iron 4-bromo-2-nitrotoluene is formed (Gluud, Ber. 1915, 48, 432). It forms a compound with chromyl chloride which on treatment with water regenerates *o*-nitrotoluene and yields a little *o*-nitrobenzaldehyde (Richter, Ber. 1886, 19, 1062). On chlorination it yields *o*-nitrobenzyl chloride, *o*-chlorotoluene, and *o*-chlorobenzyl chloride and other products (Kalle & Co., Eng. Pat. 11260 of 1897; D. R. P. 110010 of 1898).

On long keeping in contact with alcoholic or aqueous potassium hydroxide, anthranilic acid, together with the corresponding azo- and azoxybenzoic acids are formed (Preuss and Binz, Zeit. für angew. Chem. 1900, 14, 385; B. A. S. F., Eng. Pat. 18319 of 1899; Fr. Pat. 292468; D. R. P. 114839 of 1899). With nitrous esters and sodium ethoxide it yields *o*-nitrobenzaldehyde (M. L. B., D. R. P. 107095 of 1898; Fr., Pat. 290643 of 1899). When reduced by heating with iron or zinc and sodium hydroxide at 100°, it yields *o*-azoxytoluene, but when acid is added to the product, toluene-*o*-azobenzoic acid is produced. The sulphonation product of *o*-nitrotoluene differs from that of *p*-nitrotoluene in giving no red colour when boiled with alkalis (Reverdin and de la Harpe, Bull. Soc. chim. 1888, [2] 50, 44).

m-Nitrotoluene; in small quantity by nitration of toluene (cf. Holleman and co-workers under *o*-nitrotoluene; Monnet, Reverdin and Nölting, Ber. 1879, 12, 443; Nölting and Witt, Ber. 1885, 18, 1337); from nitrated *o*- or *p*-toluidine (Beilstein and Kuhlberg, Ann. 1878, 158, 335; Vanino, Präparative Chemie, 1923, vol. ii. p. 451); or from 3-nitro-*p*-toluidine (Buchka, Ber. 1889, 22, 829) by the diazo-reaction. M.p. 16°, b.p. 230°-231° (cf. Neuback, Zeitsch. physikal. Chem. 1887, 1, 658), D_{20}^{20} 1.168, n_D^{20} 1.5470, n_D^{25} 1.5275 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). It is oxidised readily to *m*-nitrobenzoic acid by chromic acid mixture and slowly by alkaline potassium ferricyanide. When oxidised electrolytically it yields chiefly *m*-nitrobenzaldehyde (Pierron, Bull. Soc. chim. 1901, [3] 25, 852) and, in sulphuric acid solution, 5-amino-*o*-cresol (Gattermann, Ber. 1894, 27, 1930). With bromine at 140° it yields *m*-nitrobenzyl bromide and *m*-nitrobenzylidene bromide (Wachendorff, Ann. 1877, 185, 266; Ber. 1876, 9, 1345). Stannous chloride and aqueous hydrochloric acid reduce it to pure *m*-toluidine, while zinc dust and aqueous hydrochloric acid yield chloro-*m*-toluidine also. *m*-Nitrotoluene is readily reduced by the method of Elbs and Kopp (Zeitsch. Elektrochem. 1898, 5, 108), forming

a yield of 91 p.c.; further it gives *m*-hydrazotoluene (Rohde, *ibid.* 1899, 5, 332). When *m*-nitrotoluene is nitrated with nitric and sulphuric acids at 80°, 3 : 4-dinitrotoluene, together with smaller amounts of 2 : 3- and 2 : 6-dinitrotoluenes, are formed, the separation of the three isomerides being effected

by fractionation *in vacuo* and freezing the distillate (Holleman and Sirks, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 280; Sirks, Rec. trav. chim. 1907, 27, 208; cf. Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 276).

p-Nitrotoluene (see also under *o*-nitrotoluene); by nitration of toluene (Rosenstiehl, Zeitsch. f. Chem. 1869, (2) 5, 190; cf. Jaworsky, *ibid.* 1865, 223); 1 part of toluene is poured into 3-4 parts of nitric acid (D 1.5) and heated to 30°. The yellow oil produced consists chiefly of *p*-nitrotoluene, which crystallises on cooling the fraction boiling above 225°.

Large thick rhombic crystals, m.p. 51.6°-51.9° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 60), 51.4° (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; cf. van der Arend, *ibid.* 1909, 28, 408), or 54° (Schiff, Ann. 1884, 223, 261; Gazz. chim. ital. 1884, 14, 181). The increase in melting-point with increase of pressure has been studied by Puschin (Chem. Soc. Trans. 1924, 125, 2628). B.p. 237.7°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 624); D_{20}^{20} 1.1392, D_{25}^{25} 1.1358 (Perkin, Chem. Soc. Trans. 1896, 69, 1239); magnetic rotatory power at 54.3° 10.17 (Perkin); n_D^{20} 1.5554, n_D^{25} 1.5346 (Holleman, Vermeulen and de Mooy). It is much less volatile with steam than the *o*-nitro-derivative. Chlorine in presence of aluminium chloride or iodine yields *p*-nitrobenzyl chloride and *p*-nitrobenzoic acid (Zimmermann and Müller, Ber. 1885, 18, 996). By the electrolysis of *p*-nitrotoluene in 5-10 parts of sulphuric acid, amino-nitro-*o*-benzyltoluene is obtained (Gattermann, Ber. 1893, 26, 1852; cf. Gattermann and Koppert, *ibid.* 2811). When heated with bromine at 140°, it yields *p*-nitrobenzyl bromide and *p*-nitrobenzylidene bromide (Wachendorff, Ann. 1877, 185, 266). It is oxidised by alkaline potassium ferricyanide to *p*-nitrobenzoic acid (Noyes, Ber. 1883, 16, 52), whilst electrolytic oxidation in acetic-sulphuric acid yields *p*-nitrobenzyl alcohol (Elbs, Zeitsch. Elektrochem. 1896, 2, 522), *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid (Fichter and Bonhöte, Helv. Chim. Acta. 1920, 3, 395). It is reduced by iron and dilute hydrochloric acid to *p*-toluidine, whilst zinc dust and dilute hydrochloric acid yield a chlorinated toluidine. Reduction in alkaline solution yields *p*-azotoluene, and in presence of formaldehyde and hydrochloric acid *p*-dimethyl-toluidine and dimethylene-di-toluidine are produced (Löb, Zeitsch. Elektrochem. 1898, 4, 428). It condenses with ethyl oxalate in presence of sodium ethoxide yielding *p*-nitrophenylpyruvic acid (Reissert, Ber. 1897, 30, 1047).

Zinc dust and sodium hydroxide yield azotoluene, m.p. 144°, two azoxy-compounds, m.p. 75° and 70° respectively, and a hydrazo-compound, m.p. 126° (Janowski and Reimann, Ber. 1889, 22, 40). For the action of sodium and caustic alkalis on *p*-nitrotoluene, see Bender and Schultz (Ber. 1886, 19, 3234), Schmidt (*ibid.* 1899, 32, 2911), Klinger (*ibid.* 1883, 16, 941), Fischer and Hepp (*ibid.* 1893, 26, 2233), Green and collaborators (*ibid.* 1897, 30, 3097; 31, 1078; Chem. Soc. Trans. 1904, 85, 1424, 1429; 1907, 91, 2076; *ibid.* 1908, 93, 1771). By heating with a solution of sulphuric acid in

in sulphuric acid it is converted into *p*-amino-benzaldehyde (Geigy & Co., D. R. P. 86874 of 1895). When treated with amyl nitrite in presence of sodium ethoxide the oxime of *p*-nitrobenzaldehyde is formed (Angeli and Angelico, Atti R. Accad. Lincei. 1900, [5] 8, ii. 32; Gazz. chim. ital. 1900, 31, i, 27; cf. M. L. B., Fr. Pat. 290643 of 1899; D. R. P. 107095 of 1898). For estimation of *p*-nitrotoluene, see Reverdin and de la Harpe (Zeit. f. analyt. Chem. 1890, 29, 215), and for volumetric estimation of *p*-nitrotoluene in crude nitrotoluene, see Glas-mann (Ber. 1903, 36, 4260; J. Russ. Phys. Chem. Soc. 1904, 36, 312).

Normal- ω -nitrotoluene, phenylnitromethane, $C_6H_5CH_2(NO_2)$; together with phthalic anhydride by decomposing a dilute aqueous solution of the disodium derivative of nitrobenzylidene-phthalide with 12 mols. of very dilute acetic acid; by boiling hydroxynitrobenzylidiphenyl-maleide with water (Cohn, Ber. 1891, 24, 3867); from toluene and nitric acid (D. 1.12) by heating for 48 hours at 100° in a sealed tube (Konowalow, Ber. 1895, 28, 1861; J. Russ. Phys. Chem. Soc. 1899, 31, 254); from benzyl chloride (Holleman, Rec. trav. chim. 1894, 13, 405) or benzyl iodide (Hantzsch and Schultze, Ber. 1896, 29, 700) and silver nitrite, or preferably mercurous nitrite (Neogi and Adhichary, Zeitsch. anorg. Chem. 1911, 40, 270); together with other products by the interaction of *iso*-nitromethane and diazo-benzene in alkaline solution (Bamberger, Schmidt and Levinstein, Ber. 1900, 33, 2053); together with phthalic anhydride by dissolving nitroxylyl-idene-phthalide in sodium hydroxide and saturating the solution with oxalic acid (Goldberg, Ber. 1900, 33, 2818), and by other methods (van Raalte, Rec. trav. chim. 1899, 18, 383).

Liquid, which does not solidify in a freezing mixture, b.p. 225°–227°, decomposing into water, nitric oxide and benzaldehyde, or b.p. 158°–160°/35 mm. with slight decomposition (Holleman); D_4^{20} 1.1756, D_4^{30} 1.1598; molecular refractive power 36.61, n_D^{20} 1.53230.

On treatment with zinc dust and dilute sulphuric acid it yields phenylamine. With fuming hydrochloric acid at 150° it is decomposed into hydroxylamine and benzoic acid (Gabriel and Koppe, Ber. 1886, 19, 1145). With alkalis it is converted into the salt of *iso*-phenylnitromethane, from which phenylnitromethane is obtained by treatment with carbon dioxide, or *iso*-phenylnitromethane by treatment with cold dilute hydrochloric acid. It is unaffected by phenyl *iso*-cyanate (Hantzsch and Schultze, Ber. 1896, 29, 2254). Its *o*-, *m*-, and *p*-nitro-derivatives melt at 72°, 94°, and 90° respectively (Holleman, Rec. trav. chim. 1896, 15, 356, 365; *ibid.* 1895, 14, 123; Hantzsch and Veit, Ber. 1899, 32, 621).

Phenyl-iso-nitromethane, $C_6H_5CH(OH)NO$; by the action of dilute hydrochloric acid on the potassium salt of phenylnitromethane (Hantzsch and Schultze, Ber. 1896, 29, 700); together with other products by oxidising benzaldoxime with Caro's acid (Bamberger, Ber. 1900, 33, 1781). It crystallises from a mixture of absolute ether and ligroin and melts at 84° when heated quickly (Hantzsch, Ber. 1896, 29, 2251). It is readily soluble in soda solution, and in contrast

to the indifferent phenylnitromethane, when treated with ammonia in presence of water-free solvents it yields the ammonium salt. It also readily reacts with phenyl *iso*-cyanate and phosphorus pentachloride (Hantzsch and Veit, Ber. 1899, 32, 620). On warming with ether or alcohol, or on keeping with hydrochloric acid, it is converted into the normal phenylnitromethane. On reduction with sodium amalgam or zinc dust in alkaline solution it yields benzaldoxime. When the sodium salt is treated with acetyl chloride acetylbenzhydroxamic acid is formed (van Raalte, *ibid.* 1899, 18, 383). When treated with benzoyl chloride, dibenzhydroxamic acid, m.p. 161°, is produced, and with *p*-nitrobenzoyl chloride it yields bis-*p*-nitrobenzoylbenzhydroxamic acid and *p*-nitrobenzoylbenzhydroxamic acid (Holleman, Rec. trav. chim. 1896, 15, 356, 365), whilst its sodium salt on treatment in aqueous solution with hydrochloric acid yields benzhydroxamic acid (Bamberger and Rust, Ber. 1902, 35, 45).

ω -Dinitrotoluene, phenyldinitromethane, large white prisms, m.p. 79° (Ponzio, Gazz. chim. ital. 1901, 31, 133; 1908, 38, 417; Ponzio and Charrier, Atti R. Accad. Sci. Torino, 1908, 43, 475).

DINITROTOLUENES.

Commercial dinitrotoluene is chiefly a mixture of the α -, β -, and γ -dinitrotoluenes, and forms a cake of yellow crystals, m.p. 66°–68°, b.p. about 300° (partial decomp.). The 2:4-dinitro-compound is present in the greatest proportion in the dinitrotoluene used in the explosive industry.

2:3-Dinitrotoluene; by heating 2:3-dinitro-*p*-toluic acid with 5 p.c. hydrochloric acid for 6 hours at 265° (Rozánski, Ber. 1889, 22, 2681); from 3-nitro-*o*-toluidine by replacing the amino-group by a nitro-group (Grell, Ber. 1895, 28, 2565). It is best obtained by nitrating aceto-*o*-toluidide with nitric acid in presence of acetic acid and treating the mixture of 3- and 5-nitro-aceto-*o*-toluidides with hydrochloric acid, the separation of the isomeric amines being accomplished by diluting the acid solution largely with water when the very feebly basic 3-nitro-*o*-toluidine is precipitated. The latter is converted into 3-nitro-2-nitrosotoluene, which is then transformed into 2:3-dinitrotoluene (Meisenheimer and Hesse, Ber. 1919, 52, 1161); also from 5:6-dinitro-*m*-toluidine by the diazo-reaction (Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 531). M.p. 61° (M. and H.) or 63° (Rozánski).

(a) 2:4-Dinitrotoluene; by nitration of toluene (Deville, Ann. 1842, 44, 307; Cahours, Compt. rend. 1847, 24, 555; Noetting and Witt, Ber. 1885, 18, 1336; Beilstein and Kuhlberg, Ann. 1870, 155, 13; Limpricht, Ber. 1885, 18, 1402), and of *o*- and *p*-nitrotoluene; by boiling 2:4-toluylenediamine with sodium peroxide solution (O. Fischer and Trost, Ber. 1893, 26, 3085); from dinitrotoluidine by elimination of the amino-group (Staedel, Ann. 1898, 259, 220). Long monoclinic needles, m.p. 70.5° (Deville), or 69.21°–69.57° (Milla, Phil. Mag. 1882, [5] 14, 27), or 69.9°–70.2° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 160). When treated for a long time with fuming nitric acid it yields 2:4-dinitrobenzoic acid. Partial reduction with ammonium sulphide in the cold yields 2-nitro-*p*-toluidine, whilst

at higher temperatures 4-nitro-*o*-toluidine is also formed (Graeff, Ann. 1885, 229, 343; Limpricht, Ber. 1885, 18, 1400). Alcoholic stannous chloride, on the other hand, yields 4-nitro-*o*-toluidine (Anschütz and Heussler, Ber. 1886, 19, 2161). When reduced completely it yields *m*-toluylenediamine (Baeyer, Ber. 1874, 7, 1638). On electrolytic oxidation it yields 2:4-dinitrobenzoic acid (Sachs and Kempf, Ber. 1902, 35, 2704). It does not react with chromium oxychloride (Richter, Ber. 1886, 19, 1062). It condenses with benzaldehyde in presence of piperidine to form stilbene derivatives (Thiele and Escales, Ber. 1901, 34, 2842); with dimethylaminobenzaldehyde to form 2':4'-dinitro-4-dimethylaminostilbene (Sachs and Steinert, Ber. 1904, 37, 1733); with nitrosodimethylamine in presence of sodium carbonate to form 2:4-dinitrobenzaldehyde-*p*-dimethylaminoanil (Sachs and Kempf, *ibid.* 1902, 35, 1224).

(B) 2:5-Dinitrotoluene; from 5-nitro-*o*-toluidine by the diazo-reaction (Grell, Ber. 1895, 28, 2565); by the action of nitrogen peroxide on toluquinonediimine in ethereal solution (Oliveri and Tortorici, Gazz. chim. ital. 1900, 30, i, 534); by treating '*p*-dinitrosotoluene' with cold fuming nitric acid (Nietzki and Guitermann, Ber. 1888, 21, 433); readily from 5-nitro-2-nitrosotoluene by oxidation with nitric acid (Meisenheimer and Hesse, Ber. 1919, 52, 1161); by heating 2:5-dinitro-*p*-toluic acid with 3 parts of 5 p.c. hydrochloric acid for 6 hours at 250° (Rozanski, Ber. 1889, 22, 2679). It appears to occur also among the products of the nitration of toluene (Limpricht, Ber. 1885, 18, 1402).

Needles or large wedge-shaped crystals, m.p. 50°-51° (Meisenheimer and Hesse), 52-5° (Rozanski) or 48° (Nietzki and Guitermann). It is reduced by alcoholic ammonium sulphide to 6-nitro-*m*-toluidine (Limpricht). On reduction with stannous chloride in presence of alcoholic hydrochloric acid it yields a mixture (m.p. 97°) of monoamines, consisting of 62 p.c. of 5-nitro-*o*-toluidine and 38 p.c. of 6-nitro-*m*-toluidine, a little 2:5-diaminotoluene being formed also (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1053).

2:6-Dinitrotoluene; from 2:6-dinitro-*p*-toluidine by the diazo-reaction (Staedel, Ann. 1883, 217, 206; Rosenstiehl, Ann. Chim. 1872, [4] 27, 470; Cunerth, Ann. 1874, 172, 222; Claus and Becker, Ber. 1883, 16, 1597; Holleman and Boeseken, Rec. trav. chim. 1897, 16, 427); together with other products during the manufacture of trinitrotoluene (Molinari and Giua, Zeit. ges. Schiess. Sprengstoffw. 1914, 9, 239; cf. Haeussermann and Grell, Ber. 1894, 27, 2209). Glistening needles, m.p. 60°-61° (Staedel), or 65-6° (H. and G.). On reduction with sulphuretted hydrogen in alcoholic ammonia a mixture, m.p. 66°, of 6-nitro-2-amino-*m*-cresol and 6-nitro-*o*-toluidine is formed, the former being produced by the action of the boiling hydrochloric acid (used to extract the amine) on the intermediate 6-nitro-*o*-tolylhydroxylamine (Cohen and Marshall, Chem. Soc. Trans. 1904, 85, 527). It condenses with dimethylaminobenzaldehyde to form a condensation product, bluish-violet lles (Sachs and Steinert, Ber. 1904, 37, 1745).

(γ) 3:4-Dinitrotoluene; together with 2:3-, 1:5-, and 3:6-dinitrotoluene by nitration of

m-nitrotoluene, and is readily separated from the mixture by fractional distillation *in vacuo* and freezing the distillate (Beilstein and Kuhlberg, Ann. 1870, 155, 25; Haeussermann and Grell, Ber. 1894, 27, 2209; Holleman and Sirks, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 280; Sirks, Rec. trav. chim. 1907, 27, 208); from 3:4- or 4:5-dinitro-*o*-toluidine by elimination of the amino-group (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1139); from 5:6-dinitro-*m*-toluidine in a similar manner (Brady, Day and Rolt, *ibid.* 1922, 121, 531); from 3-nitro-*p*-toluidine by the diazo-reaction (Haeussermann and Grell, *l.c.*); conveniently by oxidising 3-nitro-*p*-toluidine by Caro's acid to 3-nitro-4-nitrosotoluene and completing the oxidation of the latter with nitric acid (Meisenheimer and Hesse, Ber. 1919, 52, 1161). Long needles, m.p. 59°-60° (M. and H.), or 61° (H. and G.). On reduction with stannous chloride in presence of absolute alcoholic hydrochloric acid, it yields a eutectic mixture (m.p. 70°) of 4-nitro-*m*-toluidine and 3-nitro-*p*-toluidine together with a little diamine (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1053).

3:5-Dinitrotoluene; from 3:5-dinitro-*o*- or *p*-toluidine by elimination of the amino-group (Staedel, Ann. 1883, 217, 189; Ber. 1881, 14, 909; Hübner, Ann. 1884, 222, 74; Nevile and Winther, Ber. 1882, 15, 2984; Chem. Soc. Trans. 1882, 41, 416; Hönig, Ber. 1887, 20, 2418; Cohen and McCandlish, Chem. Soc. Trans. 1905, 87, 1270; Brady, Day and Rolt, *ibid.* 1922, 121, 528). It is best prepared by adding aceto-*p*-toluidide slowly to 8 times its weight of nitric acid (D. 1.79) below 0°, purifying the dinitro-derivative by extracting with hot benzene, hydrolysing with concentrated sulphuric acid (below 90°), diazotising the resulting base at -10° in concentrated sulphuric acid in presence of alcohol, warming and purifying the dinitrotoluene by extraction with alcohol (Kreman, Hönigsberg and Mauermann, Monatsch. 1923, 44, 65). Monoclinic needles or prisms readily volatile with steam, m.p. 92°-93°.

TRINITROTOLUENE.

The following method gives satisfactory results for the preparation of trinitrotoluene from toluene of about 99 p.c. purity. 50 grms. of toluene are added gradually with constant stirring to a mixture of 73.4 grms. of nitric acid (D. 1.42), and 146.8 grms. of sulphuric acid (D. 1.84), the temperature not being allowed to rise above 30°. The reaction is allowed to continue for half an hour after the addition of the toluene, and, after keeping, the spent acid is drawn off. The crude product (80-83 grms., consisting of about 60 p.c. of mono- and 40 p.c. of dinitrotoluene) is dissolved in 109.2 grms. of sulphuric acid (D. 1.84), the solution is heated to 50°, and a mixture of 54.6 grms. each of nitric acid (D. 1.5) and sulphuric acid (D. 1.84) is added gradually during a period of at least 1 hour, the temperature not exceeding 100°. The mixture is then heated for 2 hours at 90°-100°, after which it is cooled to 90°, and 145.6 grms. of oleum (15 p.c.) are added slowly followed by a mixture of 72.8 grms. each of oleum (15 p.c.) and nitric acid (D. 1.5). The addition of the acid takes 2 hours, and the temperature is not allowed

to exceed 115°. The mixture is then heated at 90°–117° for 2 hours. After keeping for at least 8 hours, the spent acid is drawn off, and the crude trinitrotoluene crushed and washed first with cold water and then several times in the molten state with hot water. A yield of 75 p.c. is obtained and the product melts at 78°–80°, a further yield of 8.5 p.c. (m.p. 69°–75°) can be recovered from the spent acid. If the product be purified by crystallising from, or washed with, a mixture of 9 volumes of 95 p.c. alcohol and 1 volume of benzene the yield is 69 p.c. (m.p. 79°–81°) and 7.5 p.c. (m.p. 78°–81°) (Hoffman, U.S. Bureau of Mines, Met. and Chem. Eng. 1916, 14, 467; cf. Humphrey, J. Ind. Eng. Chem. 1916, 8, 998; Langenscheidt, Z. ges., Schiess. u. Sprengstoffw. 1912, 7, 425). For the manufacture of TNT (trinitrotoluene) and its intermediate products, see Technical Methods of Explosives Supply, 1915–1918, No. 2, Ministry of Munitions and Department of Scientific and Industrial Research. An account of the minimum amount of water required to precipitate trinitrotoluene from its acid mother liquor is given by McHutchison and Wright (J. Soc. Chem. Ind. 1915, 34, 781).

For freezing-point solubility diagram of TNT and picric acid, see Taylor and Rinkenbach (J. Ind. Eng. Chem. 1923, 15, 795).

The specific heats of trinitrotoluene, tetryl and picric acid have been determined by Taylor and Rinkenbach (J. Amer. Chem. Soc. 1924, 46, 1504).

For quantitative experiments on the trinitration of toluene, see Gibson, Duckham and Fairbairn (Chem. Soc. Trans. 1922, 121, 282).

A review of the preparation of the six isomeric trinitrotoluenes up to date is given by Brunswig (Zeitsch. angew. Chem. 1923, 36, 75).

(a) 2:4:6-Trinitrotoluene; by prolonged boiling of toluene with nitric and sulphuric acids (Wilbrand, Ann. 1863, 128, 178) or from α - or β -dinitrotoluene in a similar manner; by treating 1 part of 2:4-dinitrotoluene dissolved in 4 parts of sulphuric acid (95–96 p.c. H_2SO_4) with 1½ parts of nitric acid (90–92 p.c. HNO_3), the mixture being heated gradually to 90°–95° with agitation for about 4–5 hours (Haeussermann, Zeitsch. angew. Chem. 1891, 5, 661); by boiling trinitrophenylacetic acid with water or alcohol (Jackson and Phinney, Ber. 1895, 28, 3067; Amer. Chem. J. 1899, 21, 431).

Pseudo-rhombic crystals, belonging to the prismatic class of the monoclinic system (Artini, Atti R. Accad. Lincei, 1915, [v.] 24, ii. 274; cf. Friedländer, Zeitsch. Kryst. Min. 1879, 3, 168), m.p. 80.52° (Mills, Phil. Mag. 1882, [5] 14, 27), 80.5° (Brunswig, Zeitsch. angew. Chem. 1923, 36, 75), 80.6° (Will, Ber. 1914, 47, 704), or 80.8°–80.85° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 60). Electrical conductivity in liquid ammonia (Franklin and Kraus, Amer. Chem. J. 1900, 23, 294); cryoscopic behaviour (Bruni and Berti, Atti R. Accad. Lincei. 1900, [v.] 9, i. 274; Gazz. chim. ital. 1900, 30, 76); behaviour with methyl alcohol, &c. (Hantzsch and Kissel, Ber. 1899, 32, 3140); solubility in organic solvents (Taylor and Rinkenbach, J. Amer. Chem. Soc. 1923, 45, 44). It forms additive compounds with hydrocarbons and with aniline (Hepp, Ann. 1882, 215, 365). On reduction with alcoholic ammonium sulphide it yields 2:6-dinitro-*p*-

toluidine (Tiemann, Ber. 1869, 3, 218), whilst in hydrochloric acid solution in presence of cupric chloride it is reduced at a copper cathode to 2:6-dinitro-*p*-toluidine and 4:6-dinitro-*o*-toluidine (Brand and Eisenmenger, J. pr. Chem. 1913, ii. 87, 487). On oxidation with nitric acid at 180° it yields 1:3:5-trinitrobenzene with evolution of carbon dioxide (Claus and Becker, Ber. 1883, 16, 1597). With acetone and ammonia it gives a deep red coloration, and is not so sensitive to alkalis as the β - and γ -compounds. In alkaline alcoholic solutions it forms coloured salts which, under the simultaneous action of oxidising agents, yield a hexanitrodiphenylethane (m.p. 212°) (Will, l.c.; Giua, Atti R. Accad. Lincei. 1914, [v.] 23, ii. 484; Gazz. chim. ital. 1915, 45, 345). When exposed to light 2:4:6-trinitrotoluene forms two substances of the formula $C_7H_5O_6N_3$ (Schultz and Ganguly, Ber. 1925, 58, 702; see also Wichert and Donat, Zeitsch. ges. Schiess-Sprengstoffw. 1925, 20, 69).

2:4:6-Trinitrotoluene condenses with diazomethane (Heinke, Ber. 1894, 31, 1399); with nitroso-dimethylaniline to form the compound $C_6H_2(NO)_3 \cdot CH \cdot N \cdot C_6H_4 \cdot N(CH_3)_2$ (Sachs and Everding, Ber. 1903, 36, 959); it combines with dimethylaminobenzaldehyde (Sachs and Steinert, *ibid.* 1904, 37, 1733); and with α - and β -naphthylamine it yields compounds which melt at 113.5° and 141.5° respectively (Sudborough, Chem. Soc. Trans. 1901, 79, 522).

(β) 2:3:4-Trinitrotoluene; together with 3:4:6-trinitrotoluene by nitration of *m*-nitrotoluene (Hepp, Ann. 1882, 215, 366); by nitration of 2:3-dinitrotoluene, and to the extent of 17 parts together with 83 parts of 3:4:6-trinitrotoluene by the nitration of 3:4-dinitrotoluene (Brady; see also Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 282); by oxidation of 2:3-dinitro-*p*-toluidine in 80 p.c. sulphuric acid with Caro's acid, followed by treatment of the nitroso-derivative with nitric acid (Scott and Robinson, Chem. Soc. Trans. 1922, 121, 846); from 3:4-dinitro-*o*-toluidine in a similar manner (Brady and Williams, *ibid.* 1920, 117, 1140). Slender leaflets or flaky needles from alcohol or thick trimetric plates from acetone, m.p. 112°. On oxidation with chromic acid mixture it yields 2:3:4-trinitrobenzoic acid, m.p. 202° (Giua; Hepp; Brunswig). With acetone and ammonia it yields a greenish-yellow coloration (Will; Giua).

2:3:4-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution yields 4-nitro-1-hydroxy-5 (or 7)-methyl-1:2:3-benzotriazole, pale yellow hexagonal prisms + H_2O , m.p. 205° (decomp.) when anhydrous. On methylation this forms exclusively the *O*-ether, brownish-yellow needles, m.p. 152°, and on acetylation an acetyl-derivative, colourless monoclinic prisms, m.p. 182° (decomp.), is formed (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 894; Brady and Day, *ibid.* 1923, 123, 2258). Converted by aqueous sodium sulphite into sodium 2:4-dinitrotoluene 3-sulphonate (Brady, Hewetson and Klein, Chem. Soc. Trans. 1924, 125, 2400).

(γ) 3:4:6-Trinitrotoluene; (see above); in a yield of 80 p.c. by adding a solution of 2 grms. of 4:5-dinitro-*o*-toluidine in 10 c.c. of 80 p.c.

sulphuric acid to Caro's acid, prepared from 10 grms. of ammonium persulphate and 7 c.c. of concentrated sulphuric acid, and pouring on to 20 grms. of crushed ice. On keeping over night and on further dilution the dinitro-nitrosotoluene separates and is oxidised by warming with 10 times its weight of nitric acid (D 1.5) (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1139); from 2:5-dinitro-*p*-toluidine in a similar manner (Scott and Robinson, *ibid.* 1922, 121, 845). Yellowish rhombohedral crystals from alcohol or rhombic plates from acetone, m.p. 104°. With alcoholic ammonia it yields 4:6-dinitro-*m*-toluidine, and with aniline, phenyl-dinitrotoluidine. With aqueous sodium sulphite it yields sodium 4:6-dinitrotoluene 3-sulphonate (Brady, Hewetson and Klein, *l.c.*). On oxidation with chromic acid mixture it yields 3:4:6-trinitrobenzoic acid, laminae, m.p. 190°–191° (decomp.) (Hepp; Giua). For the action of alkalis, aldehydes, and amines on α -, β -, and γ -trinitrotoluenes, see O'Riordan (Proc. Roy. Irish Acad. 1918, 34, 175). β - and γ -Trinitrotoluene react even with 1 p.c. sodium carbonate solution or lead oxide and alcohol with the formation of dinitrotolyl oxides. In all three cases the salts are very explosive. With acetone and ammonia it yields a blue coloration (Will, Ber. 1914, 47, 704; Giua, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 484; Gazz. chim. ital. 1915, 5, 345).

3:4:6-Trinitrotoluene when treated in boiling alcoholic solution with an excess of hydrazine hydrate yields 6-nitro-1-hydroxy-5-methyl-1:2:3-benzotriazole, yellow prisms, i.p. 194° (decomp.). The latter compound on methylation yields a mixture of the *O*-methyl ether, long, pale canary-yellow needles, m.p. 35°, and the *N*-methyl ether, canary-yellow aethery tufts, m.p. 265° (decomp.), and on acetylation an acetyl derivative, faintly pink monoclinic needles, m.p. 166° (decomp.), is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; cf. Brady and Bowman, *ibid.* 1921, 119, 894).

(ξ) 2:3:5-Trinitrotoluene; from 3:5-dinitro-*o*-toluidine. Large, slightly yellow prisms, belonging to the bi-pyramidal class of the rhombic system. It melts at 97° (Brunswick, Zeitsch. angew. Chem. 1923, 36, 75). It dissolves in acetone containing a few drops of ammonia giving a rose-red coloured solution, which changes to red, then brown, and finally black. With chromic acid it yields 2:3:5-trinitrobenzoic acid, m.p. 82° (+2H₂O) or 171° (anhydrous) (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, i. 888). With aqueous sodium sulphite it yields sodium 3:5-dinitrotoluene 2-sulphonate (Brady, Hewetson and Klein, *l.c.*).

2:3:5-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution forms nitro-1-hydroxy-4-methyl-1:2:3-benzotriazole, pale yellow prisms, m.p. 225° (decomp.). The latter on methylation yields a mixture of *O*-ether, needles, m.p. 137°, and the *N*-ether, low needles, m.p. 220° (decomp.), and on acetylation an acetyl-derivative, almost colourless cubic crystals, m.p. 142°, is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; Brady and Bowman, *ibid.* 1921, 119, 894).

(ϵ) 2:3:6-Trinitrotoluene; by direct nitra-

tion of toluene (Drew, Chem. Soc. Trans. 1920, 117, 1615); together with 2:3:4- and 3:4:6-trinitrotoluene by nitration of *m*-nitrotoluene (Marqueyrol, Koehler and Jovinet, Bull. Soc. chim. 1920, [v.] 27, 420; Drew, *l.c.*; Brady, Chem. Soc. Trans. 1922, 121, 328); in a yield of 15 p.c. together with other products by nitration of 2:3- and 2:5-dinitrotoluene (Drew); from 2:4:6-trinitrotoluene by reduction, bromination, elimination of the amino-group, and replacement of the bromine atom by an amino-group, followed by conversion of the 2:6-dinitro-*m*-toluidine into 2:3:6-trinitrotoluene via the diazo-nitrate (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339); from 3:6- or 5:6-dinitro-*o*-toluidine by treatment with Caro's acid and oxidation of the dinitro-nitroso-toluene produced (Brady and Taylor, Chem. Soc. Trans. 1920, 117, 876); from 2:6-dinitro-*m*-cresol (Drew).

Molinari and Giua (Zeitsch. ges. Schiess-Sprengstoffw. 1914, 9, 239) obtained in the manufacture of trinitrotoluene a compound, m.p. 79.5°, which they stated might be 2:3:6-trinitrotoluene, together with 3- and 4-nitrotoluene, 2:4-, 2:5-, 2:6-, 3:4-dinitrotoluenes, and 2:4:6-trinitrotoluene. Brady and Taylor, however, showed that this compound was probably a mixture of 2:3:4- and 3:4:6-trinitrotoluenes.

The formation of 2:3:6-trinitrotoluene by the direct nitration of toluene has been questioned by Giua (Gazz. chim. ital. 1921, 51, ii. 113), but Drew's contention that 2:3:4-, 2:4:5-, and 2:3:6-trinitrotoluene are formed by the nitration of *m*-nitrotoluene is further supported by Brady (*l.c.*).

Shining white needles belonging to the prismatic class of the monoclinic system, m.p. 111°. By treatment with alcoholic ammonia in a sealed tube at 110°–120° it yields 3:6-dinitro-*o*-toluidine, m.p. 151°, and a complex mixture of substances, m.p. 128°. It yields 2:3:6-trinitrobenzoic acid, m.p. 55° (+2H₂O) or 160° (anhydrous), on oxidation with chromic acid (Körner and Contardi; cf. Brunswick, *l.c.*).

(δ) 3:4:5-Trinitrotoluene; from 3:5-dinitro-*p*-toluidine. Greenish-yellow transparent prisms or plates, belonging to the prismatic class of the monoclinic system, m.p. 137.5°. With chromic acid it yields 3:4:5-trinitrobenzoic acid (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 464; 1915, [v.] 24, i. 888; cf. Brunswick, Zeitsch. angew. Chem. 1923, 36, 75). With aqueous sodium sulphite it forms sodium 3:5-dinitrotoluene 4-sulphonate (Brady, Hewetson and Klein, Chem. Soc. Trans. 1924, 125, 2400).

3:4:5-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution yields 4-nitro-1-hydroxy-6-methyl-1:2:3-benzotriazole, yellow needles, m.p. 241° (decomp.), the monohydrate of which, deep orange prisms, loses water at 90°–95°. The triazole on methylation yields exclusively the *O*-ether, yellow plates, m.p. 183°, and on acetylation an acetyl-derivative, colourless prismatic crystals, m.p. 210° (decomp.), is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; cf. Brady and Bowman, *ibid.* 1921, 119, 894).

Up to the present, the formation of higher nitro-derivatives by the nitration of toluene has

failed, for if the reaction is promoted by heat or pressure either trinitrobenzoic acid or even tetranitromethane is obtained, whilst 3:5-dinitrotoluene could not be nitrated to yield any trinitro-derivative (Will, Ber. 1914, 47, 704).

o-Nitrobenzyl chloride; together with the *p*-isomeride by nitration of benzyl chloride (Noelting, Ber. 1884, 17, 385; Kumpf, Ann. 1884, 224, 100; Ber. 1884, 17, 1073; cf. Beilstein and Geitner, Ann. 1866, 139, 337); from *o*-nitrobenzyl alcohol and phosphorus pentachloride (Geigy and Königs, Ber. 1885, 18, 2401; Gabriel and Borgmann, Ber. 1883, 16, 2066); by the action of chlorine on a mixture of *o*-nitrotoluene and sulphur at 130°–140° (Haeussermann and Beck, Ber. 1892, 25, 2445). Calcspar-like crystals, m.p. 47.9°; $n_D^{25} 1.5557$ (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). With potassium iodide it yields *o*-nitrobenzyl iodide. With stannous chloride and hydrochloric acid it is reduced to *o*-benzylene-imide (Lellmann and Stickel, Ber. 1886, 19, 1604; Thiele and Weil, Ber. 1895, 28, 1650), whilst on reduction with stannous chloride in presence of alcoholic hydrochloric acid *o*-aminobenzyl ethyl ether is obtained: By reduction with excess of stannous chloride in aqueous or ethereal solution in presence of hydrogen chloride, followed by treatment with hydrogen sulphide, *o*-diaminobenzyl sulphide is produced (Thiele and Dimroth, Ann. 1899, 305, 112, 122; Ber. 1895, 28, 914). With aluminium chloride in presence of benzene it yields *o*-nitrodiphenylmethane and other products (Freund, Monatsh. 1896, 17, 395). When reduced with sodium in methyl alcoholic solution *o*-nitrobenzyl chloride yields *o*-nitrobenzyl methyl ether (Thiele and Dimroth).

m-Nitrobenzyl chloride; from *m*-nitrobenzyl alcohol and phosphorus pentachloride (Gabriel and Borgmann, Ber. 1883, 16, 2064); together with *o*- and *p*-nitrobenzyl chloride by treating benzyl chloride in the cold with nitric acid (D 1.5) (Abelli, Gazz. chim. ital. 1883, 13, 98; Kumpf, l.c.). Yellow needles, volatile with steam, m.p. 44.8°, $n_D^{25} 1.5577$ (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). When treated with sodium sulphite it yields the sodium salt of *m*-nitrobenzyl sulphonic acid (Purgotti and Monti, Gazz. chim. ital. 1900, 30, ii, 246).

p-Nitrobenzyl chloride; by nitration of benzyl chloride (Beilstein and Geitner, Ann. 1866, 139, 337; Strakosch, Ber. 1873, 6, 1056); by the action of 1 mol. of chlorine on *p*-nitrotoluene at 185°–190° (Wachendorff, Ann. 1877, 185, 271). Needles, m.p. 72.4°, $n_D^{25} 1.5647$ (Holleman, Vermeulen and de Mooy, l.c.). Chlorine at 190°–190° is without any action. It is oxidised by alkaline pyrogallol to *p*-nitrotoluene (Pellizzari, Gazz. chim. ital. 1884, 14, 481). For its reduction with stannous chloride under various conditions, see Thiele and Dimroth (l.c.); Roser, (Ann. 1887, 238, 364). With zinc and hydrochloric acid it is reduced to *p*-toluidine (Rudolph, D.R.P. 34234 of 1885). With sodium acetoxime in warm alcohol it yields *p*:*p*-dinitrostilbene (Schröter and Peschkes, Ber. 1900, 33, 1981). It forms colouring matters with primary, secondary, and tertiary amines, as well as with phenols in the presence of oxidising agents

(Greiff, D. R. P. 15120 of 1881; Lembach and Schleicher, D. R. P. 14945 of 1880).

2:4:6-Trinitrobenzyl chloride; m.p. 85° (Ganguly, Ber. 1925, 59, 708).

2:3:4-Trichloro-6-nitro-benzyl chloride. Needles, m.p. 122° (Ganguly, l.c.).

o-Nitrobenzylidene chloride; in a yield of 23.3 p.c. by nitration of benzylidene chloride. M.p. 25.7° (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; cf. Kliegel, Ber. 1907, 40, 4937).

m-Nitrobenzylidene chloride; m.p. 64.5°. Yield 33.8 p.c. (Holleman, &c.).

p-Nitrobenzylidene chloride; m.p. 42.8°. Yield 42.9 p.c. (Holleman, &c.).

CHLORONITROTOLUENES.

The nitration of *o*-chlorotoluene leads to formation of all the possible chloromononit derivatives, 2:3-, 2:4-, 2:5-, and 2:6-, although the 2:4-isomeride is difficult to detect. Using 10 grms. of *o*-chlorotoluene and nitrating with 40 grms. of nitric acid (D 1.52) at 0°, the percentage yields of the products in the above order are 19.2, 17.0, 43.3, and 20.5 respectively. In the case of *m*-chlorotoluene the 3:6-, 3:5-, 3:4-, and 3:2-chloromononitrotoluenes are obtained in a yield of 58.9 p.c., very little, 32.3 p.c. and 8.8 p.c. respectively (Holleman and Wibaut, Proc. K. Akad. Wetensch. Amsterdam, 1912, 15, 594). The nitration of *o*-chlorotoluene with nitric and sulphuric acids primarily at 8°–10°, and finally at the temperature of the water-bath, leads to the formation of four isomeric dinitro-derivatives in the following proportions: 2-chloro-3:5-dinitrotoluene, 55–60 p.c.; 2-chloro-5:6-dinitrotoluene, 18–20 p.c.; 2-chloro-4:5-dinitrotoluene, 18–20 p.c.; 2-chloro-4:6-dinitrotoluene, 1–2 p.c. (Morgan and Drew, Chem. Soc. Trans. 1921, 117, 793).

2-Chloro-3-nitrotoluene; from 3-nitro-*o*-toluidine by the diazo-reaction (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151; cf. Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1127). M.p. 21° (Holleman, Rec. trav. chim. 1908, 27, 455), $n_D^{20} 1.5327$ (Wibaut, *ibid.* 1913, 32, 244).

2-Chloro-4-nitrotoluene; from *p*-nitrotoluene and phosphorus pentachloride (Lellmann, Ber. 1884, 17, 534) or antimony pentachloride (Wachendorff, Ann. 1877, 185, 273); in a yield of 95 p.c. by chlorination of *p*-nitrotoluene at 65°–75° in presence of antimony trichloride (Davies, Chem. Soc. Trans. 1921, 119, 868; 1922, 121, 809); from 4-nitro-*o*-toluidine (Green and Lawson, *ibid.* 1891, 59, 1017), or 6-chloro-4-nitro-*m*-toluidine (Morgan and Drew, *ibid.* 1920, 117, 789), or 2-chloro-4-nitro-*m*-toluidine (Morgan and Glover, *ibid.* 1921, 119, 1704) by the diazo-reaction. Long white pointed needles, m.p. 68° (Green and Lawson), or m.p. 62.3°, $n_D^{20} 1.5470$ (Wibaut, Rec. trav. chim. 1913, 32, 244), b.p. 257°–260°/756 mm. (Davies, l.c.). Volatile with steam and develops an intense red coloration with hot alcoholic sodium hydroxide.

2-Chloro-5-nitrotoluene; by nitration of *o*-chlorotoluene; from 5-nitro-*o*-toluidine (Goldschmidt and Hönig, Ber. 1886, 19, 2439; 1887, 20, 199), or 2-chloro-5-nitro-*p*-toluidine (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1334); together with 4-chloro-7-nitroindazole from

6-chloro-3-nitro-*o*-toluidine (Morgan and Drew, *ibid.* 1920, 117, 787) by the diazo-reaction. Yellowish pyramids, m.p. 44°, b.p. 248°/711 mm. (G. and H.), or m.p. 42-43°, n_D^{20} 1.5511 (Wibaut, *Rec. trav. chim.* 1913, 32, 244).

2-Chloro-6-nitrotoluene; from 6-nitro-*o*-toluidine (Green and Lawson, *l.c.*; Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 787) by the diazo-reaction; by the reduction of 2:6-dinitrotoluene by means of hydrogen sulphide in ammoniacal solution followed by the diazo-reaction (Wibaut, *Rec. trav. chim.* 1913, 32, 244); together with considerable amounts of 4-chloro-2-nitrotoluene by chlorination of *o*-nitrotoluene (Cohn, *Monatsh.* 1901, 22, 471; cf. Janson, D. R. P. 107505 of 1898). Needles, m.p. 35-37°, n_D^{20} 1.5377 (Wibaut), or m.p. 37° (Green and Lawson), b.p. 236°-238° (Janson). Readily volatile with steam. On reduction with zinc dust and sodium hydroxide it yields 6-chloro-*o*-toluidine, *o*-*o'*-dichloroazotoluene, and *o*-*o'*-dichlorotolidine (Cl:CH₃:NH₂=2:3:4) (Cohn, *l.c.*; cf. Akt. Ges. f. Anilfabr., D. R. P. 82140 of 1894).

3-Chloro-2-nitrotoluene; by chlorination of 6-nitro-aceto-*o*-toluidine in glacial acetic acid, followed by hydrolysis and elimination of the amino-group (Cohen and Hodsman, *Chem. Soc. Trans.* 1907, 91, 974). M.p. 23-24° (Holleman and Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 594), n_D^{20} 1.5204 (Wibaut, *Rec. trav. chim.* 1913, 32, 244). It may also exist in a metastable form. It is oxidised to 3-chloro-2-nitrobenzoic acid (Brand and Zöller, *Ber.* 1907, 40, 3324).

3-Chloro-4-nitrotoluene; from 5-chloro-4-nitro-*o*-toluidine. M.p. 24-25°, n_D^{20} 1.5428 (Wibaut, *l.c.*).

3-Chloro-5-nitrotoluene; from 5-nitro-*m*-toluidine by the diazo-reaction (Hönig, *Ber.* 1887, 20, 2419). Yellow needles, volatile with steam m.p. 55° (Hönig), m.p. 58-60°, n_D^{20} 1.5404 (Wibaut, *Rec. trav. chim.* 1913, 32, 244), m.p. 61° (Wynne and Greeves, *Chem. Soc. Proc.* 1895, 11, 151).

3-Chloro-6-nitrotoluene; from 6-nitro-*m*-toluidine (Cohen and Hodsman, *Chem. Soc. Trans.* 1907, 91, 975) or 2-nitro-5-chloro-*p*-toluidine (Brand and Zöller, *l.c.*). It appears to exist in a stable form, m.p. 24-25°, and a metastable form, m.p. 24-25°, n_D^{20} 1.5495 (Wibaut, *l.c.*).

4-Chloro-2-nitrotoluene; together with the 4:3-isomeride by nitration of *p*-chlorotoluene (Engelbrecht, *Ber.* 1874, 7, 797; Goldschmidt and Hönig, *ibid.* 1886, 19, 2440; cf. Wroblewsky, *Ann.* 1873, 168, 203); from 2-nitro-*p*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, *Ann.* 1871, 158, 336; Green and Lawson, *Chem. Soc. Trans.* 1891, 59, 1019). Long needles, m.p. 38°, b.p. 239-240°/718 mm., readily volatile with steam. On reduction it yields *p*-chloro-*o*-toluidine (Goldschmidt and Hönig).

4-Chloro-3-nitrotoluene; together with the 4:3-isomeride by nitrating *p*-chlorotoluene (see under 4-chloro-2-nitrotoluene); from 3-nitro-*p*-toluidine by the diazo-reaction (Gattermann and Kaiser, *Ber.* 1888, 12, 2800). Oil which solidifies in a freezing mixture, m.p. 7°, b.p. 260°/745 mm. n_D^{20} 1.297 (Gattermann and Kaiser).

2-Chloro-3:4-dinitrotoluene; from 3:4-di-

nitro-*o*-toluidine by the Sandmeyer reaction. Colourless needles, m.p. 89°. With warm aqueous sodium hydroxide the following colour-changes occur: yellow, yellowish-brown, brownish-red; with alcoholic sodium hydroxide, pale green, dark green, greenish-blue, brownish-black, and after heating and keeping for 2 hours, pale red; with alcoholic ammonia, faint yellow (Morgan and Glover, *Chem. Soc. Trans.* 1921, 119, 1703).

2-Chloro-3:5-dinitrotoluene; from 3:5-dinitro-*o*-toluidine by the diazo-reaction (Körner and Contardi, *Atti R. Accad. Lincei*, 1915, [v.] 24, i. 888; Rabaut, *Bull. Soc. chim.* 1895, [3] 13, 634; *Compt. rend.* 1895, 120, 1123); together with other products by nitration of *o*-chlorotoluene (Nietzki and Rehe, *Ber.* 1892, 25, 3005; Borsche and Fiedler, *ibid.* 1911, 45, 270; Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 784); best prepared by heating 2-chloro-3-nitrotoluene or 2-chloro-5-nitrotoluene with a mixture of equal parts of sulphuric and fuming nitric acids for 2 hours on the water-bath (Borsche and Fiedler, *l.c.*). Stout yellow rhombs, or large prisms; m.p. 63°-64.5° (Borsche and Fiedler). With anhydrous liquid ammonia it yields an intense violet to bluish-violet colour (red by transmitted light) changing to greenish-black; with alcoholic ammonia a greenish to azure-blue colour changing to red; with alcoholic sodium hydroxide a pale yellow colour changing through greenish-blue to intense rose-red and on heating to bright orange-red (Morgan and Drew).

2-Chloro-4:5-dinitrotoluene; from 4:5-dinitro-*o*-toluidine by the Sandmeyer reaction (Morgan and Glover, *Chem. Soc. Trans.* 1921, 119, 1703); in 85 p.c. yield together with upwards of 4 p.c. of 2-chloro-4:6-dinitrotoluene by nitration of 2-chloro-4-nitrotoluene (Morgan and Challenor, *ibid.* 1921, 119, 1539); in 18-20 p.c. yield by direct nitration of *o*-chlorotoluene (Morgan and Drew, *ibid.* 1920, 117, 786, 792). Colourless hexagonal leaflets or prismatic needles, m.p. 88-89°. It yields a transparent orange-red colour with anhydrous liquid ammonia which changes to bluish- and brownish-black, a transparent orange-red coloration with alcoholic ammonia, and with alcoholic sodium hydroxide a pale yellow colour which changes through emerald-green to brownish-red (Morgan and Drew).

2-Chloro-4:6-dinitrotoluene; in a yield of about 1-2 p.c. by nitration of *o*-chlorotoluene; in a yield of 12 p.c. by nitration of 2-chloro-4-nitrotoluene (Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 786, 792); in small yield, together with 2-chloro-5:6-dinitrotoluene by nitration of 2-chloro-6-nitrotoluene (Morgan and Jones, *ibid.* 1921, 119, 187). Colourless rectangular prisms or prismatic needles, m.p. 49°. With anhydrous liquid ammonia it yields an intense violet coloration which changes to bluish-violet, magenta, and finally deep crimson; with alcoholic ammonia a bright red colour which changes to bluish-green, intense azure blue, red by transmitted light to deep crimson, and with alcoholic sodium hydroxide an intense blue changing to greenish-blue and finally black, and on heating to reddish-black and finally to transparent deep orange-red (Morgan and Drew).

2-Chloro-5:6-dinitrotoluene; as the chief product, together with a small amount of 2-chloro-4:6-dinitrotoluene, by the gradual addition of 2-chloro-6-nitrotoluene to a mixture of nitric acid (D 1.42) and sulphuric acid at 20°, the temperature being raised subsequently to 70° for 1 hour (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 187; cf. Janson, D. R. P. 107805 of 1898; Cohn, Monatsh. 1901, 22, 475; Morgan and Drew, Chem. Soc. Trans. 1920, 117, 787). Colourless needles or prisms, m.p. 106.5°. With anhydrous liquid ammonia it yields a transparent yellow colour which changes to orange-red, with alcoholic ammonia a transparent yellow colour, and with alcoholic sodium hydroxide a faint transparent yellow colour which on heating changes from orange to deep orange-red, fading to transparent brownish-yellow and finally to light orange (Morgan and Drew).

3-Chloro-2:4-dinitrotoluene; by the action of cupric chloride on 2:4-dinitro-*m*-tolyl-hydrazine. Long silky pale yellow needles, m.p. 92° (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 897). These authors consider that the compound, m.p. 73°, obtained by Borsche and Fiedler (Ber. 1913, 46, 2117) is identical with 3-chloro-2:6-dinitrotoluene.

3-Chloro-2:6-dinitrotoluene; large, almost colourless prisms, m.p. 75° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339; cf. Borsche and Fiedler, *l.c.*).

3-Chloro-4:6-dinitrotoluene; from 6-nitro-*m*-toluidine by replacement of the amino-group by chlorine, followed by nitration with fuming nitric acid and sulphuric acid; or by nitration of *m*-chlorotoluene (Reverdin and Crépeux, Ber. 1900, 33, 2506; Bull. Soc. chim. 1900, (3) 23, 838). Pale yellow needles, or shining leaflets, volatile with steam, m.p. 91°. When reduced with an alcoholic solution of ammonium sulphite it yields a *chloronitrotoluidine* (3:4:6- or 3:6:4-), yellow leaflets, m.p. 120°, *acetyl derivative*, m.p. 262° (Reverdin and Crépeux; cf. Borsche and Fiedler, Ber. 1913, 46, 2117). On nitration it yields 3-chloro-2:4:6-trinitrotoluene.

4-Chloro-2:3-dinitrotoluene; by nitration of *p*-chlorotoluene with nitric acid (D 1.4). Small yellow needles, m.p. 76° (Goldschmidt and Hönig, Ber. 1886, 19, 2439; Hönig, *ibid.* 1887, 20, 2420).

4-Chloro-2:5-dinitrotoluene; by oxidation of 4-chloro-2:5-dinitrosotoluene with warm concentrated nitric acid. Short amber-yellow prisms, m.p. 107° (Kahrmann, Silva and Keleti, Ber. 1915, 48, 2021).

4-Chloro-2:6-dinitrotoluene; by nitration of 4-chloro-2-nitrotoluene with mixed acid. Long white needles, m.p. 101° (Hönig, Ber. 1887, 20, 2420).

4-Chloro-3:5-dinitrotoluene; by nitration of 4-chloro-3-nitrotoluene (Hönig, Ber. 1887, 20, 2420; Borsche and Fiedler, Ber. 1912, 45, 1839; 1913, 46, 2117); in small quantity by the action of toluene *p*-sulphonyl chloride on 3:5-dinitro-*p*-cresol in presence of diethylaniline (Borsche and Fiedler). In preparing the compound by the first method, a substance, m.p. 106°, probably 4-chloro-2:5-dinitrotoluene, is formed simultaneously. 4-Chloro-3:5-dinitrotoluene is prepared also from the corresponding nitrate by the

action of cuprous or cupric chloride (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 22, ii. 464). Colourless needles, m.p. 115°-116° (Borsche and Fiedler), or stout yellow rhombic prisms, m.p. 114.5° (Körner and Contardi). Hönig gave the melting point as 48°.

3-Chloro-2:4:6-trinitrotoluene; by nitration of 3-chloro-4:6-dinitrotoluene at 150°-175°, or of 3-chlorotoluene with sulphuric acid (D 1.84) and nitric acid (D 1.51) (Reverdin, Drosel and Delétra, Bull. Soc. chim. 1904, [3] 31, 631); by condensation of trinitro-*m*-cresol with toluene *p*-sulphonyl chloride in presence of diethylaniline (Ullmann and Náday, Ber. 1908, 41, 1870). Long colourless needles or spangles, m.p. 148.5°.

2:3-Dichloro-4-nitrotoluene; by the action of cold fuming nitric acid on 2:3-dichlorotoluene. Fine needles, m.p. 50.5°-51.5° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1128; 1902, 81, 1327, 1347; cf. Seelig, Ann. 1887, 237, 163).

2:3-Dichloro-5-nitrotoluene; from 3-chloro-5-nitro-*o*-toluidine by the diazo-reaction (Wyne and Greeves, Chem. Soc. Proc. 1895, 11, 151). Pale yellow needles, m.p. 83°.

2:4-Dichloro-5-nitrotoluene; by nitration of 2:4-dichlorotoluene with cold fuming nitric acid. Needles, m.p. 54°-55° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1129; 1902, 81, 1334, 1348; cf. Seelig, *l.c.*).

2:5-Dichloro-3-nitrotoluene; from 5-chloro-3-nitro-*o*-toluidine by the diazo-reaction. Long slender needles, volatile with steam, m.p. 54°-55° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

2:5-Dichloro-4-nitrotoluene; by nitration of 2:5-dichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1130; 1902, 81, 1347); from 6-chloro-4-nitro-*m*-toluidine by the diazo-reaction (Morgan and Drew, *ibid.* 1920, 117, 789). Fine needles, m.p. 50°-51° (C. and D.).

2:5-Dichloro-6-nitrotoluene, m.p. 68°-70°, from 5-chloro-6-nitro-*o*-toluidine by the diazo-reaction (Cohen and Hodsman, *ibid.* 1907, 81, 975).

2:6-Dichloro-3-nitrotoluene; m.p. 52°-53°, by nitrating 2:6-dichlorotoluene in the cold with fuming nitric acid (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1346).

2:6-Dichloro-4-nitrotoluene; together with other products in a yield of more than 30 p.c. by the monochlorination of 2-chloro-4-nitrotoluene in the presence of antimony trichloride or ferric chloride. Thick colourless faintly odorous blunt needles, m.p. 65°, b.p. 278°-279°/760 mm. It is very stable towards potassium permanganate solution (Davies, Chem. Soc. Trans. 1922, 121, 810).

3:4-Dichloro-5-nitrotoluene; from 3-chloro-5-nitro-*p*-toluidine by the diazo-reaction. Pale yellow needles, volatile with steam, m.p. 49°-50°. On further nitration it yields a *dinitro-derivative*, m.p. 80°-81° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1338, 1349).

3:4-Dichloro-6-nitrotoluene; by nitration of 3:4-dichlorotoluene. Fine long needles, m.p. 63°-64° (Cohen and Dakin, *ibid.* 1902, 81, 1349).

3:5-Dichloro-2-nitrotoluene; by nitration of 3:5-dichlorotoluene. Needles, m.p. 62° (Cohen and Dakin, *ibid.* 1902, 81, 1348).

A *dichloro-4-nitrotoluene*, m.p. 16°, b.p. 274°, is obtained from dichlorotoluene and fuming nitric acid as described by Wroblewsky (Ann. 1873, 166, 212).

The following dichlorodinitro-derivatives are obtained by nitrating the corresponding dichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1111; 1902, 81, 1224, 1344; Cohen and Hodman, *ibid.* 1907, 91, 975; Davies, *ibid.* 1922, 121, 812; Seelig, Ann. 1887, 237, 129).

2:3-Dichloro-4:6-dinitrotoluene; m.p. 71°-72° (C. and D.).

2:4-Dichloro-3:5-dinitrotoluene; prisms, m.p. 103°-104° (C. and D.; S.).

2:5-Dichloro-4:6-dinitrotoluene; m.p. 100°-101° (C. and D.; C. and H.).

2:6-Dichloro-3:4-dinitrotoluene; by nitrating 2:6-dichloro-4-nitrotoluene with nitric acid (D 1.5) and concentrated sulphuric acid at the temperature of the water-bath for 1 hour. Long colourless needles, m.p. 130°-131° (D).

2:6-Dichloro-3:5-dinitrotoluene; colourless needles, m.p. 121° (C. and D.); also prepared from 2:6-dichloro-3-nitro-*p*-toluidine by eliminating the amino-group followed by nitration (D).

3:4-Dichloro-2:6-dinitrotoluene; long, most colourless needles, m.p. 91.5°-92.5° (C. and D.).

3:5-Dichloro-2:6-dinitrotoluene, long white needles, m.p. 99°-100° (C. and D.).

3:5-Dichloro-2:4:6-trinitrotoluene; by heating ethyldichlorotrinitrophenyl acetate in a sealed tube with concentrated hydrochloric acid at 150°-160°. Long flat white prisms, m.p. 200°-201° (Jackson and Smith, Amer. Chem. J. 1904, 32, 168).

2:6-Dichloro-3:4:5-trinitrotoluene; by prolonged nitration of 2:6-dichloro-3:5-dinitrotoluene with a mixture of nitric acid (D 1.5) and fuming sulphuric acid (20 p.c. SO₃) at 155°-160°. Small colourless needles, m.p. 160°-161° (Davies, Chem. Soc. Trans. 1922, 121, 812).

The following trichloronitrotoluenes have been obtained by nitrating the corresponding dichlorotoluenes (Seelig, Ann. 1887, 237, 140; Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1224, 1344).

2:3:4-Trichloronitrotoluene; white needles, m.p. 60°-61° (S.).

2:3:5-Trichloronitrotoluene; felted needles, m.p. 58°-59° (C. and D.).

2:3:6-Trichloronitrotoluene; long needles, m.p. 57°-58° (C. and D.).

3:4:5-Trichloronitrotoluene; needles or prisms, m.p. 91°-92° (S.) (cf. Beilstein and Kahlberg, Ann. 1869, 152, 240; Schultz, Ann. 1871, 167, 277).

3:4:6-Trichloro-3-nitrotoluene; m.p. 54° (Beilstein) (C. and D.).

3:4:5-Trichloro-3-nitrotoluene; prisms, m.p. 51°-52° (C. and D.).

The following trichlorodinitrotoluenes have been obtained by nitrating the corresponding dichlorotoluenes (Seelig, Ann. 1887, 237, 140; Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1224, 1344).

2:3:4-Trichloro-4:6-dinitrotoluene; small needles, m.p. 141° (S.).

2:3:5-Trichloro-4:5-dinitrotoluene; prisms, m.p. 140°-142° (C. and D.).

2:4:5-Trichloro-3:6-dinitrotoluene; small needles, m.p. 227° (S.).

2:4:6-Trichloro-3:5-dinitrotoluene; m.p. 178°-180° (C. and D.).

3:4:5-Trichloro-2:6-dinitrotoluene, prismatic needles, m.p. 163°-164° (C. and D.).

The following tetrachloronitrotoluenes have been obtained in a similar manner (Cohen and Dakin, *ibid.* 1904, 85, 1274; 1906, 89, 1483).

2:3:4:5-Tetrachloro-6-nitrotoluene; m.p. 159°.

2:3:4:6-Tetrachloro-5-nitrotoluene; m.p. 131°-134° (not pure).

2:3:5:6-Tetrachloro-4-nitrotoluene; small hexagonal plates, m.p. 150°-152°.

2-Bromo-4-nitrotoluene, by elimination of the amino-group from 6-bromo-4-nitro-*m*-toluidine (Neville and Winther, Chem. Soc. Trans. 1881, 39, 85; Ber. 1881, 14, 418); by heating *p*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 171); by the action of hydrobromic acid on *p*-nitrotoluene-*o*-diazopiperidide (Wallach, Ann. 1886, 235, 248). Needles, m.p. 77.5° (S.) or 74°-75° (N. and W.).

2-Bromo-5-nitrotoluene; from 5-nitro-*o*-toluidine (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429); by heating *m*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 180); from 2-bromo-5-nitro-*p*-toluidine or 6-bromo-3-nitro-*o*-toluidine by the diazo-reaction (Blankma, Chem. Weekblad. 1912, 9, 968). It melts at 78° (S.).

2-Bromo-6-nitrotoluene; from 6-nitro-*o*-toluidine (Friedländer, Bruckner and Deutsch, Ann. 1912, 388, 23; Nölting, Ber. 1904, 37, 1915). Yellowish-white needles, m.p. 41° (N.) or 35° (F. B. and D.).

3-Bromo-2-nitrotoluene; from 2-nitro-3-bromo-*m*-toluidine by the diazo-reaction. Liquid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 630; Ber. 1880, 13, 1945).

3-Bromo-5-nitrotoluene; from 3-bromo-5-nitro-*p*-toluidine, 5-bromo-3-nitro-*o*-toluidine, or 3-bromo-5-nitro-*o*-toluidine by the diazo-reaction. Prisms, m.p. 81.4°-81.5° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429; Ber. 1880, 13, 564) or m.p. 86°, b.p. 269°-270° (Wroblewsky, Ann. 1878, 192, 203).

4-Bromo-2-nitrotoluene; from 2:4-dinitrotoluene by replacing the *p*-nitro-group by bromine (Beilstein and Kahlberg, Ann. 1871, 158, 340); together with 4-bromo-3-nitrotoluene by nitrating *p*-bromotoluene (Wroblewsky, Ann. 1873, 168, 176); by the action of bromine on *o*-nitrotoluene in presence of iron (Gland, Ber. 1915, 48, 432). Slender yellowish needles or large monoclinic tables, m.p. 45° (Beilstein and Roes, Ber. 1873, 6, 609), m.p. 43°, b.p. 257° (Wroblewsky), m.p. 157.5° (Hodman, Rec. trav. chim. 1915, 34, 262). Its reaction with sulphuric acid on electrolysis yields 4-bromo-2-amino-3-creosol (Gattermann, Ber. 1904, 37, 1921).

4-Bromo-3-nitrotoluene; together with 4-bromo-2-nitrotoluene by nitrating *p*-bromotoluene (Wroblewsky, Ann. 1873, 168, 176).

(D 1.52) cooled in ice a mixture of 4-bromo-2-nitrotoluene and 4-bromo-3-nitrotoluene, in the relative proportions of 56.3 : 43.7, is obtained. Analysis by decomposition with sodium methoxide showed the mixture to contain 41.5 p.c. of the 3:4-isomeride, whilst calculation from theoretical considerations gave the relative proportions as 2:4/3 = 52.4 : 47.6 (Holleman, Rec. trav. chim. 1915, 34, 283); from 3-nitro-*p*-toluidine by the diazo-reaction (Neville and Winther, Chem. Soc. Trans. 1880, 37, 442; Ber. 1880, 13, 972); by treating *m*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 180). M.p. 33°.

η_D^{20} 1.5682 (Holleman; cf. Hübner and Rods), b.p. 255°–256°, D_{20}^{20} 1.631 (Wroblewsky). By the electrolysis of its solution in sulphuric acid, 4-bromo-5-amino-2-cresol is obtained (Gatterman, Ber. 1893, 27, 1931).

2-Bromo-3:5-dinitrotoluene; slender white prisms or large prisms, m.p. 86.2° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339; Blanksma, Rec. trav. chim. 1901, 20, 425).

3-Bromo-4:6-dinitrotoluene; by nitrating *m*-bromotoluene or *m*-bromomononitrotoluene with fuming nitric acid (Grete, Ann. 1873, 168, 258; Ber. 1875, 8, 567; Bentley and Warren, Amer. Chem. J. 1890, 12, 1); by the decomposition of ethyl bromodinitrophenylmalonate (Jackson and Robinson, Amer. Chem. J. 1889, 11, 541). Long pale yellow prisms or needles, m.p. 103°–104° (G.).

4-Bromo-3:5-dinitrotoluene; from 3:5-dinitro-*p*-toluidine by the diazo-reaction; by nitration of 4-bromo-3-nitrotoluene with nitric acid (D 1.52). Yellow prisms, m.p. 118.4° (Jackson and Ittner, Amer. Chem. J. 1897, 19, 7, 199, 205; Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 464).

3-Bromo-2:4:6-trinitrotoluene; by boiling 10 grms. of 3-bromo-4:6-dinitrotoluene with 20 c.c. of a mixture of 1 vol. of concentrated sulphuric acid and 2 vols. of concentrated nitric acid (Bentley and Warren, Amer. Chem. J. 1890, 12, 4); from 3-bromo-2:6-dinitro-*p*-toluidine (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339). Small needles, m.p. 143°. With alcoholic ammonia it yields 2:4:6-trinitro-*m*-toluidine.

2:3-Dibromo-4- (or 6) nitrotoluene; by nitrating 2:3-dibromotoluene. Needles, m.p. 56.5°–57.5° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 434; Ber. 1881, 14, 419) or 59° (Wroblewsky, Ann. 1873, 168, 184).

2:3-Dibromo-5-nitrotoluene; from 3-bromo-5-nitro-*o*-toluidine by the diazo-reaction. It melts at 105.4° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429; Ber. 1880, 13, 965; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 512).

2:4-Dibromo-5-nitrotoluene; by nitration of 2:4-dibromotoluene (Davis, Chem. Soc. Trans. 1902, 81, 872; cf. Neville and Winther, l.c.); from 2-bromo-5-nitro-*p*-toluidine by the diazo-reaction. Colourless needles, m.p. 85° (Blanksma, Chem. Weekblad. 1912, 9, 968) or 81°–82° (Davis).

2:4-Dibromo-6-nitrotoluene (?); by nitrating dibromotoluenes derived from dibromo-*m*-toluidine (m.p. 75°). It melts at 80°–81° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 441; Ber. 1881, 14, 419).

2:5-Dibromo-3-nitrotoluene; from 5-bromo-3-nitro-*o*-toluidine by the diazo-reaction. It melts at 69.5°–70.2° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 448; Ber. 1881, 14, 419).

2:5-Dibromo-4-nitrotoluene; by nitrating 2:5-dibromotoluene; from 6-bromo-4-nitro-*m*-toluidine by the diazo-reaction (Neville and Winther, Chem. Soc. Trans. 1880, 37, 445; Ber. 1881, 14, 419); together with other products by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids (Claus, J. pr. Chem. 1888, [2] 37, 18). Needles, m.p. 87°–89° (N. and W.), 89° (C.).

2:6-Dibromo-3-nitrotoluene; by nitration of 2:6-dibromotoluene with nitric acid (D 1.45) the 3-nitro-compound is formed and not the 4-nitro-derivative as stated by Neville and Winther; from 6-bromo-3-nitro-*o*-toluidine. Pale yellow crystals, m.p. 50° (Blanksma, l.c.; cf. Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 502).

2:6-Dibromo-4-nitrotoluene; from *p*-nitrotoluene by the action of bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 178); from 2:6-dibromo-4-nitro-*m*-toluidine (Neville and Winther). Needles, m.p. 57°–58° (S.) or 56.8°–57° (N. and W.).

3:4-Dibromo-5-nitrotoluene; from 3-bromo-5-nitro-*p*-toluidine. Leaflets, m.p. 62°–63.6° (Neville and Winther, l.c.) or 63°–65° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 510).

3:4-Dibromo-6-nitrotoluene; by nitration of 3:4-dibromotoluene (Wroblewsky, Ann. 1873, 168, 184; Neville and Winther, Chem. Soc. Trans. 1880, 37, 429; Ber. 1881, 14, 417); from 5-bromo-2-nitro-*p*-toluidine (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 515). Needles, m.p. 86.5°–87.5° (Neville and Winther) or 83.5°–84.5° (Cohen and Dutt).

3:5-Dibromonitrotoluene; by nitration of 3:5-dibromotoluene. Prisms, m.p. 124° (Wroblewsky, Ann. 1873, 168, 189).

3:5-Dibromo-2-nitrotoluene; obtained together with a *by-product* of higher melting-point by the diazotisation of 3:5-dibromo-2-nitro-*p*-toluidine. It melts at 67°, and on nitration with nitric acid (D 1.52) it yields a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene, but in presence of sulphuric acid 3:5-dibromo-2:4:6-trinitrotoluene is obtained (Blanksma, Chem. Weekblad, 1909, 6, 728).

3:5-Dibromo-4-nitrotoluene; obtained together with a *compound*, m.p. about 250°, from 3:5-dibromo-4-nitro-*o*-toluidine by the diazo-reaction. Colourless crystals, m.p. 84° (Blanksma, l.c.).

2:4-Dibromo-3:5-dinitrotoluene; by nitration of 2:4-dibromotoluene or 2:4-dibromo-5-nitrotoluene. Light yellow prisms, m.p. 127.5° (Davis, Chem. Soc. Trans. 1902, 81, 873) or 130° (Blanksma, Chem. Weekblad, 1912, 9, 968).

2:5-Dibromo-4:6-dinitrotoluene; by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids. Small acicular needles, or large yellow prisms, m.p. 142°. It sublimes readily in leaflets (Claus, J. pr. Chem. 1888, [2] 37, 16).

2:6-Dibromodinitrotoluene; by nitration of 2:6-dibromotoluenes. It melts at 161.6°–162.2°

(Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 437; *Ber.* 1880, 13, 967).

2:6-Dibromo-3:5-dinitrotoluene; by nitration of 2:6-dibromo-3-nitrotoluene. Colourless crystals, m.p. 161° (Blanksma, *l.c.*).

3:5-Dibromo-2:4-dinitrotoluene; when 3:5-dibromotoluene is added slowly to four times its weight of nitric acid (D 1.52) and the mixture is warmed for 10 minutes at 100°, 3:5-dibromo-2:4-dinitrotoluene, needles, m.p. 157°, is obtained, together with a product, cubes, m.p. 106°–108°, which appears to be a mixture of the above substance with the 2:6-isomeride (Blanksma, *Rec. trav. chim.* 1904, 23, 125; *cf.* Neville and Winther, *l.c.*); also prepared by nitration of 3:5-dibromo-4-nitrotoluene and, together with the 2:6-isomeride, by nitration of 3:5-dibromo-2-nitrotoluene (Blanksma, *Chem. Weekblad*, 1909, 6, 728).

3:5-Dibromo-2:6-dinitrotoluene; (*see above*); from 3:5-dibromo-2:6-dinitro-*p*-toluidine. White needles or flat plates, m.p. 120° (Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v.] 25, ii. 339) or 117° (Blanksma, *l.c.*).

3:5-Dibromo-2:4:6-trinitrotoluene; by nitration of 3:5-dibromotoluene in presence of sulphuric acid (Blanksma, *Rec. trav. chim.* 1904, 23, 125); by nitration of 3:5-dibromo-4-nitrotoluene, 3:5-dibromo-2:4-dinitrotoluene, and of 3:5-dibromo-2-nitrotoluene, the nitration in the last case being carried out in presence of sulphuric acid (Blanksma, *Chem. Weekblad*, 1909, 6, 728); from 3:5-dibromo-2:6-dinitro-*p*-toluidine by the action of nitrous gases on a suspension in concentrated nitric acid at 0° (Körner and Contardi, *l.c.*). White flat needles, m.p. 240°; Palmer (*Ber.* 1888, 21, 3501; 1896, 29, 1346) describes it as long yellow prisms, m.p. 229°–230°.

2:3:4-Tribromonitrotoluene; by nitration of 2:3:4-tribromotoluene. M.p. 107°–108° (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 446; Cohen and Dutt, *l.c.*).

2:3:5-Tribromonitrotoluene; on nitration 2:3:5-tribromotoluene yields two mononitroderivatives, m.p. 67°–68° and 88.5°–89° respectively, the former in greater quantity (Cohen and Dutt, *l.c.*).

2:3:6-Tribromonitrotoluene; m.p. 91°–92° (C. and D.; N. and W.).

2:4:5-Tribromonitrotoluene; colourless crystals, m.p. 131°–131.5° (C. and D.).

2:4:6-Tribromonitrotoluene; m.p. 215° (Wroblewsky, *Ann.* 1873, 168, 195).

2:4:6-Tribromonitrotoluene; colourless crystals, m.p. 74°–75.5° (C. and D.).

2:5:6-Tribromo-4-nitrotoluene; from 2:6-dibromo-4-nitro-*m*-toluidine. It melts at 106.5°–107° (C. and D.; N. and W.).

3:4:5-Tribromonitrotoluene; colourless crystals, m.p. 104°–105° (C. and D.).

3:5:6-Tribromo-2-nitrotoluene; from 3:5-dibromo-6-nitro-*o*-toluidine. It melts at 93° (Blanksma, *Chem. Weekblad*, 1914, 11, 185).

2:3:4-Tribromodinitrotoluene; m.p. 197°–199° (C. and D.).

2:2:5-Tribromodinitrotoluene; m.p. 209°–210° (C. and D.).

2:3:6-Tribromodinitrotoluene; light yellow prisms, m.p. 202°–203° (C. and D.).

2:4:5-Tribromodinitrotoluene; colourless crystals, m.p. 276°–278° (C. and D.).

2:4:6-Tribromodinitrotoluene; colourless crystals, m.p. 217°–218° (C. and D.; N. and W.).

3:4:5-Tribromodinitrotoluene; colourless prisms, m.p. 211.5° (C. and D.).

3:5:6-Tribromodinitrotoluene; by nitration of 3:5:6-tribromo-2-nitrotoluene. Colourless crystals, m.p. 208° (Blanksma, *Chem. Weekblad*, 1914, 11, 185).

2:3:4:5-Tetrabromo-6-nitrotoluene, m.p. 212° (N. and W.).

2:3:4:6-Tetrabromo-5-nitrotoluene, m.p. 215°–216° (N. and W.).

2:3:5:6-Tetrabromo-4-nitrotoluene; by nitration of 2:3:5:6-tetrabromotoluene (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 450); from 2-bromo-4-nitrotoluene by bromination in presence of ferrous bromide (Scheufelen, *Ann.* 1885, 231, 179). It melts at 213° (Neville and Winther) or 227° (Scheufelen).

m-Chloro-*p*-bromonitrotoluene; by nitration of chlorinated *p*-bromotoluene. Needles, m.p. 61° (Willgerodt and Salzmann, *J. pr. Chem.* 1889, [2] 39, 478).

o-Chlorobromonitrotoluene; by nitration of brominated *o*-chlorotoluene. Needles, m.p. 68° (W. and S.).

Dichloro-*p*-bromonitrotoluene; by nitration of dichloro-*p*-bromotoluene. Pearly leaflets, m.p. 106° (W. and S.).

Trichloro-*p*-bromonitrotoluene; by nitration of trichloro-*p*-bromotoluene. Needles, m.p. 162° (W. and S.).

2-Iodonitrotoluene; by nitration of 2-iodotoluene. Microscopic needles, m.p. 103°–104° (Beilstein and Kuhlberg, *Ann.* 1871, 158, 347).

2-Iodo-3-nitrotoluene; from 3-nitro-*o*-toluidine. Light yellow plates, m.p. 67°–68° (Wheeler and Liddle, *Amer. Chem. J.* 1909, 42, 441).

2-Iodo-4-nitrotoluene; from 4-nitro-*o*-toluidine. Yellowish plates, m.p. 51° (Reverdin, *Ber.* 1897, 30, 3000) or rhombic plates, m.p. 58° (Willgerodt and Kok, *Ber.* 1908, 41, 2077). It yields a dichloride, sulphur-yellow prisms, m.p. 83°, which on treatment with sodium carbonate or sodium hydroxide yields 2-iodo-4-nitrotoluene, yellowish-white powder, exploding at 180°–181°. The latter on treatment with hypochlorous acid is converted into 2-iodoxy-4-nitrotoluene, white flocculent precipitate, exploding at 204° (Willgerodt and Kok, *l.c.*).

2-Iodo-5-nitrotoluene; from 5-nitro-*o*-toluidine by the diazo-reaction (Reverdin); by gradual treatment of *o*-iodo-toluene with nitric acid (D 1.51) (Reverdin; Beilstein and Kuhlberg, *Ann.* 1871, 158, 347). It melts at 103°–104° and forms a dichloride, m.p. 102° (decomp.), when chlorine is passed into a saturated solution in chloroform (McCrae, *Chem. Soc. Trans.* 1878, 73, 693).

2-Iodo-6-nitrotoluene; from 6-nitro-*o*-toluidine. It forms thick yellowish-white crystals, m.p. 35.5° (Nölting, *Ber.* 1904, 37, 1015) or yellow needles, m.p. 34°–35° (Cohen and Miller, *Chem. Soc. Trans.* 1904, 85, 1627).

3-Iodo-2-nitrotoluene; from 5-iodo-6-nitro-*o*-toluidine. Colourless prismatic plates, m.p. 65°, volatile with steam (Wheeler and Brautlecht, *Amer. Chem. J.* 1910, 44, 126).

3-Iodo-5-nitrotoluene; from 5-nitro-*m*-toluidine. Yellow rectangular prisms, m.p. 77°

(Wheeler and Scholes, Amer. Chem. J. 1910, 44, 126).

3-Iodo-6-nitrotoluene; from 6-nitro-*m*-toluidine. Orange needles, volatile with steam, m.p. 84° (Artmann, Monatsh. 1905, 26, 1091).

3-Iodo-nitrotoluene; by nitration of 3-iodotoluene. Small needles, m.p. 108°–109° (Beilstein and Kuhlberg).

4-Iodo-2-nitrotoluene; from 2:4-dinitrotoluene by replacing the *p*-nitro-group by iodine (Heynemann, Ann. 1871, 158, 337); together with other products by the nitration of *p*-iodotoluene (Reverdin, Ber. 1897, 30, 3001). Pale yellow crystals, m.p. 60.5°–61°, b.p. 286° (decomp.).

4-Iodo-3-nitrotoluene; from 3-nitro-*p*-toluidine. Flat yellow needles, m.p. 55°–56° (Beilstein and Kuhlberg, Ann. 1871, 158, 344). Yields a *dichloride*, large yellow plates, m.p. 71° (Willgerodt and Simonis, Ber. 1906, 39, 269).

2-Iodo-3:5-dinitrotoluene; from 3:5-dinitrotoluene-2-diazonium nitrate and cupric iodide. Small lemon-yellow plates or long prisms, m.p. 119.5° (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, i. 888).

3-Iodo-2:4-dinitrotoluene; by boiling an alcoholic solution of 2:4-dinitro-3-tolylhydrazine with excess of iodine. Yellow leaflets, m.p. 117° (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 897).

3-Iodo-2:6-dinitrotoluene; large aggregates of small colourless plates, m.p. 90° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339).

4-Iodo-3:5-dinitrotoluene; by nitration of *p*-iodotoluene (Glassner, Ber. 1875, 8, 561); from 3:5-dinitro-*p*-toluidine. Lemon-yellow needles, m.p. 158° (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 464); Glassner gave m.p. 137°–138°.

Di-iodonitrotoluene (?); formed together with other products by nitration of *p*-iodotoluene with nitric acid (D 1.51); m.p. 112° (Reverdin, l.c.).

2:3-Di-iodo-4-nitrotoluene; from 3-iodo-5-nitro-*o*-toluidine. Light brown prismatic needles, m.p. 143° (Wheeler, etc., Amer. Chem. J. 1910, 44, 126, 493).

2:5-Di-iodo-3-nitrotoluene; from 5-iodo-3-nitro-*o*-toluidine. Colourless prisms, m.p. 95° (Wheeler, etc.).

2:5-Di-iodo-4-nitrotoluene; from 5-iodo-4-nitro-*o*-toluidine. Buff coloured prismatic plates, m.p. 117° (Wheeler, etc.).

2:5-Di-iodo-6-nitrotoluene; from 5-iodo-6-nitro-*o*-toluidine. Colourless needles, m.p. 105° (Wheeler, etc.).

3:4-Di-iodo-5-nitrotoluene; from 3-iodo-5-nitro-*p*-toluidine. Rectangular orange prisms, m.p. 84°–85° (Wheeler, etc.).

3-Bromo-2-iodonitrotoluene; by nitration of 3-bromo-2-iodotoluene. Prisms (Wroblewsky, Ann. 1873, 168, 165).

2-Bromo-4-iodonitrotoluene; by nitration of *o*-bromo-*p*-iodotoluene. Yellow needles, m.p. 92° (Hirtz, Ber. 1896, 29, 1405).

3-Bromo-4-iodonitrotoluene; by nitration of 3-bromo-4-iodotoluene. Needles, m.p. 118° (Wroblewsky, Ann. 1873, 168, 160).

3:5-Dibromo-4-iodo-2-nitrotoluene; by nitration of 3:5-dibromo-4-iodotoluene. Large needles, volatile with steam, m.p. 69° (Wroblewsky, Ann. 1878, 192, 210).

3:5-Dibromo-2:4-di-iodonitrotoluene; by nitration of 3:5-dibromo-2:4-di-iodotoluene (m.p. 68°). Plates, m.p. 129° (Wroblewsky).

SULPHINIC AND SULPHONIC ACID DERIVATIVES.

Toluene *o*-sulphinic acid; by boiling *o*-tolyltoluenesulphazide with baryta water (Limpricht, Ber. 1887, 20, 1241); by dropping toluene *o*-sulphonyl chloride into a warm mixture of zinc dust and water (Troeger and Voigtländer, J. pr. Chem. 1896, [2] 54, 513); by treating an ice-cold solution of *o*-toluenediazonium sulphate in sulphuric acid saturated with sulphur dioxide with copper (Gattermann, Ber. 1899, 32, 1140; Fr. Bayer & Co., Eng. Pat. 26139 of 1896; Fr. Pat. 252787 and addn.; D. R. P. 95830 of 1896); by the action of sulphur dioxide on an ethereal solution of *o*-tolyl magnesium bromide (Rosenheim and Singer, Ber. 1904, 37, 2152). Long needles, m.p. 80° (Limpricht). $\text{NaA}' + 4\text{H}_2\text{O}$, glistening plates; $\text{CaA}'_2 + 3\text{H}_2\text{O}$, crystalline powder; $\text{BaA}'_2 + 3\text{H}_2\text{O}$, nodules; $\text{SrA}'_2 + 3\text{H}_2\text{O}$, crystalline powder. On passing hydrogen sulphide into the methyl alcoholic solution, a mixture of *o*-tolyl tetra- and pentasulphide is formed. On boiling with water for about 3 hours, the sulphinic acid is converted into *o*-toluic disulphoxide and toluene *o*-sulphonic acid (T. and V.). For its behaviour with diazo-compounds, see Troeger and Ewers (J. pr. Chem. 1900, [2] 62, 369).

Toluene *m*-sulphinic acid; from diazotised *m*-toluidine, sulphur dioxide and copper powder. Unstable oil (Troeger and Hill, J. pr. Chem. 1905, (2) 71, 201).

Toluene *p*-sulphinic acid; prepared as in the case of the *o*-sulphinic acid (Limpricht); by treating toluene *p*-sulphonyl chloride with sodium amalgam, zinc-dust or sodium sulphite (Otto, Ann. 1867, 142, 92; 1868, 145, 19; Ber. 1876, 9, 1586; Bloomstrand, Ber. 1869, 3, 965); by Gattermann's reaction (Ber. 1899, 32, 1141); by the action of sulphur dioxide and aluminium chloride on toluene or its halogen derivatives at low temperatures (Knoevenagel and Kenner, Ber. 1908, 41, 3315). Plates, m.p. 86°–87° (Thomas, Chem. Soc. Trans. 1909, 95, 344). $\text{KA}' + 2\text{H}_2\text{O}$, leaflets (Casanova, Ber. 1887, 20, 2088); $\text{CaA}'_2 + 4\text{H}_2\text{O}$; BaA'_2 , small leaflets; $\text{ZnA}'_2 + 2\text{H}_2\text{O}$ (Otto); $\text{NH}_4\text{A}'$, small needles, m.p. 175°; *hydrazine salt*, glistening plates, decomposing at 140°; *aniline salt*, m.p. 118°; *o*-toluidine salt, m.p. 124°; *p*-toluidine salt, m.p. 140°; *m*-xylylidine salt, m.p. 129.5° (Hälsig, J. pr. Chem. 1897, [2] 56, 213); *phenylhydrazine salt*, m.p. 114° (Köhler and Reimer, Amer. Chem. J. 1904, 31, 163; cf. Hälsig). On electrolytic oxidation it yields *p*-sulphobenzonic acid (Sehor, Zeitsch. Elektrochem. 1903, 9, 370). When treated with an excess of thionyl chloride, it yields the *sulphonyl chloride*, m.p. 54°–58° (Hilditch and Smiles, Ber. 1908, 41, 4113). When ammonia is passed into an alcoholic or ethereal solution of toluene *p*-sulphinic acid, the corresponding ammonium salt is formed, whilst in benzene solution a mixture of *p*-tolyl disulphoxide and toluene *p*-sulphonic acid is produced (Heiduschka, Verh. Ges. deut. Naturforsch. Aerzte, 1907, 11, 170; Hälsig, J. pr. Chem. 1897, 56, 213).

For the action of toluene *p*-sulphinic acid on nitrobenzene and phenylhydroxylamine, see

Bamberger and Rising (Ber. 1901, 34, 228, 241), and for further reactions, see Kohler and Macdonald (Amer. Chem. J. 1899, 22, 235), von Meyer, Nacke and Gmeiner (J. pr. Chem. 1901, 63, 167), von Meyer (*ibid.* 1903, 68, 263), Hälsig (*ibid.* 1897, 56, 213), Troeger and Ewers (*ibid.* 1900, 62, 369), Hantzsch and Horn (Ber. 1902, 35, 877), Ullmann and Lehner (*ibid.* 1905, 38, 729), Kohler and Reimer (Amer. Chem. J. 1904, 31, 163).

Toluene p-sulphinic anhydride; melts at 75° (Knoevenagel and Polack, Ber. 1908, 41, 3323).

Methyl ester; a very unstable yellow oil. Oxidation yields the corresponding sulphonate (Otto, J. pr. Chem. 1893, [2] 47, 166).

Ethyl ester; from sodium toluene *p*-sulphinate and ethyl chlorocarbonate. Oil, D₂₀^o 1.1212. On treatment with hydrogen sulphide, (CH₃)C₆H₄SO₃H, C₂H₅SH, (CH₃)C₆H₄SH, [(CH₃)C₆H₄]₂S₂ and sulphur are produced (Otto and Rössing, Ber. 1885, 18, 2504; 1886, 19, 1226; 1887, 20, 2278; 1893, 26, 310).

Nitrotoluene sulphinic acid; from *o*(?)-nitrotoluene *p*(?)-sulphonic acid and sodium amalgam in ethereal solution. Crystals, NaA' + $\frac{1}{2}$ H₂O (Otto and Grüber, Ann. 1868, 145, 24).

2:6-Dinitrotoluene 4-sulphinic acid; from the corresponding sulphonyl chloride and zinc dust. Solidifies after prolonged keeping over sulphuric acid. KA', crusts; BaA'₂ + xH₂O, pearly leaflets; PbA'₂ + 3H₂O, microscopic prisms (Perl, Ber. 1885, 18, 71).

Toluene 2:4-disulphinic acid; obtained as its zinc salt by the action of zinc dust on the corresponding disulphonyl chloride. The free acid is an oil, zinc salt, white needles, sodium and barium salts, white crystals. When heated with water the free acid yields toluene 2:4-disulphonic acid and tolylene-toluene-2:4-dithio-sulphonate, C₆H₄(SO₂)₂:C₆H₄ (Tröger and Meine, J. pr. Chem. 1903, [2] 68, 313).

Benzyl sulphinic acid; by treating benzyl sulphonyl chloride with zinc dust or sodium amalgam. The free acid is very unstable and is readily decomposed with evolution of sulphur dioxide; NaA', small leaflets (Otto and Lüders, Ber. 1880, 13, 1287).

Sulphonation of toluene: The quantities of the three isomeric monosulphonic acids produced are dependent upon the temperature, the concentration, and the amount of the sulphonating agent. Increase of temperature favours the production of toluene *p*- and *m*-sulphonic acids. The concentration of acid between the limits of 96–100 p.c. appears to be without influence. Increase in the amount of acid favours the production of the *o*-isomeride at low temperatures, but this influence is neutralised at higher temperatures by the effect due to rise of temperature. The addition of potassium sulphate, mercurous sulphate, and silver sulphate has no effect. At 35° and 75° the transformation of the *o*- and *p*-isomerides into one another occurs very slowly, whilst toluene *m*-sulphonic acid is unaltered after heating with sulphuric acid for 6 hours at 100°. With chlorosulphonic acid the chief product is also the *p*-isomeride (Holleman, Culand, van der Linden and Wibaut, Ber. 1911, 44, 2504). If fuming sulphuric acid be used and the temperature of the reaction is kept at the b.p.

of toluene, the main product is the *p*-acid, but if the temperature be not allowed to rise above 100° and ordinary concentrated acid is employed, 40–50 p.c. of the *o*-sulphonic acid is obtained (Fahlberg, Fr. Pat. 163797; D. R. P. 35211 of 1884; Fabr. de Thann, Eng. Pat. 14390 of 1901; Fr. Pat. 312797; D. R. P. 137935 of 1901; Eng. Pat. 10810 of 1897; Norton and Otten, Amer. Chem. J. 1885, 10, 140; Bourgeois, Chem. Zentr. 1900, i, 253; Reverdin, Ber. 1909, 42, 1523).

Toluene o-sulphonic acid; in small quantity together with the *p*-isomeride by dissolving toluene in hot fuming sulphuric acid (Engelhardt and Latschinoff, Zeit. f. Chem. 1869, (2) 5, 617; Wolkoff, *ibid.* (2) 6, 321; Bourgeois, Rec. trav. chim. 1899, 18, 436); by gradual addition of concentrated sulphuric acid to boiling toluene only the *p*-isomeride is formed (Chrutschoff, Ber. 1874, 7, 1167), whilst, according to Fahlberg (Ber. 1879, 12, 1048) no *m*-sulphonic acid is produced; in a yield of 40–50 p.c. by sulphonating below 100° with concentrated sulphuric acid with efficient agitation (Fahlberg and List; cf. D. R. PP. 35211, 35717 of 1884, and 137935 of 1901); from the sulphonyl chloride obtained together with the *m*- and *p*-isomerides by the action of chlorosulphonic acid on toluene (Klason and Vallin, Ber. 1879, 12, 1848; Noyes, Amer. Chem. J. 1886, 8, 176; Gilliard, Monnet and Cartier, D. R. P. 98030 of 1894); from 4-bromotoluene 2-sulphonic acid by reduction with sodium amalgam (Terry, Ann. 1873, 169, 27); from 4-nitrotoluene 2-sulphonic acid by elimination of the nitro-group (Jenssen, Ann. 1874, 172, 235); by treating diazo-derivatives of *o*-toluidine with sulphurous acid (Müller and Wiesinger, Ber. 1879, 12, 1348); by treatment of *p*-diazo-toluene *o*-sulphonic acid with sodium methoxide in methyl alcoholic solution (Moale, Amer. Chem. J. 1898, 20, 298); by warming the salts of *o*-sulphotoluene-*p*-hydrazine sulphonie acid, (CH₃)C₆H₄(SO₂H)·NH·NH·SO₃H, with potassium hydroxide (Ges. f. Chem. Ind. D. R. P. 68708 of 1892). For separation of the *o*- and *p*-acids by means of magnesium and zinc salts, see Fahlberg (Eng. Pat. 17401 of 1896; D. R. PP. 103299 of 1898, and 103943 of 1895), or by means of sulphuric acid, see Lange (Fr. Pat. 232539; D. R. P. 57391 of 1890).

Free acid, thin leaflets containing 2H₂O; NH₄A', thin leaflets; NaA' + H₂O, tables; KA' + H₂O, monoclinic plates; KA', needles; CaA'₂, leaflets; BaA'₂ + H₂O, plates; ZnA'₂ + 7H₂O; CdA'₂ + 2H₂O; PbA'₂ + 4H₂O, needles (Terry; Hübner and Post); +H₂O (Klason and Vallin); MnA'₂ + 2H₂O; CuA'₂ + 4H₂O; AgA'; MnA'₂ + 2H₂O; ZnA'₂ + 7H₂O; MgA'₂ + 7H₂O (Klason and Vallin, *loc. cit.*; Hübner and Post, Ann. 1873, 169, 1).

Chloride, by the action of chlorine on toluene *o*-sulphinic acid in presence of dilute sodium hydroxide or hydrochloric acid at temperatures below 35° (Basler Chemische Fabrik, Eng. Pat. 4525 of 1900, and 12585 of 1900; U.S. Pat. 667861; D. R. P. 124407 of 1900), or on potassium toluene *o*-sulphinate in aqueous solution (Ullmann and Lehner, Ber. 1905, 38, 729). Oil, b.p. 126°/10 mm., D₁₇^o 1.3443 (U. and L.), or b.p. 151°/33 mm., 154°/36 mm. (Davies, Chem.

Soc. Trans. 1921, 119, 878). See also Fahlberg and List (*l.c.*), and Majert and Ebers (D. R. P. 95338 of 1898); Fabr. de Thann, Eng. Pat. 14390 of 1901; U.S. Pat. 692598; Fr. Pat. 312797; D. R. P. 142116 of 1901; Eng. Pat. 2304 of 1905; M. L. B., D. R. P. 154493 of 1902; Eng. Pat. 6581 of 1897; 4525 of 1900; 11077 and 11078 of 1898; 16299 of 1903.

Bromide; by the action of bromine on an aqueous solution of toluene *o*-sulphinic acid. M.p. 13°, b.p. 137.5°–138°/10 mm.

Tröger's compound (J. pr. Chem. 1896, [2] 54, 523) contains some of the *p*-isomeride (Ullmann and Lehner, *l.c.*).

Amide; octahedra, m.p. 154° (Noyes), m.p. 156.3° (McKie, Chem. Soc. Trans. 1918, 113, 799; cf. Wolkoff, *l.c.*; Klason and Vallin, Ber. 1879, 12, 1850; Heffter, Ann. 1883, 221, 208; Miller, Chem. Soc. Trans. 1892, 61, 1030; Thomas, *ibid.* 1909, 95, 343; Noyes, *l.c.*; Fahlberg and List, *l.c.*). It can be separated from the *p*-isomeride by fractional precipitation from an alkaline solution by means of acids or by fractional crystallisation of the sodium salts (von Heyden, D. R. P. 76881 of 1892, and 77435 of 1894; cf. Barger and Givaudan, Eng. Pat. 848 of 1903; D. R. P. 154655 of 1903). When oxidised in alkaline solution with potassium manganate or potassium permanganate it yields *o*-sulphaminobenzoic acid, in neutral solution benzoic sulphinide is the chief product, whilst in acid solution the product is *o*-sulphobenzoic acid (Fahlberg and List, Ber. 1888, 21, 242; cf. Fahlberg and Remsen, Ber. 1879, 12, 469). It is converted in 4*N*-ammoniacal solution in the presence of ammonium sulphate at 40° at a platinum gauze anode into 'saccharin'; the material yield being 43.7 p.c. and the current yield 9.2 p.c. The most favourable results, however, (material yield 75.4 p.c., current yield 42.6 p.c.) are obtained by the electrolysis of a suspension in 2*N*-sodium carbonate solution at about 60° with a platinum gauze anode and a rotating lead cathode (Fichter and Löwe, Helv. Chim. Acta, 1922, 5, 60; vide SACCHARIN).

Methylamide, thin striated plates, m.p. 73°–75°, when oxidised with alkaline potassium permanganate yields potassium *o*-methylsulphaminobenzoate (Remsen and Clark, Amer. Chem. J. 1903, 30, 247).

Toluene *m*-sulphonic acid; in small quantities by sulphonation of toluene (Holleman and co-workers, *l.c.*); from *o*-bromotoluene *m*-sulphonic acid, (Müller, Ann. 1873, 169, 47) or 4-bromotoluene 3-sulphonic acid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 628) and sodium amalgam; or from 2-bromotoluene 5-sulphonic acid and zinc dust in alkaline solution (Miller, Chem. Soc. Trans. 1892, 61, 1030); from *p*-toluidine 3-sulphonic acid (Pechmann, Ann. 1874, 173, 202; Neville and Winther, *l.c.*), *o*-toluidine *m*-sulphonic acid (Pagel, Ann. 1875, 176, 297) or *o*-toluidine 5-sulphonic acid (Neville and Winther, *l.c.*); by treating *m*-toluidine diazo-salts with sulphur dioxide (Müller and Wiesinger, Ber. 1879, 12, 1348); from *p*-diazo-toluene *m*-sulphonic acid by treatment with zinc dust in ethyl alcoholic solution (Griffin, Amer. Chem. J. 1897, 19, 173, 189).

The free acid forms thin deliquescent scales +H₂O (Klason and Vallin); NH₄A', scales;

NaA' + ½H₂O (Miller); + ½H₂O (Vallin, Ber. 1886, 19, 2953), +H₂O (G.); KA' + ½H₂O, scales (M.), +H₂O (K. and V.); CaA' + 2½ or 5H₂O (V.), +3H₂O (K. and V.), +2H₂O, tables (G.); BaA', +H₂O, rectangular tables (G.); ZnA', +7H₂O, thin rectangular plates (K. and V.), +6H₂O, long thin prisms; CdA', +6H₂O (V.), +7H₂O, tables (K. and V.); PbA', +H₂O (Pechmann), +2H₂O (M.; Pagel; V.), +3H₂O (K. and V.); MnA', +6H₂O (V.), +7H₂O (K. and V.); CuA', +7H₂O (V.), +4H₂O (K. and V.), +½H₂O (G.); AgA', glistening prisms (V.), rectangular tables (G.).

Chloride; oil.

Amide; monoclinic needles or tables (Noyes and Walker, Amer. Chem. J. 1886, 8, 188), hexagonal scales, fernlike aggregates from water, or monoclinic prisms from alcohol (Griffin); m.p. 108° (Klason and Vallin, *l.c.*; Klason, Ber. 1886, 19, 2887; Griffin, Amer. Chem. J. 1897, 19, 176) or 91° (Noyes, Amer. Chem. J. 1886, 8, 177). According to Noyes, the amide, m.p. 108°, is a mixture of the *o*- and *p*-isomerides. On oxidation with potassium permanganate or chromic acid mixture it yields *m*-sulphaminobenzoic acid.

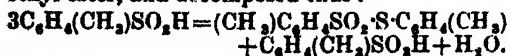
Toluene *p*-sulphonic acid; chief product of sulphonation of boiling toluene (Deville, Ann. Chim. 1841, (3) 3, 172; Fittig and Tollens, Ann. 1864, 131, 310; Märcker, *ibid.* 1865, 136, 85; Engelhardt and Latschinoff, Zeit. f. chem. 1869 (2) 5, 617; Jaworski, *ibid.* 1865, 221; Otto and Grüber, Ann. 1867, 142, 92; 1868, 145, 10; Chrustchoff, Ber. 1874, 7, 1167; Fahlberg, Ber. 1879, 12, 1048); from toluene and chlorosulphonic acid (Klason and Vallin, Ber. 1879, 12, 1848); by the action of sulphurous acid on *p*-diazo-toluene salts (Müller and Wiesinger). Thick plates or flat prisms +H₂O (K. and V.), m.p. 92° (Norton and Otten, Amer. Chem. J. 1888, 10, 140), or 35°, b.p. 146°–147°/0 mm. (Krafft and Wilke, Ber. 1900, 33, 3208). Fusion with potash yields *p*-cresol and *p*-hydroxybenzoic acid. Fusion with sodium formate yields *p*-toluic acid (Remsen, Ber. 1875, 8, 1412). Hydrolysis with steam commences at 150° (Armstrong and Miller, Chem. Soc. Trans. 1884, 45, 148). On electrolytic oxidation in 10–20 p.c. sulphuric acid using a lead anode at 70°, it yields *p*-sulphobenzoic acid (Sebor, Zeitsch. Elektrochem. 1903, 9, 370).

NH₄A' (K. and V.); NaA' + 2H₂O, or +4H₂O, rectangular tables (Vallin, Ber. 1886, 19, 2953); KA' + H₂O, six-sided plates, prisms or trimetric crystals (Otto and Köbig, Ber. 1886, 19, 1834); BaA', crystallises in anhydrous leaflets above 30° and as needles +3H₂O below 30° (Kelbe, Ber. 1883, 16, 622); CaA', +4H₂O, monoclinic prisms (K. and V.); MgA', +6H₂O, large tables (K. and V.); ZnA', +6H₂O, tables (K. and V.); CdA', +6H₂O, tables (K. and V.); PbA', long needles (K. and V.); MnA', +6H₂O, tables (K. and V.); CuA', +6H₂O, tables or needles (K. and V.); AgA', large tables (K. and V.).

The following salts with organic bases are described by Norton and Otten (*l.c.*): NH₄(CH₃)C₆H₄SO₃, rosettes, m.p. 128°; NH(CH₃)C₆H₄SO₃, m.p. 78°; N(CH₃)C₆H₄SO₃, m.p. 92°; NH₄(C₂H₅)C₆H₄SO₃, m.p. 111°; NH(C₂H₅)C₆H₄SO₃, m.p. 85°; N(C₂H₅)C₆H₄SO₃, m.p. 65°.

Chloride; rhombic tablets or triclinic crystals (Otto and Köbig, Ber. 1888, 19, 1835), m.p. 69°, b.p. 145°-146°/15 mm. (Krafft and Roos, Ber. 1892, 25, 2259), 136°-1°/11 mm., 151°-6°/20 mm. (Bourgeois, Rec. trav. chim. 1899, 18, 436), 164°/33 mm. (Davies, Chem. Soc. Trans. 1921, 119, 878), 80°/0 mm. (Krafft and Wilke, l.c.). On warming with alkaline solutions, or better, by boiling with 80 p.c. sulphuric acid, it yields *o*-chloro-toluene (Ges. für. Chem. Ind., D. R. P. 133000 of 1901). Toluene *p*-sulphonyl chloride when heated with ethylene chlorohydrin yields β -chloroethyltoluene *p*-sulphonate, b.p. 210°/21 mm., which is a valuable reagent for introducing the chloroethyl-group into amines and phenols (Clemo and W. H. Perkin, Chem. Soc. Trans. 1922, 121, 642; B. D. C., W. H. Parkin and Clemo, Eng. Pat. 193618 of 1922).

Toluene *p*-sulphonyl chloride when treated at 70°-75° with antimony pentachloride yields a mixture of the 2:6-di- and 2:3:6-trichloro-derivatives, converted on hydrolysis into the corresponding sulphonic acids, or, on removing the acyl-group into a mixture of 2:6-di- and 2:3:6-trichlorotoluene (Geigy & Co., D. R. P. 210856 of 1908). When electrolysed in 2*N*. alcoholic hydrochloric acid solution it yields as the main product, the corresponding sulphonic acid, which is partially converted into its ethyl-ester, and decomposed thus:



In the presence of titanium trichloride using a nickel gauze cathode, the main product is *p*-tolyl mercaptan, which is also produced by reducing a suspension of the sulphonyl chloride in aqueous sulphuric acid at 80° at a lead cathode (Fichter and Bernouilli, Zeitsch. Elektrochem. 1907, 13, 310). Toluene *p*-sulphonyl chloride on nitration on the water-bath with fuming nitric and concentrated sulphuric acids yields 2:6-dinitrotoluene 4-sulphonic acid in almost theoretical yield (Reverdin and Crépieux, Ber. 1901, 34, 2992).

Bromide; from toluene *p*-sulphonic acid and bromine. Monoclinic prisms, m.p. 96° (Otto, Ann. 1867, 142, 98) or 93°-94° (Zincke and Frohberg, Ber. 1910, 43, 837).

Iodide; from sodium toluene *p*-sulphinate and iodine. Yellow powder, m.p. 84°-85°. By heating with water or alcohol it is decomposed into toluene *p*-sulphonic acid, iodine and little *p*-toluene disulphoxide, whilst by heating with potassium hydroxide it yields toluene *p*-sulphonic acid. Zinc-ethyl yields the zinc sulphinate (Otto and Trüger, Ber. 1891, 24, 479).

Ethyl ester; from the chloride (Jaworski, Zeit. f. chem. 1865, 1221) or the bromide (Otto, Ann. 1867, 142, 100); by treating the ethyl ester of toluene *p*-sulphonic acid with potassium permanganate and acetic acid (Otto and Rössing, 1890, 19, 1236). Monoclinic crystals, m.p. 32°-33°, b.p. 73°/15 mm., $D_{20}^{25} 1.1736$, $n_D^{20} 1.5776$ (Krafft and Roos, Ber. 1892, 25, 2259).

The phenyl, *o*-, *m*-, and *p*-tolyl esters melt at 95°-96°, 54°-55°, 51°, and 69°-70° respectively (Reverdin and Crépieux, Bull. Soc. chim. 1901, (3) 25, 1044; 1902, (3) 27, 741; Ber. 1902, 35, 214, 1422). For other esters, see Reverdin and Crépieux (l.c.); Bamberger and Rietz (Ber. 1901, 34, 338). For the use of

methyl- and ethyl-toluene *p*-sulphonates as alkylating agents, see Ullmann and Wenner (Ann. 1903, 327, 120); Finzi (Annali. Chim. Appl., 1925, 15, 41).

Anhydride; formed together with the chloride by heating toluene *p*-sulphonic acid with pure thionyl chloride. Crystals, m.p. 122°-125° (Meyer and Schlegel, Monatsh. 1913, 34, 561).

Amide; leaflets, m.p. 137°-137.5° (Claesson and Wallin, Ber. 1879, 12, 1853; McKie, Chem. Soc. Trans. 1918, 113, 799). It forms a potassium salt, $C_6H_4SO_3NHK$ (Wolkoff, Ber. 1872, 5, 140; Zeit. f. Chem. 1870, (2) 6, 323, 580). **Methylamide**, m.p. 76°-77°; **ethylamide**, m.p. 64°; **dimethylamide**, m.p. 76°; **diethylamide**, m.p. 59°-60°; **anilide**, m.p. 103°; **methylanilide**, m.p. 95°; **ethylanilide**, m.p. 88°; ***p*-toluidide**, m.p. 118° (van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1902, 616; cf. Rec. trav. chim. 1884, 3, 7; Jaeger, Proc. K. Akad. Wetensch. Amsterdam, 1920, 23, 347; Remsen and Palmer, Amer. Chem. J. 1886, 8, 241; Marckwald and von Droste-Hulshoff, Ber. 1898, 31, 3262; 1899, 32, 561; D. R. P. 105870 of 1897); **propylamide**, m.p. 52° (Marckwald, Ber. 1899, 32, 3509); **propylisobutylamide**, m.p. 59° (M.); **bromoallylamide**, m.p. 45°-46° (Rudziak, Ber. 1901, 34, 3543); **benzylamide**, m.p. 116° (Chattaway, Chem. Soc. Trans. 1905, 87, 145); **benzylmethylamide**, m.p. 95° (Holmes and Ingold, Chem. Soc. Trans. 1925, 127, 1813); **anilide**, m.p. 103° (R. and P.); **3-iodoanilide**, m.p. 128° (Ullman, Ann. 1904, 332, 38); **2:4-dinitroanilide**, m.p. 219°; ***o*-toluidide**, m.p. 108°, on nitration yields the 5-nitro-*o*-toluidide, and a little 3-nitro-*o*-toluidide and 3:5-dinitro-*o*-toluidide, which, on hydrolysis, yield 5-nitro-*o*-toluidine, 3-nitro-*o*-toluidine, and 3:5-dinitro-*o*-toluidine, respectively; ***m*-toluidide**, m.p. 114°; ***p*-toluidide**, m.p. 117°, on nitration yields the 3-nitro-*p*-toluidide; ***p*-phenetide**, m.p. 106°-107°; the amides with *o*-, *m*-, and *p*-phenylenediamine melt at 201°-202°, 172° and above 250°, respectively; ***di-p*-toluene-sulphonbenzide**, m.p. 243°, and its **dimethyl-derivative**, m.p. 235° (Reverdin and Crépieux; Willstätter and Kalb, Ber. 1904, 37, 3761). For other derivatives, see Esch and Marckwald (Ber. 1900, 33, 762); Howard and Marckwald (l.c.); von Meyer (J. pr. Chem. 1901, 63, 167). For *N*-halogen derivatives of the amides see Chattaway (Chem. Soc. Trans. 1905, 87, 145).

Benzylsulphonic acid; by oxidising benzyl disulphide with nitric acid (Barbaglia, Ber. 1872, 5, 270, 688); by boiling benzyl chloride with aqueous potassium or sodium sulphite (Böhler, Ann. 1870, 154, 50; 1883, 221, 216; Mohr, ibid. 1883, 221, 216; Otto and Lüden, Ber. 1890, 13, 1286); by heating benzyl methyl ketone with sulphuric acid (Krocker, Ber. 1888, 19, 2625). Very hygroscopic crystals. The potassium salt when heated with phosphorus pentachloride yields benzotrichloride; with potassium cyanide it yields benzyl cyanide (Barbaglia, l.c.), and on fusion with potassium hydroxide it yields toluene and benzoic acid (Otto, Ber. 1890, 13, 1288).

NH_4A' ; $KA' + H_2O$, rhombic, m.p. 104°; $CaA' + 2H_2O$, crystalline scales; $FeA' + 2H_2O$, $PbA' + Pb(OH)_2$, crystalline powder.

tate; PbA' , plates; AgA' , crystalline scales (Böhler, *l.c.*).

The *o*-chloro-derivative, obtained by treating *o*-chlorobenzyl chloride with sulphites, forms a dinitro-derivative whose calcium salt forms needles. The free acid on heating with ammonia at 135° – 140° yields a nitroaminohydroxybenzyl sulphonic acid (Kalle and Co., D. R. P. 141783 of 1902).

Chloride; prisms, m.p. 92° . Decomposes on heating into benzyl chloride and sulphur dioxide (Pechmann, Ber. 1873, 6, 534; Otto and Lüders, Ber. 1880, 13, 1286).

Amide; small prisms, m.p. 102° (O. and L.) or 105° (P.).

(a) *Toluene 2:4-disulphonic acid*; by sulphonation of toluene, toluene-*o*- or *p*-sulphonic acid (Hakansson, Ber. 1872, 5, 1085; Claesson and Berg, *ibid.* 1880, 13, 1170; Gnehm and Forrer, *ibid.* 1877, 10, 542, 1276; Klason, *ibid.* 1887, 20, 354; Senhofer, Ann. 1872, 164, 126); by the action of iodine and potassium iodide on potassium toluene disulphinate (Tröger and Meine, J. pr. Chem. 1903, (2) 68, 313); by heating toluene *p*-sulphonyl chloride with sulphuric acid (Fahlberg, Ber. 1879, 12, 1052; Amer. Chem. J. 1879, 1, 170; 1880, 2, 182); from *p*-toluidine 2-sulphonic acid and *o*-toluidine 4-sulphonic acid by the xanthate method (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 754).

$(\text{NH}_4)_2\text{A}'' + \text{H}_2\text{O}$; $\text{K}_2\text{A}'' + \text{H}_2\text{O}$; $\text{BaA}'' + \text{H}_2\text{O}$, silky needles (W. and B.) or $\text{BaA}'' + (?)2\text{H}_2\text{O}$, prisms (H.); $\text{ZnA}'' + 8\text{H}_2\text{O}$; $\text{CuA}'' + 8\text{H}_2\text{O}$, four-sided prisms; $\text{As}_2\text{A}'' + 2\text{H}_2\text{O}$ (Senhofer).

Chloride; elongated prisms or prismatic needles, m.p. 56° (W. and B.) or 51° – 52° (H.).

Bromide; white solid, m.p. 78° (Tröger and Meine).

Amide; prisms, m.p. 185° – 186° . On oxidation with potassium permanganate it yields disulphaminobenzoic acid (Fahlberg).

Anilide; small prisms or tufts of needles, m.p. 187° (W. and B.).

o-Toluidide; m.p. 170° – 171° (T. and M.).

m-Toluidide; m.p. 138° (T. and M.).

(β) *Toluene 2:5-disulphonic acid*; by sulphonation of toluene; by heating toluene *o*-sulphonic acid with fuming sulphuric acid at 160° (Hakansson, *l.c.*), or toluene *m*-sulphonic acid with sulphuric acid at 180° (Klason, *l.c.*); from *o*-toluidine 5-sulphonic acid by replacing the amino-group by a mercaptan group and oxidising the thiocresol sulphonic acid obtained with permanganate (Klason, Ber. 1887, 20, 354); from *p*-toluidine 2:5-disulphonic acid by conversion into the hydrazine and treatment of the latter with copper sulphate, or from *o*-toluidine 5-sulphonic acid by the xanthate method (Wynne and Bruce).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$; $\text{BaA}'' + \text{H}_2\text{O}$.

Chloride; four-sided plates or prisms, m.p. 98° (W. and B.).

Amide; microscopic prisms, m.p. 224° (K.).

Anilide; slender prismatic needles, m.p. 178° (W. and B.).

(c) *Toluene 2:6-disulphonic acid*; by reduction of 4-bromo- or 4-chlorotoluene 2:6-disulphonic acid with sodium amalgam (Kornatzki, Ann. 1883, 221, 199; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 771).

$\text{K}_2\text{A}''$, anhydrous flat prisms; $\text{BaA}'' + 2\text{H}_2\text{O}$,

rhombs (above 50°), or $+4\text{H}_2\text{O}$, flat needles (below 50°).

Chloride; monoclinic prisms, m.p. 88° .

Amide; long slender needles, melting above 260° (Kornatzki).

Anilide; minute diamond-shaped prisms, m.p. 162° (W. and B.).

Toluene 3:4-disulphonic acid; from *p*-toluidine 3-sulphonic acid by conversion into *p*-thiocresol 3-sulphonic acid and oxidation of the latter with potassium permanganate (Klason Ber. 1887, 20, 356), or by diazotisation, treatment with potassium xanthate, saponification and oxidation with potassium permanganate (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 751).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, needles; $\text{BaA}'' + 2\text{H}_2\text{O}$, prisms.

Chloride; scales, m.p. 111° , or prismatic crystals, m.p. 70° – 80° , from benzene, containing benzene of crystallisation, which is lost rapidly on exposure to air when the melting-point rises to 111° (Klason; Wynne and Bruce).

Amide; m.p. 235° – 239° (slight decomp.) (Klason).

Anilide; small prisms or clusters of minute plates, m.p. 190° (W. and B.).

(γ or δ) *Toluene 3:5-disulphonic acid*; from *o*-toluidine 3:5-disulphonic acid by conversion into the hydrazine and treatment with copper sulphate (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 748); together with the 2:5-acid by sulphonation of toluene *m*-sulphonic acid (Klason, Ber. 1886, 19, 2889; 1887, 20, 352); by treatment of *p*-iodotoluene disulphonic acid with sodium amalgam (Limpricht and Richter, Ber. 1885, 18, 2179; Richter, Ann. 1885, 230, 326).

$\text{K}_2\text{A}''$, anhydrous microscopic scales; $\text{BaA}'' + 3\frac{1}{2}\text{H}_2\text{O}$, small scales, becoming anhydrous on exposure to air (W. and B.). The product obtained by Richter is the 3:5-disulphonic acid and not the 2:6- or 2:3- isomeride, as he was led to believe from the experiments of Hasse (Ann. 1885, 230, 286), whilst the compound described by Hasse is not the 3:5-acid.

Chloride; pale yellow prismatic crystals, m.p. 95° (W. and B.) (Hasse gives m.p. 132°).

Amide; short prisms, m.p. 214° (K.) or 216° (R.) (Hasse gives m.p. above 230°).

Anilide; thin scales, m.p. 153° (W. and B.).

Toluene 2:4:6-trisulphonic acid; by heating 1 mol. of potassium toluene 2:4-disulphonate with 3 mols. of chlorosulphonic acid at 240° . The product is converted, *via* the barium and potassium salts, into the sulphonyl chloride, which is then heated with 12 parts of water at 130° – 140° .

Long slender needles $+6\text{H}_2\text{O}$, which lose $3\text{H}_2\text{O}$ at 100° and melt at 145° .

$\text{KA}''' + 3\frac{1}{2}\text{H}_2\text{O}$, large rhombic tables; $\text{Ba}_2\text{A}_2''' + 14\text{H}_2\text{O}$; $\text{Pb}_2\text{A}_2''' + 8\text{H}_2\text{O}$, amorphous crystals (Klason, Ber. 1881, 14, 307).

Chloride; tables, m.p. 153° (K.).

Amide; microscopic crystals, m.p. above 300° (K.).

4-Fluorotoluene 2-sulphonic acid; from *p*-toluidine 2-sulphonic acid.

$\text{KA}' + 2\text{H}_2\text{O}$, large scales; $\text{BaA}' + \text{H}_2\text{O}$, small scales.

Chloride; oil, b.p. 145° – $150^{\circ}/20$ mm.

Amide; large prisms or long white needles, m.p. 140° or 155° . When oxidised with per-

manganate it yields *p*-chlorobenzoic sulphinide, 'fluoraccharin,' colourless needles or rhombs, m.p. 200°, which is very sweet but has a somewhat bitter after-taste (Roode, Amer. Chem. J. 1891, 13, 219; Holleman, Rec. trav. chim. 1906, 25, 330).

p-Chlorotoluene on sulphonation yields chiefly 4-chlorotoluene 3-sulphonic acid together with 4-chlorotoluene 2-sulphonic acid (Wynne, Chem. Soc. Trans. 1892, 61, 1082; Wynne and Bruce, Chem. Soc. Proc. 1895, 11, 152; Vogt and Henninger, Ann. Chim. 1865, (4) 27, 133; Ann. 1873, 165, 362), whilst toluene *o*-sulphonic acid or its soluble salts when chlorinated in cold aqueous solution yields a mixture of 4- and 6-chlorotoluene *o*-sulphonic acids. The latter mixture is readily separable owing to the much greater insolubility of the salts of the 4-chloro-acid. Chlorination in more dilute solution at a temperature not exceeding 60° yields a mixture of dichloro- and trichlorotoluene *o*-sulphonic acids (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920).

On disulphonation with 20 p.c. fuming sulphuric acid *p*-chlorotoluene yields a mixture of the 2:6- and 2:5-disulphonic acids in the proportion of about 3 parts of the former to 1 part of the latter, together with some of the 3:5-disulphonic acid. A similar mixture is obtained also when 4-chlorotoluene 2-sulphonic acid is treated in this manner (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 768).

3-Chlorotoluene *o*-sulphonic acid; from *m*-chlorotoluene and 100 p.c. sulphuric acid.

$\text{NaA}' + \text{H}_2\text{O}$, monosymmetric rhombs; KA' , monosymmetric rhombs; $\text{BaA}'_2 + \text{H}_2\text{O}$, small nacreous plates (Wynne, Chem. Soc. Trans. 1892, 61, 1075).

Chloride; orthorhombic prisms, m.p. 53° (W.).

Amide; thin scales, m.p. 182° (W.).

4-Chlorotoluene 2-sulphonic acid; sulphonation of *p*-chlorotoluene (above) or chlorination of toluene *o*-sulphonic acid (above); from *p*-toluidine 2-sulphonic acid by the diazo-reaction (Jonsen, Ann. 1874, 172, 239; Roode, Amer. Chem. J. 1891, 13, 221; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 761; cf. Wynne, *ibid.* 1892, 61, 1078).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, rectangular scales; KA' , anhydrous prismatic needles (W. and B.; R.), $+ \text{H}_2\text{O}$ (Hübner and Majert, Ber. 1873, 6, 793); $\text{BaA}'_2 + \text{H}_2\text{O}$, microscopic plates (H. and M.), or prismatic aggregates (W. and B.; Jonsen); $\text{CaA}'_2 + 6\text{H}_2\text{O}$ (H. and M.); $\text{PbA}'_2 + 8\text{H}_2\text{O}$ (H. and M.); $\text{CuA}'_2 + 7\text{H}_2\text{O}$ (H. and M.).

Chloride; large four-sided elongated plates, m.p. 24° (W. and B.).

Amide; slender needles, m.p. 142° (W. and B.; Heffter, Ann. 1883, 221, 209, gives m.p. 128°).

Anilide; monosymmetric plates, m.p. 144° (W. and B.).

When oxidised with potassium permanganate it yields *p*-chlorobenzoic sulphinide, pearly scales, m.p. 218°, with a sweet taste but bitter after-taste (R.). On heating at 150° with 20 p.c. fuming sulphuric acid the free acid yields a mixture of the 2:5- and 2:6-disulphonic acids in the approximate proportions of 1:3 (W. and B.).

4-Chlorotoluene 3-sulphonic acid; by sul-

phonation of *p*-chlorotoluene (Vogt and Henninger, *l.c.*); from *p*-toluidine 3-sulphonic acid by diazotisation and treatment with cuprous chloride (Wynne and Bruce, *l.c.*).

$\text{NaA}' + \text{H}_2\text{O}$, long needles or flat prisms (Wynne); $\text{NaA}' + 5\text{H}_2\text{O}$ (Hübner and Majert, *l.c.*); $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$ (Wynne), $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, laminae, $\text{KA}' + \text{H}_2\text{O}$, rectangular plates or prismatic needles (W. and B.); $\text{BaA}'_2 + \frac{1}{2}\text{H}_2\text{O}$ (H. and M.), $\text{BaA}'_2 + \text{H}_2\text{O}$, thin scales, $\text{BaA}'_2 + 2\text{H}_2\text{O}$, rectangular prisms (W. and B.), $\text{BaA}'_2 + 7\text{H}_2\text{O}$ (Engelbrecht, Ber. 1874, 7, 796); $\text{CdA}'_2 + 2\text{H}_2\text{O}$; $\text{PbA}'_2 + 6\text{H}_2\text{O}$; $\text{CuA}'_2 + 10\text{H}_2\text{O}$. When heated with 20 p.c. fuming sulphuric acid at 150° it yields a mixture of the 2:5- and 3:5-disulphonic acids.

Chloride; large elongated hexagonal plates, m.p. 56° (W. and B.).

Amides; spear-shaped crystals, m.p. 156° (W. and B.).

Anilide; small monosymmetric prisms or needles, m.p. 188° (W. and B.).

6-Chlorotoluene 2-sulphonic acid; non-deliquescent laminae, m.p. about 72°, is obtained from the sulphonyl chloride which is produced in a yield of 38.6 p.c., together with other isomerides, by chlorinating toluene *o*-sulphonyl chloride at 75°-90° in presence of antimony pentachloride.

$\text{NaA}' + \text{H}_2\text{O}$, large laminae; $\text{BaA}'_2 + \text{H}_2\text{O}$, small lustrous flakes.

Chloride; large thick white prisms or plates, softening at 71°, m.p. 72°.

Amide; glistening scales, m.p. 180°. On oxidation with alkaline permanganate at 96°-97° in the presence of carbon dioxide, it yields 6-chloro-*o*-benzoic sulphinide ('6-chloro-saccharin'), small plates, m.p. 210°-212°. The latter product is more than half as sweet as saccharin, but has a somewhat astringent taste except in very great dilution (Davies, Chem. Soc. Trans. 1921, 119, 878).

6-Chlorotoluene 3-sulphonic acid; from *o*-chlorotoluene and fuming sulphuric acid (Hübner and Majert, *l.c.*; Wynne, Chem. Soc. Trans. 1892, 61, 1073); from *o*-toluidine 5-sulphonic acid by the diazo-reaction (Wynne, *l.c.*, 1040). It crystallises with $\frac{1}{2}\text{H}_2\text{O}$.

$\text{NH}_4\text{A}' + \text{H}_2\text{O}$; $\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, thin plates; $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, large quadrate tables or scales; $\text{CaA}'_2 + 2\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, leaflets or long thin prisms; $\text{PbA}'_2 + 2\text{H}_2\text{O}$; $\text{CuA}'_2 + \frac{1}{2}\text{H}_2\text{O}$.

The potassium salt on sulphonation with 20 p.c. fuming sulphuric acid at 150° yields *o*-chlorotoluene 3:5-disulphonic acid, which is also produced by sulphonating *o*-chlorotoluene under similar conditions.

Chloride; long, pearly prisms, m.p. 60° or 65°.

Bromide; thin flat prisms, m.p. 67.5°.

Amide; thin glistening scales, m.p. 128°.

Anilide; thin irregular scales or anorthic plates, m.p. 92° (Wynne, *l.c.*; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 731).

2-Chlorotoluene 4-sulphonic acid; from *o*-toluidine 4-sulphonic acid by diazotisation and treatment with cuprous chloride (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 764); by hydrolysis of the amide with hydrochloric acid at 150° (Payson, Ann. 1883, 221, 213).

$\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, large hexagonal (W. and B.) or anhydrous pearly leaflets (P.

small scales; $\text{BaA}'_2 + \text{H}_2\text{O}$, thin scales (W. and B.), anhydrous (P.); CaA'_2 , glistening rhombic leaflets (P.).

Chloride; long massive prisms, m.p. 37° , b.p. $178^\circ/36$ mm. (W. and B.; Davies, Chem. Soc. Trans. 1921, 119, 860).

Amide; in the usual manner (W. and B.) or by treating the sulphonamide of diazoaminotoluene with hydrochloric acid (P.). Long slender needles, m.p. 137° (Davies).

Anilide; rhomb-shaped plates, m.p. 96° (W. and B.).

On sulphonation with 35 p.c. fuming sulphuric acid at 150° potassium *o*-chlorotoluene 4-sulphonate yields a mixture of the 4:5- and 4:6-disulphonic acids (W. and B.).

2:3-Dichlorotoluene sulphonic acid; 2:3-dichlorotoluene is stated by Wynne and Greeves (Chem. Soc. Proc. 1895, 11, 151) and Wynne (Chem. Soc. Trans. 1892, 61, 1045) to yield two sulphonic acids on sulphonation, which are separated by their barium salts. The acid from the less soluble barium salt yields a very soluble *chloride*, radiating needles, m.p. 45° , and an *amide*, m.p. 221° , whilst that from the more soluble barium salt is the 5-sulphonic acid, and yields a *chloride*, prisms, m.p. 85° , *amide*, m.p. 183° . Cohen and Dakin (Chem. Soc. Trans. 1901, 79, 1129) could only isolate one sulphonic acid, forming the sulphonamide, m.p. 222° .

$\text{NaA}' + \text{H}_2\text{O}$, large pearly leaflets; $\text{CaA}'_2 + \text{H}_2\text{O}$, leaflets; $\text{BaA}'_2 + \text{H}_2\text{O}$, leaflets (Seelig, Ann. 1887, 237, 159).

2:4-Dichlorotoluene 5-sulphonic acid; by sulphonation of 2:4-dichlorotoluene.

$\text{NaA}' + 1\frac{1}{2}\text{H}_2\text{O}$, long thin needles; $\text{CaA}'_2 + 3\text{H}_2\text{O}$, long thin needles; $\text{BaA}'_2 + 2$ or $4\text{H}_2\text{O}$ (Seelig; Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151; Cohen and Dakin).

Chloride; elongated scales or hard prisms, m.p. 71° (W. and G.; C. and D.); *amide*, m.p. 176° – 177° (W. and G.; C. and D.).

2:5-Dichlorotoluene *p*-sulphonic acid; (see 2:3:6-trichlorotoluene *p*-sulphonic acid): by chlorination of toluene *p*-sulphonic acid (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920). *Chloride* is formed together with 2:6-dichlorotoluene *p*-sulphonyl chloride by chlorination of 2-chlorotoluene *p*-sulphonyl chloride (Davies, Chem. Soc. Trans. 1921, 119, 874).

2:5-Dichlorotoluene sulphonic acid; by sulphonation of 2:5-dichlorotoluene.

KA' , long needles which break up into a crystalline powder; $\text{NaA}' + 1\frac{1}{2}\text{H}_2\text{O}$, long slender needles; $\text{BaA}'_2 + \text{H}_2\text{O}$, diamond-shaped plates and large prismatic needles (Wynne, l.c.).

Chloride; brownish coloured tables, m.p. 43° (W.) or colourless plates, m.p. 46° (C. and D.).

Amide; long thin flat needles, m.p. 191° – 192° (W.; C. and D.; cf. Seelig, Ann. 1887, 237, 159).

2:6-Dichlorotoluene *p*-sulphonic acid; colourless deliquescent plates.

$\text{NaA}' + \text{H}_2\text{O}$, colourless fan-like needles; $\text{BaA}'_2 + 3\text{H}_2\text{O}$, minute silky needles.

Chloride; by chlorinating at 65° – 70° a fused mass of 2-chloro-*p*-toluene sulphonyl chloride for 2 hours until the necessary increase in weight has been attained. Large flat plates, m.p. 69° . A substance, hair-like colourless needles, m.p. 218° , apparently pentachlorotoluene, is obtained as a by-product.

Amide; scales, m.p. 191° (Davies, Chem. Soc. Trans. 1921, 119, 871).

2:6-Dichlorotoluene sulphonic acid; by sulphonation of 2:6-dichlorotoluene.

Chloride; prismatic needles, m.p. 60° .

Amide; m.p. 204° (Wynne and Greeves, l.c.; cf. Cohen and Dakin, l.c.).

3:4-Dichlorotoluene sulphonic acid; from 3:4-dichlorotoluene and 5 p.c. fuming sulphuric acid.

KA' , long thin prismatic needles; NaA' , long slender brittle needles; $\text{BaA}'_2 + 2(?)\text{H}_2\text{O}$, long slender needles.

Chloride; long monosymmetric prisms, m.p. 82° .

Amide; elongated prisms, m.p. 189° (Wynne, Chem. Soc. Trans. 1892, 61, 1060) or 190° – 191° (Cohen and Dakin, l.c.).

3:5-Dichlorotoluene sulphonic acid; by sulphonation of 3:5-dichlorotoluene.

Chloride; thick prisms, m.p. 45° .

Amide; needles, m.p. 168° – 169° (Wynne and Greeves; Cohen and Dakin).

2-Chlorotoluene 3:5-disulphonic acid; by sulphonating 2-chlorotoluene 5-sulphonic acid and from *o*-toluidine 3:5-disulphonic acid by the diazo-reaction. Very small needles.

$\text{K}_2\text{A}'' + 2\frac{1}{2}\text{H}_2\text{O}$, massive irregular crystals, or $+2\text{H}_2\text{O}$, small needles; $\text{BaA}'' + 4\frac{1}{2}\text{H}_2\text{O}$, minute needles.

Chloride; short slender needles, m.p. 85° .

Anilide; small elongated flat prisms, m.p. 183° (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 750).

2-Chlorotoluene 4:5-disulphonic acid; by sulphonation of potassium *o*-chlorotoluene-4-sulphonate and from *o*-toluidine 4:5-disulphonic acid by the diazo-reaction.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, long prismatic needles; $\text{BaA}'' + 2\text{H}_2\text{O}$, small rectangular prisms (W. and B.).

Chloride; plates or monosymmetric prisms, m.p. 158° .

Anilide; small prisms, m.p. 183° (W. and B.).

2-Chlorotoluene 4:6-disulphonic acid; from 2-chlorotoluene 4-sulphonic acid and 35 p.c. fuming sulphuric acid at 150° .

$\text{K}_2\text{A}'' + 2\text{H}_2\text{O}$, large prisms; $\text{BaA}'' + 6\text{H}_2\text{O}$, microscopic prisms; $\text{BaA}'' \cdot \text{K}_2\text{A}'' + 3\text{H}_2\text{O}$, very small needles.

Chloride; octahedral prisms or four-sided plates, m.p. 88° .

Anilide; small plates, m.p. 180° (W. and B.).

4-Chlorotoluene 2:5-disulphonic acid; from *p*-toluidine 2:5-disulphonic acid. Small scales.

$\text{K}_2\text{A}'' + 2\text{H}_2\text{O}$, small scales; $\text{BaA}'' + \text{H}_2\text{O}$, minute prisms.

Chloride; very small prisms, m.p. 144° .

Anilide; small diamond-shaped scales or large prisms, m.p. 245° (W. and B.).

4-Chlorotoluene 2:6-disulphonic acid; by sulphonation of 4-chlorotoluene 2-sulphonic acid with 20 p.c. fuming sulphuric acid at 150° .

$\text{K}_2\text{A}''$, anhydrous scales; $\text{BaA}'' + 3\frac{1}{2}\text{H}_2\text{O}$, small prisms.

Chloride; large prisms or large pale-yellow monosymmetric plates, m.p. 108° .

Anilide; small lustrous scales, m.p. 188° (W. and B.).

4-Chlorotoluene 3:5-disulphonic acid; from *p*-toluidine 3:5-disulphonic acid. Long colourless needles.

$\text{K}_2\text{A}'' + 6\text{H}_2\text{O}$, long thin needles, which

rapidly becomes anhydrous on exposure to air; $\text{BaA}'' + 3\text{H}_2\text{O}$, prisms.

Chloride; small monosymmetric prisms from benzene, containing $\frac{1}{2}\text{O}_2\text{H}_2$, which is lost rapidly at 140° , or plates from light petroleum. Both forms melt at 118° with previous softening (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 740; Pope, Z. f. Krist., 1900, 31, 128).

2:3:4-Trichlorotoluene; when shaken with fuming sulphuric acid at 60° yields two sulphonic acids, α -acid, $\text{NaA}' + 4\frac{1}{2}\text{H}_2\text{O}$, fine needles or leaflets, and the β -acid, $\text{NaA}' + \text{H}_2\text{O}$, leaflets (Seelig, Ann. 1887, 237, 136).

2:3:6-Trichlorotoluene 4-sulphonic acid; obtained together with the 2:5-dichloro-isomeride by neutralising 680 grams of toluene *p*-sulphonic acid with sodium hydroxide dissolved in sufficient water to make about 11 litres and chlorinating until 10 c.c. of the solution have acquired an acidity equivalent to 5.5 c.c. of N-alkali. Nearly the whole of the sodium trichlorosulphonate crystallises, and the dichloro-sulphonate is recovered practically pure by evaporating the mother-liquor (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920).

3:4:5-Trichlorotoluene sulphonic acid; $\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, needles; KA' , scales; $\text{BaA}'_2 + \text{H}_2\text{O}$, scales.

Chloride; short needles, m.p. 88° (Wynne, Chem. Soc. Trans. 1892, 61, 1069).

2-Bromotoluene 4-sulphonic acid; from *o*-toluidine 4-sulphonic acid by the diazo-reaction (Hayduck, Ann. 1874, 172, 205); together with *p*-bromotoluene and *p*-bromobenzyl bromide by brominating potassium toluene *p*-sulphonate (Miller, Chem. Soc. Trans. 1892, 61, 1027).

KA' , white plates (M.); $\text{BaA}'_2 + 2\text{H}_2\text{O}$, plates (M.) or microscopic tables (H.);

$\text{PbA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$ (H.).

Chloride; m.p. 54° (H.).

Amide; microscopic prisms, m.p. 151° (H.).

2-Bromotoluene 5-sulphonic acid; from *o*-bromotoluene by sulphonation (Miller, Chem. Soc. Trans. 1892, 61, 1029; Hübner and Post, Ann. 1873, 169, 31; cf. Dmochowsky, Ber. 1872, 5, 333); from brominated *p*-toluidine 3-sulphonic acid by elimination of the amino-group (Pechmann, Ann. 1874, 173, 212); from *o*-toluidine by sulphonation and replacement of the amino-group by bromine (Pagel, Ann. 1875, 176, 394; Neville and Winther, Chem. Soc. Trans. 1880, 37, 628; Ber. 1880, 13, 1943; Wynne, Chem. Soc. Trans. 1892, 61, 1041; cf. Gerver, Ann. 1873, 169, 384).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, striated prisms; $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, rhomboidal tables; $\text{PbA}'_2 + 2\text{H}_2\text{O}$ (H. and P.) or $3\text{H}_2\text{O}$ (P.).

Chloride; elongated flat prisms, m.p. 61° (W.), 56° (N. and W.), 53° (P.).

Bromide; glistening scales, m.p. 63.5° (W.).

Amide, needles, m.p. 147° (W.; N. and W.) or 135° (P.).

2-Bromotoluene 6-sulphonic acid; in small yield, together with 2-bromotoluene 5-sulphonic acid by sulphonating *o*-bromotoluene. The two acids are separated by means of their barium salts, when the barium salt of the 5-acid crystallises first.

KA' ; $\text{BaA}'_2 + \text{H}_2\text{O}$, minute scales (Miller, l.c.).

According to Wroblewsky (Ann. 1873, 188, 186), *m*-bromotoluene when dissolved in fum.

sulphuric acid yields three sulphonic acids of which the α -acid is formed in greatest quantity. Separation is effected by means of their barium salts.

Grete (Ber. 1874, 7, 795; 1875, 8, 565; Ann. 1875, 177, 233) only obtained one acid corresponding to the α -acid of Wroblewsky.

α -Acid or 3-bromotoluene 2-sulphonic acid; $\text{BaA}'_2 + \text{H}_2\text{O}$; $\text{CaA}'_2 + 2\text{H}_2\text{O}$; $\text{SrA}'_2 + \text{H}_2\text{O}$; $\text{MgA}'_2 + 6\text{H}_2\text{O}$; $\text{PbA}'_2 + 3\text{H}_2\text{O}$; $\text{CuA}'_2 + 4\text{H}_2\text{O}$.

β -Acid or 3-bromotoluene 6-sulphonic acid; KA' ; $\text{CaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$; $\text{PbA}'_2 + 3\text{H}_2\text{O}$.

γ -Acid; formed in smallest quantity; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$.

m-Bromotoluene *o*-sulphonic acid; by bromination of *p*-toluidine 2-sulphonic acid, followed by elimination of the amino-group (Weckwarth, Ann. 1874, 172, 191).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, scales or nodules; $\text{KA}' + \text{H}_2\text{O}$, yellow rhombic plates; $\text{SrA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, yellow needles; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, scales or plates; $\text{PbA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, grouped prisms; $\text{PbA}'_2 + 5\text{H}_2\text{O}$, yellow prisms; $\text{CuA}'_2 + \frac{1}{2}\text{H}_2\text{O}$; yellowish-green plates or thick prisms.

Chloride; liquid, solidifying in a freezing mixture.

Amide; thick yellow needles from chloroform, m.p. 162° – 165° .

This acid appears to be identical with Wroblewsky's β -acid, although some of the salts differ in the content of water of crystallisation.

3-Bromotoluene 5-sulphonic acid; from 3-bromo-*o*-toluidine 5-sulphonic acid or 5-bromo-*p*-toluidine 3-sulphonic acid by elimination of the amino-group (Neville and Winther, Chem. Soc. Trans. 1880, 41, 420; Ber. 1880, 13, 1944).

Chloride; m.p. 52° (N. and W.).

Amide; m.p. 138° – 139° (N. and W.).

Bromotoluene sulphonic acid; from toluene by sulphonation, nitration, reduction and replacement of the amino-group by bromine (Weckwarth, Ann. 1874, 172, 193; Hayduck, *ibid.* 1875, 177, 57). $\text{BaA}'_2 + \text{H}_2\text{O}$.

Chloride; oil, solidifying on cooling.

Amide; nodules, which do not melt at 230° .

4-Bromotoluene 2-sulphonic acid; chief product, together with the 3-acid by sulphonating *p*-bromotoluene (Hübner and Post, Ann. 1873, 169, 6; Zeit. f. Chem. 1871, (2) 7, 618; Miller, Chem. Soc. Trans. 1892, 61, 1026) from *p*-toluidine 2-sulphonic acid by the diazo-reaction (Jensen, Ann. 1874, 172, 237). Free acid, large plates. Oxidised by chromic acid mixture to *p*-bromosulphobenzoic acid and reduced to toluene *o*-sulphonic acid by sodium amalgam.

$\text{NaA}' + \text{H}_2\text{O}$; $\text{KA}' + \text{H}_2\text{O}$, scales (Roode, Amer. Chem. J. 1891, 13, 222); $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$ (Miller); $\text{MgA}'_2 + 8\frac{1}{2}\text{H}_2\text{O}$ (?); $\text{CaA}'_2 + 4\text{H}_2\text{O}$, rhombic needles; $\text{SrA}'_2 + \text{H}_2\text{O}$; $\text{BaA}'_2 + \text{H}_2\text{O}$; $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (M.); $\text{PbA}'_2 + 3\text{H}_2\text{O}$, needles; $\text{PbA}'_2 + 2\text{H}_2\text{O}$ (M.); $\text{CuA}'_2 + 7\text{H}_2\text{O}$.

Chloride; plates, m.p. 35° (H. and P.).

Amide; long fine needles, m.p. 165° – 167° (H. and P.). When oxidised with permanganate it yields *p*-bromobenzoic sulphamide, which is somewhat sweet with a bitter after-taste (R.).

4-Bromotoluene 3-sulphonic acid; (see above); by sulphonation of *p*-bromotoluene; from *p*-toluidine 3-sulphonic acid by replacing the amino-group by bromine (K. Richter, Ann. 1873, 188, 186; Post and Reibey, *ibid.* 1874, 177, 57).

169, 7; Pechmann, *ibid.* 1874, 173, 208; Neville and Winther, Chem. Soc. Trans. 1880, 37, 631). Laminee + H_2O , m.p. $105^\circ\text{--}110^\circ$ (P.). Oxidation with chromic acid mixture yields *p*-bromobenzoic-*m*-sulphonic acid.

$\text{BaA}'_2 + 7\text{H}_2\text{O}$, long rhombic needles; $\text{SrA}'_2 + 7\text{H}_2\text{O}$; $\text{PbA}'_2 + 3\text{H}_2\text{O}$.

Chloride; oil, solidifying on keeping, m.p. 62° (P.; N. and W.).

Amide; long needles, m.p. $151^\circ\text{--}152^\circ$ (H. and P.).

2-Bromotoluene 3:5-disulphonic acid; from *o*-toluidine 3:5-disulphonic acid by the Sandmeyer reaction (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 749; Hasse, Ann. 1885, 230, 295).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, small needles; $\text{BaA}'' + 4\text{H}_2\text{O}$, short slender needles (W. and B.).

Chloride; white needles, m.p. 102° .

Anilide; small square prisms or irregular needles, m.p. 194° (W. and B.); the products obtained by Hasse were impure).

4-Bromotoluene disulphonic acid; by passing sulphur trioxide into a mixture of *p*-bromotoluene and sulphuric acid (Kornatzki, Ann. 1883, 221, 192). Very deliquescent crystals. On boiling with nitric acid it yields dibromonitrotoluene disulphonic acid, nitrotoluene disulphonic acid, and disulphobromobenzoic acid.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, fine needles or large rhombic prisms; $\text{BaA}'' + 5\text{H}_2\text{O}$, thick prisms or fine needles or plates; $\text{PbA}'' + 2\text{H}_2\text{O}$, glistening needles.

Chloride; large rhombic plates, m.p. 99° (K.).

Amide; irregular crystals, m.p. above 260° (K.).

p-Bromotoluene disulphonic acid; from *p*-toluidine disulphonic acid by replacement of the amino-group by bromine (Limpriht, Ber. 1885, 18, 2179; Richter, Ann. 1885, 230, 324). Crystalline mass.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, silky felted needles; $\text{BaA}'' + 6\text{H}_2\text{O}$, silky needles.

Chloride; prisms, m.p. 133° (R.).

Amide; long prisms, m.p. above 240° .

2:1-Dibromotoluene 5-sulphonic acid; from 2-bromotoluene 5-sulphonic acid by nitration and replacement of the nitro-group by bromine (Schäfer, Ann. 1874, 174, 365). Syrup.

$\text{NaA}' + 2\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$ (S.).

5:6-Dibromotoluene 3-sulphonic acid; from 3-bromo-*o*-toluidine 5-sulphonic acid by the Sandmeyer reaction (Wynne, Chem. Soc. Trans. 1892, 61, 1038).

$\text{NaA}' + \text{H}_2\text{O}$, long flat needles; KA' , long needles; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, long thin needles.

Chloride; small four-sided prisms or needles, m.p. 93° (W.).

Bromide; needles, m.p. 97° (W.).

Amide; small prisms, m.p. 214° (W.).

2:3:5-Tribromotoluene 4-sulphonic acid; from *o*-toluidine *p*-sulphonic acid by dibromination and replacement of the amino-group by bromine (Hayduck, Ann. 1874, 174, 354); or from 3:5-dibromo-*o*-toluidine 4-sulphonic acid by replacement of the amino-group by bromine (Claus and Immel, Ann. 1891, 265, 677). Free acid is deliquescent.

KA' , white needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, white mammillary mass (H.).

Chloride; syrup.

Amide; amorphous powder, charring without melting when heated.

2-(or 6)-Nitrotoluene 3-sulphonic acid; from *p*-toluidine *m*-sulphonic acid by nitration, reduction and elimination of the amino-group (Pechmann, Ann. 1874, 173, 214).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, plates.

Chloride, m.p. 58.5° (Foth, Ann. 1885, 230, 308).

Amide; m.p. 163.5° (F.).

2-Nitrotoluene 4-sulphonic acid; together with other products by nitrating *o*-nitrotoluene *p*-sulphonamide (Reverdin and Crépieux, Ber. 1901, 34, 2992); by sulphonating *o*-nitrotoluene or nitrating toluene *p*-sulphonic acid (Beilstein and Kuhlberg, Ann. 1871, 155, 18; Engelhardt and Bck, Zeit. f. Chem. 1869, (2) 5, 209; Kornatzki, Ann. 1883, 221, 180).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, scales; $\text{PbA}'_2 + 2\text{H}_2\text{O}$. On electrolysis in sulphuric acid solution it yields 6-amino-3-cresol 4-sulphonic acid (Gattermann, Ber. 1894, 27, 1938).

Chloride, by nitration of toluene *p*-sulphonyl chloride. M.p. 45° (van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1902, 616; cf. Otto and Grüber, Ann. 1868, 145, 23) or 36° (Reverdin and Crépieux). A suspension in alcoholic sulphuric acid is readily reduced at a lead electrode below 20° . The product is 2-aminotolyl-4-mercaptan sulphate which readily changes to the sulphate of 2-aminotolyl-4-disulphide on keeping in a loosely closed vessel (Fichter and Bernouilli, Ber. 1909, 42, 4308).

Amide; four-sided rhombic columns, m.p. 128° (O. and G.), 139° (K.), 144° (Reverdin and Crépieux, Ber. 1901, 34, 2992, 2996; Neale, Ann. 1880, 203, 73). When heated with fuming nitric acid two mononitrotoluene sulphonic acids, of which one is 2-nitrotoluene 4-sulphonic acid, and a dinitrotoluene sulphonic acid are obtained (Reverdin and Crépieux, *l.c.*).

For the preparation and properties of the *anilide*, *p*-toluidide, 2:4-dinitroanilide, α - and β -naphthalide, the diamide of *o*-, *m*-, and *p*-phenylenediamine; and also the esters of phenol, *o*-, *m*-, and *p*-cresol, *p*-nitrophenol, resorcinol and nitroresorcinol, &c., see Reverdin and Crépieux (Ber. 1901, 34, 2992, 2996; 1902, 35, 314, 1439; Bull. Soc. chim. 1901, (3) 25, 1044; 1902, (3) 27, 745). For the *N*-halogen derivative of the amides, see Chattaway (Chem. Soc. Trans. 1905, 87, 145).

2-Nitrotoluene 5-sulphonic acid; by heating the diazo-compound of 2-nitro-*p*-toluidine 5-sulphonic acid with absolute alcohol at 100° (Foth, Ann. 1885, 230, 305).

KA' , reddish-yellow thick prisms; barium and lead salts, readily soluble in water and alcohol.

Chloride; thick prisms, m.p. 50° (F.).

Amide; long glistening needles, m.p. 133.5° (F.).

m-Nitrotoluene sulphonic acid; by sulphonating *m*-nitrotoluene (Beilstein and Kuhlberg, Ann. 1870, 155, 27).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, nodules; $\text{PbA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, small granules.

von Pagel (Ann. 1875, 176, 304) has described a nitrotoluene sulphonic acid obtained by nitrating *p*-toluidine *o*-sulphonic acid and eliminating the amino-group.

$\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, tufts of red needles.

4-Nitrotoluene 2-sulphonic acid; by nitrating toluene *o*-sulphonic acid or by sulphonating

p-nitrotoluene (Jaworsky, Zeit. f. Chem. 1865, 1, 222; Beilstein and Kuhlberg, l.c.; Jenssen, Ann. 1874, 172, 230; Hart and Remsen, Ber. 1877, 10, 1046; Amer. Chem. J. 1879, 1, 349; Schwanert, Ann. 1877, 186, 351; Ber. 1877, 10, 29; Noyes, Amer. Chem. J. 1886, 8, 168; Haussner, Bull. Soc. chim. 1890, (3) 3, 797); by sulphonating *p*-cymene to its *o*-sulphonic acid and treating the sulphonation mixture at 40°–60° with nitric and sulphuric acids (Hintikka, Eng. Pat. 123548 of 1918; Can. Pat. 200291; cf. Osakeyhtio, D. R. P. 327051 of 1918). Prisms or rhombic tables + 2½H₂O, or prisms + aq., m.p. 133°–5° (Hintikka, Ann. Acad. Sci. Fennicae, 1917 (A), 10, 1).

For the action of sodium hydroxide, see Fischer and Hepp, Ber. 1893, 26, 2233; 1895, 28, 2281; Bender, *ibid.* 1895, 28, 422; Green and Wahl, *ibid.* 1897, 30, 3099; Kalle & Co., D. R. P. 79241 of 1892; Cassella & Co., D. R. P. 75369 of 1893; Leonhardt & Co., D. R. PP. 96107 of 1893, 46252 of 1888, and 38735 of 1886; for the action of zinc and sodium hydroxide, see Neale, Ann. 1880, 203, 80; Kornatzki, Ann. 1883, 221, 182; Bender and Schultz, Ber. 1886, 19, 3235; for the action of sodium hypochlorite, see Ris and Simon, Ber. 1897, 30, 2618; 1898, 31, 354; Geigy & Co., Fr. Pat. 269466; D. R. P. 98760 of 1897; Green and Wahl, Ber. 1897, 30, 3097; 1898, 31, 1078; Levinstein, D. R. P. 106961 of 1897; Green, Chem. Soc. Trans. 1904, 85, 1424; for dye formation by condensation with *p*-diamines in presence of alkalis, see Geigy & Co., Eng. Pat. 15671 of 1890; U.S. Pat. 455952; Fr. Pat. 208626; D. R. PP. 99290 of 1890, 75326 of 1893.

NH₄A', long prisms not decomposed by sulphuric acid at 100°; NaA' + 2H₂O, prisms (Haussner); KA' (Noyes); CaA'₂ + H₂O (Schwanert), or + 4H₂O, needles (H. and R.), or + 6H₂O (Hart); BaA'₂ + 3H₂O (Jaworsky); PbA'₂ + 3H₂O, needles (Beilstein and Kuhlberg), or + 2H₂O (Schwanert).

Chloride; rhombic tables, m.p. 43°–44°–5°.

Amide; long needles, m.p. 186°. With permanganate it is oxidised to anhydro-*p*-nitro-sulphaminobenzoic acid (Noyes).

o-Nitrobenzyl sulphonic acid; by boiling *o*-nitrobenzyl chloride with sodium sulphite solution (Eug. Fischer, Fr. Pat. 193686; D. R. P. 8722 of 1888; Marckwald and Frahne, Ber. 1898, 31, 1855). Very hygroscopic crystals.

NaA' + H₂O, silver-white scales; BaA'₂ - 3H₂O; AgA' + H₂O, needles.

m-Nitrobenzyl sulphonic acid; from *m*-nitrobenzyl chloride and sodium sulphite (Purgotti and Monti, Gazz. chim. ital. 1900, 30, ii. 247). White crystals + H₂O, m.p. 74°.

NaA' + H₂O, needles; BaA'₂ + 3H₂O; PbA'₂, needles; AgA', leaflets.

Chloride; m.p. 100°.

Amide; m.p. about 159° (decomp.).

Methyl ester; m.p. 77°.

p-Nitrobenzyl sulphonic acid; from *p*-nitrobenzyl chloride and alkali sulphites (Dahl & Co., R. P. 55138 of 1889; Purgotti and Monti, *ibid.*); by nitration of barium nitrobenzyl sulphonic acid (Böhler, Ann. 1870, 154, 55). A little acid is formed also (Mohr, *ibid.* 1883, 221, 16). If the crude mixture is oxidised with potassium permanganate *p*-nitrobenzoic acid and a little *o*-nitrobenzoic acid are formed.

The following salts are described by Böhler, and are probably those of *p*-nitrobenzyl sulphonic acid.

BaA'₂ + 2H₂O, needles; PbA'₂ + 3H₂O, needles; PbOHA', crystals.

Chloride; oil.

Amide; prisms, m.p. 204° (Mohr).

Nitrotoluene disulphonic acid; together with other acids by boiling *p*-bromotoluene disulphonic acid with fuming nitric acid (Kornatzki, Ann. 1883, 221, 198).

K₂A', fine needles.

The same acid (?) is obtained by warming toluene disulphonic acid, obtained from *p*-bromotoluene disulphonic acid and sodium amalgam, with nitric acid for 2 hours (Kornatzki, l.c., 201).

K₂A'', fine needles; BaA'' + 3H₂O, small needles.

2:6-Dinitrotoluene 4-sulphonic acid; by nitration of toluene *p*-sulphonic acid (Beilstein and Kuhlberg, Ann. 1870, 155, 21; Schwanert, Ann. 1877, 186, 342; Ber. 1877, 10, 28; cf. Marckwald, Ann. 1893, 274, 349); in almost theoretical yield by nitrating toluene *p*-sulphonyl chloride with fuming nitric and concentrated sulphuric acids (Reverdin and Crépieux, Ber. 1901, 34, 2992; Bull. Soc. chim. 1901, (3) 25, 1043).

Pale yellow flat rhombic prisms + 2H₂O, m.p. 165° (anhydrous) (Schwanert).

NH₄A', flat rhombic prisms; KA'; CaA'₂ + 2H₂O, needles or scales; BaA'₂ + 4H₂O, prisms; PbA'₂ + 2H₂O, clumps of needles; PbA'₂ + 3H₂O, laminæ (Schwanert).

Chloride; rhombic needles, m.p. 125° (S.).

Amide; white needles or laminæ, m.p. 203° (S.).

Dinitrobenzyl sulphonic acid; by warming nitrobenzyl sulphonic acid with nitric and sulphuric acids (Mohr, Ann. 1883, 221, 225).

KA', yellow leaflets; BaA'₂ + 4H₂O, yellowish nodules; PbA'₂ + 4H₂O, yellow crystals.

Chloronitrotoluene sulphonic acid; from liquid (α)-chloronitrotoluene and fuming sulphuric acid (Wroblewsky, Ann. 1873, 168, 204).

BaA'₂ + 4H₂O, needles.

5-Chloro-4-nitrotoluene 2-sulphonic acid; by successive sulphonation and nitration of *m*-chlorotoluene.

BaA'₂ + 2H₂O, yellowish-brown plates or needles (Schraube and Romig, Ber. 1893, 26, 579).

6-Chloro-4-nitrotoluene 2-sulphonic acid; slightly hygroscopic, colourless flattened needles (Davies, Chem. Soc. Trans. 1921, 119, 881, 885).

NaA' + H₂O, plates; BaA'₂ + H₂O, needles.

Chloride; formed in about 60 p.c. yield together with about 40 p.c. of 6-chloro-3-nitrotoluene *o*-sulphonyl chloride by nitrating 6-chlorotoluene *o*-sulphonyl chloride at 20°–30° (D.).

Amide; minute needles, m.p. 161°. A red colour is formed by boiling for a few minutes with ammonia solution (D.).

6-Chloro-3-nitrotoluene o-sulphonic acid (see above). Very deliquescent microscopic prisms.

NaA' + 3½ or 4H₂O, needles; BaA'₂ + 7H₂O, small needles, decomposing at about 140°.

Chloride; long colourless needles, m.p. 60°. When boiled with sodium hydroxide the sulphonyl group is replaced by hydroxyl (Davies, l.c.).

2-Chloro-5-nitrotoluene *p*-sulphonic acid; small non-deliquescent crystals which after drying at 120° melt at 123°–128° (Davies).

$\text{NaA}' + 2\text{H}_2\text{O}$, pale yellow or colourless needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, colourless scales.

Chloride; formed together with 2-chloro-6-nitrotoluene *p*-sulphonyl chloride, by gradual addition of 2-chlorotoluene *p*-sulphonyl chloride with stirring to a cold mixture of nitric acid (D 1.5) and sulphuric acid.

Large colourless prisms, m.p. 99.2° (D.).

Amide, small needles, m.p. 181° (D.).

2-Chloro-6-nitrotoluene *p*-sulphonic acid (see above); deliquescent plates.

NaA' , colourless microscopic plates; KA' , colourless laminæ; $\text{BaA}'_2 + 3\text{H}_2\text{O}$, colourless leaflets (Davies).

Chloride; long colourless needles, m.p. 70° (D.).

Amide; needles or scales, m.p. 182° (D.).

***o*-Bromonitrotoluene *m*-sulphonic acid**; by nitration of barium-*o*-bromotoluene sulphonate (Müller, Ann. 1873, 169, 42; Pagel, *ibid.* 1875, 176, 299).

Free acid is crystalline and very deliquescent.

$\text{NaA}' + \text{H}_2\text{O}$; KA' ; $\text{BaA}'_2 + \text{H}_2\text{O}$, small needles or nodules; $\text{PbA}'_2 + 2\text{H}_2\text{O}$, microscopic crystals.

***o*-Bromonitrotoluene *p*-sulphonic acid**; by nitration of barium *o*-bromotoluene-*p*-sulphonate with nitric acid (D 1.5) (Hayduck, Ann. 1874, 174, 347); from *o*-toluidine *p*-sulphonic acid by nitration and replacement of the amino-group by bromine (Hayduck, *ibid.* 1874, 172, 219). Microscopic needles.

$\text{BaA}'_2 + 3\text{H}_2\text{O}$, needles.

Chloride; crystals which do not melt at 220°.

Amide; does not melt at 200°.

***m*-Bromonitrotoluene *o*-sulphonic acid**; by nitration of barium (β) *m*-bromotoluene *o*-sulphonate (Wroblewsky, Ann. 1873, 168, 169).

$\text{CaA}'_2 + 4\frac{1}{2}\text{H}_2\text{O}$, large prismatic crystals; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles; $\text{PbA}'_2 + 3\text{H}_2\text{O}$, prismatic crystals.

***m*-Bromonitrotoluene *o*-sulphonic acid**; by nitration of *m*-bromotoluene *o*-sulphonic acid (Weckwarth, Ann. 1874, 172, 200).

NaA' , yellow granules; $\text{CaA}'_2 + 5\text{H}_2\text{O}$, pale yellow prisms; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, yellow needles.

Nitro-*p*-bromotoluene *o*-sulphonic acid; by nitrating *p*-bromotoluene *o*-sulphonic acid (Hässelbarth, Ann. 1873, 169, 22). Deliquescent laminæ.

$\text{BaA}'_2 + 2\text{H}_2\text{O}$; $\text{SrA}'_2 + 7\text{H}_2\text{O}$; $\text{PbA}'_2 + 3\text{H}_2\text{O}$; $\text{CuA}'_2 + 6\text{H}_2\text{O}$; AgA' .

Nitro-*p*-bromotoluene *m*-sulphonic acid; by nitrating barium *p*-bromotoluene *m*-sulphonate (Hässelbarth, *l.c.*). Small deliquescent needles.

$\text{BaA}'_2 + 5\text{H}_2\text{O}$ or H_2O ; $\text{SrA}'_2 + 5\text{H}_2\text{O}$;

$\text{PbA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$.

Dibromonitrotoluene sulphonic acid; together with other acids by boiling *p*-bromotoluene disulphonic acid with nitric acid (Kornatzki, Ann. 1883, 221, 197).

$\text{KA}' + \text{H}_2\text{O}$, nodules; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, thin plates.

AMINO DERIVATIVES.

***o*-Toluidine**; by reduction of *o*-nitrotoluene (Beilstein and Kuhlberg, Ann. 1871, 158, 77);

by catalytic reduction by passing the vapours mixed with hydrogen over heated reduced copper or nickel (Sabatier and Senderens, Compt. rend. 1901, 133, 321); and by other methods of catalytic reduction (Hänke and Browne, J. Physikal. Chem. 1923, 27, 52); by heating 1 part of *o*-cresol with 1 part of ammonium chloride and 4 parts of ammonium-zinc chloride for 40 hours at 330°–340° (Merz and Müller, Ber. 1887, 20, 547); together with *p*-toluidine by the action of hydroxylamine on toluene in presence of aluminium or ferric chloride (Graebe, Ber. 1901, 34, 1778). Colourless, thick, refractive liquid, which does not solidify at –20°, b.p. 199.7°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 621) or 198.4°–198.5°/735.4 mm. (Brühl, Ann. 1880, 200, 189); D_4^{25} 1.0112; D_{15}^{25} 1.0031; D_{25}^{25} 0.997; D_{50}^{50} 0.9852 (Perkin, Chem. Soc. Trans. 1896, 69, 1245); D_{30}^{30} 1.003; D_{25}^{25} 0.998 (B. and K.); magnetic rotatory power at 15° 17.18 (Perkin); heat of combustion at constant volume 963.8 Cal.; at constant pressure 964.7 Cal. (Petit, Ann. Chim. 1889, [6] 18, 152; Compt. rend. 1888, 107, 266); refractive index, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 216); surface tension, Dutoit and Friderich (Compt. rend. 1900, 130, 328); cryoscopic behaviour, Ampola and Rimatori, (Gazz. chim. ital. 1897, 27, i. 43, 63). May be separated from *p*-toluidine by means of the acid oxalates (Ihle, J. pr. Chem. 1876, (2) 14, 449; Bindschedler, Ber. 1873, 6, 448; Miniati, Booth and Cohen, J. Soc. Chem. Ind. 1887, 6, 418); by freezing (Rosenstiehl, Bull. Soc. chim. 1871, (2) 17, 7); by means of the nitrate (Schad, Ber. 1873, 6, 1361); by means of the hydrochloride, sulphates or phosphates (Lewy, Zeitsch. anal. Chem. 1884, 23, 269; Ber. 1886, 19, 1717, 2728; D. R. P. 22139 of 1882; cf. Wülling, Ber. 1886, 19, 2132). The crude product contains about 63 p.c. *o*-, 2 p.c. *m*-, and 35 p.c. *p*-toluidine.

According to Friswell (J. Soc. Chem. Ind. 1908, 27, 258) the best method of separation is to freeze in presence of water or ice. *p*-Toluidine forms a hydrate (Walker and Beveridge, Chem. Soc. Trans. 1907, 91, 1797) which can be readily separated from the other isomerides. A full description of the method and apparatus is given by Friswell.

The proof that 2-aminotoluene is identical with 6-aminotoluene is given by Wroblewsky (Ann. 1878, 192, 213).

Estimation of aniline and *o*- and *p*-toluidine, see Reinhardt, Zeitsch. anal. Chem. 1894, 33, 90; Dobriner and Schranz, *ibid.* 1895, 34, 734; Liebmann and Studer, J. Soc. Chem. Ind. 1899, 18, 111; for estimation of small quantities of *p*-toluidine in *o*-toluidine, see Haenemann, Zeitsch. anal. Chem. 1887, 26, 750; estimation of *o*- and *p*-toluidine by specific gravity determination, see Zeitsch. anal. Chem. 1885, 24, 489; by solidification point of the mixed acetyl derivatives (Holleman, Rec. trav. chim. 1900, 27, 458; Proc. K. Akad. Wetensch. Amsterdam, 1904, 7, 395).

For other methods, see Raube, Chem. Zeit. 1891, 15, 116, 179. For the two modifications of *o*-toluidine, see Ostromislensky, Zeitsch. physikal. Chem. 1906, 57, 341).

A colour test to distinguish between aniline

and the three toluidines is described by Murray (Chem. News, 1925, 130, 23).

Salts (see Beilstein and Kahlberg, Ann. 1870, 156, 76; Rosenstiehl, *l.c.*), $B'HCl + H_2O$, scales, m.p. $214.5-215^\circ$ b.p. $240.2^\circ/728$ mm. or $242.2^\circ/760$ mm. (Ullmann, Ber. 1898, 31, 1699); $B'H_2Cl_2.CuCl_2$ (Pomey, Compt. rend. 1887, 104, 365); $B'HBr$, trimetric prisms (Stadel, Ber. 1883, 16, 28); $B'HI$, slender rhombic prisms (Stadel); $B'HNO_3$, leaflets; $B'H_2SO_4$, small crystals; $B'H_2SO_4$ (Wellington and Tollens, Ber. 1885, 18, 3313); $B'H_2SO_4 + H_2O$ (Hitzel, Bull. Soc. chim. 1894, (3) 11, 1054); $B'H_3PO_4$ (Lewy, Ber. 1886, 19, 1718); $B'C_2H_5ClO_2$, m.p. 95° (Reisser, Ber. 1888, 21, 1260); oxalate, small plates; $B'H_2FeC_2N_4$ (Eisenberg, Ann. 1880, 205, 271; Ber. 1879, 12, 2234); $B'H_2SnCl_4$, silky needles, m.p. 164° ; $B'H_2SnCl_4 + H_2O$, short pale pink needles, beginning to decompose at 210° (Druce, Chem. Soc. Trans. 1918, 113, 716); ($B'HC$), $ZnCl_2 + 2H_2O$, tables (Base, Amer. Chem. J. 1898, 20, 653); $B'2HgCl_2$, plates (Swan, *ibid.* 1898, 20, 622); $B'HC.HgCl_2$ (Swan); ($B'HC$), $HgCl_2$ (Swan); $B'HC.HgBr_2$ (Swan); ($B'HC$), $SnCl_2 + \frac{1}{2}H_2O$, colourless prisms (Slagle, Amer. Chem. J. 1898, 20, 640); ($B'HC$), $SnCl_2 + 2H_2O$, (Slagle); ($B'HC$), $SbCl_3$ (Higbee, *ibid.* 1900, 23, 150); ($B'HC$), $BiCl_3$ (Hauser and Vanino, Ber. 1900, 33, 2271); ($B'HB$), $ZnBr_2 + 2H_2O$ (Base); ($B'HB$), $SbBr_3$ (Higbee); $B'H_2PtCl_4$, decomposed by boiling water, unlike the salt of *p*-toluidine (de Coninck, Bull. Soc. chim. 1886, 45, 131); $B'_2ZnCl_2 + 2H_2O$ (Lachovich, Monat. 1888, 9, 513); B'_2HgCl_2 , m.p. 115° (lein, Ber. 1878, 11, 743); B'_2MnCl_2 ; B'_2gBr_2 , leaflets, m.p. 104° (Klein, Ber. 1879, 12, 835); B'_2ZnBr_2 (Leeds, Jahresbericht, 1880, 503); B'_2ZnI_2 ; B'_2CdI_2 ; $B'_2HgC_2N_4$; $H_2FeC_2N_4$; $B'_2H_2Cu_2(SO_4)_2$ (Deniges, Compt. rend. 1870, 112, 870); $B'_2HgH_2(SO_4)_2 + H_2O$; H_2PO_4 and $B'_2H_2PO_4$ could not be prepared; $HSCN(CN)(SCN)_2.2NH_3$, red plates (Christensen, pr. Chem. 1892, (2) 45, 362); *picrate* mononitric crystals, m.p. $212-215^\circ$ (Jerusalem, Chem. Trans. 1909, 95, 1284; Carrasso and Padova, ti R. Accad. Lincei, 1906, (v.) 15, i, 699). $HISbI_3$, red needles (Higbee); ($B'HI$), $(SbI_3)_2$, orange leaflets (H.); B'_2MgCl_2 (Tombeck, mpt. rend. 1896, 124, 963, 1532; Ann. Chim. (7) 21, 397); B'_2ZnBr_2 (Tombeck, Ann. chim. 1900, (7) 21, 466); B'_2CdCl_2 ; B'_2CdBr_2 ; B'_2CdSO_4 ; B'_2AgNO_3 ; $B'_2Ag_2SO_4$; $3B' + 2SiF_6$ (Pomey and Jackson, Amer. Chem. J. 1888, 10, 2). *Chlorate*, white plates exploding at 88 (atta and Choudhury, J. Amer. Chem. Soc. 16, 38, 1079); $B'CdCl_2$, tables (Lachowicz, Monat. 1889, 10, 898); $B'HgCl_2$ (Lachowicz); $B'HgCl_2$ (7), m.p. $113-115^\circ$ (Klein, Ber. 1878, 11, 744); $2B'HgBr_2$, laminated crystals, m.p. -104° (Klein, Ber. 1880, 13, 835); $2B'HgI_2$, decomposes at $40-50^\circ$ (Klein); $4B' + AgNO_3 + AgNO_3$ (Lachowicz, Monat. 1889, 10, 3B' + $2CuSO_4 + H_2O$ (Lachowicz); Br_2 ; $2B'ZnI_2$; $2B'CdI_2$; $2B'HgCl_2$; $(CN)_2$; $2B'MnCl_2$ (Leeds). *Benzene sulfo acid salt*, m.p. 127° (Norton and Weston, Amer. Chem. J. 1888, 10, 135); *toluene p-sulfo acid salt*, long prisms, m.p. 180° and *Oliven*, *ibid.* 144); *amide sul.* $C_6H_4NOHSO_3NH_2$, m.p. 131° (and Ber. 1894, 2162); *toluene*

succinic acid salt, $(C_6H_4N)_2C_4H_4Cl_2O_4 + C_6H_5OH$, crystalline powder (van der Riet, Ann. 1894, 280, 232); *toluene p-sulphonic acid salt*, needles, m.p. 124° (Hälsig, J. pr. Chem. 1897, (2) 56, 217); B'_2Ca (Erdmann and Smitten, Ann. 1908, 361, 52).

o-Toluidine forms precipitates with salts of the rare metals (Jefferson, J. Amer. Chem. Soc. 1902, 25, 540).

o-Toluidine dissolved in diluted sulphuric acid and treated with chromic acid and sulphuric acid yields a blue colour, converted into red-violet on dilution (Rosenstiehl, Bull. Soc. chim. 1868, (2) 10, 200), whilst a solution of *o*-toluidine in diluted sulphuric acid gives an orange coloration with nitric acid (Lorenz, Ann. 1874, 172, 180). When an equal volume of water is added to a solution of the base in ether, and a very dilute solution of bleaching powder is added drop by drop, the aqueous layer is coloured yellow or brown, and the ethereal layer on shaking with sulphuric acid colours this reddish-violet (Rosenstiehl). If a trace of a salt of *o*-toluidine be added to a solution of a salt of 2:5-toluylenediamine, followed by ferric chloride, potassium dichromate, or manganese dioxide, a green colour is formed (distinction from *m*- and *p*-toluidine) (Nietzki, Ber. 1877, 10, 1157).

When passed through a hot tube *o*-toluidine is converted into ditolylamine, with evolution of ammonia and hydrogen (Seyberth, Ber. 1896, 29, 2594), whilst under the influence of an electric discharge it yields a little ammonia and forms a strongly basic polyamine (Berthelot, Compt. rend. 1898, 126, 780). It is oxidised in alkaline solution forming azotoluene, oxalic acid and ammopla, whilst in acid solution it forms quinones. Azoderivatives are formed also with nitric acid (Nietzki, Ber. 1877, 10, 662; Ullmann and Forgan, Ber. 1901, 34, 3805; cf. Bradshaw, Amer. Chem. J. 1906, 35, 326). Its hydrochloride when electrolysed or when treated with potassium dichromate yields dyestuffs (Goppels-roeder, Dingl. poly. J. 1877, 223, 347, 634; Coninck, Compt. rend. 1898, 127, 1221).

o-Toluidine printed on the fibre can be oxidised to a moderately permanent dark violet dye by means of sodium chlorate and potassium ferrocyanide; *m*-toluidine under these conditions yields a blackish-violet colour and *p*-toluidine a chestnut-brown colour (Kirpitschnikoff, Zeitsch. Farb. Text. Ind. 1905, 4, 233).

It gives a violet colouring matter with thallium chloride (Renz, Ber. 1902, 35, 2768). When treated with hydrogen in the presence of reduced nickel it yields methyl cyclo-hexylamine (Sabatier and Senderens, Bull. Soc. chim. 1904, (3) 31, 769).

It reacts with diazo-compounds (Mehner, J. pr. Chem. 1902, 65, 401); with methylene iodide (Senier and Goodwin, Chem. Soc. Trans. 1902, 81, 280); with phenyl urethane (Dixon, *ibid.* 1901, 79, 102); with phosphoryl trithiocyanate (*ibid.* 541); with a number of aldehydes (Kilbner and Peltzer, Ber. 1900, 33, 3480; Fosse, Bull. Soc. chim. 1901, (3) 25, 375; Stard, *ibid.* 1883, (2) 39, 530; Pistot, Ber. 1886, 19, 1663; Sachs and Kempf, Ber. 1902, 35, 2704; Oohn and Blau, Monat. 1904, 25, 365; Walker and Rector, J. pr. Chem. 1905, 65, 285).

o-Toluidine on treatment with strong alkalis

cyanate either at 1°–3° or at the boiling point yields chiefly acetyl-*o*-tolylthiocarbamide, m.p. 184° (Doran and Dixon, Chem. Soc. Trans. 1905, 67, 338). With dichloroacetic acid, *o*-toluidine yields chiefly *o*-methylaminophenyl-*o*-toluidine-acetic acid, prismatic needles, m.p. 239°–240°, as well as some *o*-tolyl-*o*-methylmesatin $C_8H_7ON_2$, golden-yellow leaflets, m.p. 225° (Ostromislensky, Ber. 1907, 40, 4972; cf. Meyer, Ber. 1883, 16, 2261). The magnesium iodide derivative of *o*-toluidine reacts with ethyl chloroacetate to yield iodoaceto-*o*-toluidide, long white needles, m.p. 142° (decomp.) (Bodroux, Compt. rend. 1905, 141, 195), and with α -iodopropionate and α -iodobutyrate to form α -iodopropion-*o*-toluidide, m.p. 148°, and α -iodobutyr-*o*-toluidide, m.p. 135°–139°, respectively (Bodroux and Taboury, *ibid.* 1907, 144, 1437).

The diazoamino-compounds derived from the three toluidines and diphenylamine are described by Vignon and Simonet (Compt. rend. 1905, 140, 788).

Formyl-derivative; by continuous boiling of *o*-toluidine with formic acid (Ladenburg, Ber. 1877, 10, 1129; Tobias, *ibid.* 1882, 15, 2446). Plates, m.p. 62° (Nef, Ann. 1892, 270, 310), b.p. 288°. When boiled for a long time it decomposes into *o*-toluidine, methenylditolylamine, carbon monoxide and carbon dioxide. For solid and liquid modifications, see Orloff (J. Russ. Phys. Chem. Soc. 1905, 37, 439).

Silver salt, amorphous precipitate (Comstock and Clapp, Amer. Chem. J. 1891, 13, 526); **sodium salt** (Wheeler, *ibid.* 1900, 23, 466); **ethyl-*o*-tolylformimino ether**,



from silver *o*-formotoluidide and chloroformic ester, liquid, b.p. 101°/12 mm. (Wheeler and Boltwood, Amer. Chem. J. 1896, 18, 389); **methylether**; from the silver salt and methyl iodide. Liquid, b.p. 211°–213° (C. and C.).

Thioformyl-derivative; by heating the formyl-derivative with phosphorus pentasulphide at 120°. Another method of preparation is given by Nef (Ann. 1892, 270, 313). Yellow needles, m.p. 96° (Senier), or colourless needles, m.p. 100°–101° (Nef). On distillation *in vacuo* it forms methenyldi-*o*-tolylamine. On heating under pressure for 7 hours at 190° it yields a crystalline compound, $C_{10}H_{11}N_2S$, m.p. 160° (Senier, Ber. 1885, 18, 2292; Chem. Soc. Trans. 1885, 47, 762).

Acetyl-derivative; by heating the base with acetic acid (Beilstein and Kuhlberg, Ann. 1870, 156, 77; Alt, *ibid.* 1889, 252, 318), or by shaking with water and acetic anhydride (Hinsberg, Ber. 1890, 23, 2962). See also Lumière and Barbier (Bull. Soc. chim. 1905, (3) 33, 784); Pawlewski (Ber. 1902, 35, 110). Long monoclinic crystals, m.p. 110° (Alt; Sudborough, Chem. Soc. Trans. 1901, 79, 537) or 107°–109° (Bedson and King, Chem. Soc. Trans. 1890, 37, 753), b.p. 296° (Beilstein and Kuhlberg).

With potassium permanganate it yields acetyl-*o*-aminobenzoic acid and with phosphorus pentachloride an unstable iminochloride, $CH_3COCl=NC_6H_4$, which on careful heating yields a base $C_8H_7N=C(CH_3)CH_2CCl=NC_6H_4$, m.p. 53°. When treated hot with bromine it yields the derivative $CH_3C_6H_4Br_2NHCH_2C_6H_4BrO$, whilst bromide in acetic acid solution yields the

6-bromo-derivative. When treated with a mixture of hydrochloric and nitric acids it yields a dichloroaceto-*o*-toluidide, m.p. 155°–156° (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20).

Aceto-*o*-toluidide forms compounds with sodium hydroxide, $C_8H_7ON+NaOH$, with sodium methoxide, $C_8H_7ON+CH_3ONa$, and with sodium ethoxide, $C_8H_7ON+C_2H_5ONa$ (Cohen, Archdeacon and Brittain, Chem. Soc. Trans. 1896, 69, 93; 1898, 73, 161).

With methyl iodide in presence of dry silver oxide, aceto-*o*-toluidide yields a mixture of methyl aceto-*o*-toluidide and *N*-*o*-tolylacetimino-methylether, whilst with ethyl iodide it yields *N*-*o*-tolylacetimino-ethylether (Lander, Chem. Soc. Trans. 1901, 79, 690). Chloroacetyl in the presence of aluminium chloride yields chloroacetyl-*o*-toluidine, m.p. 160° (Kunchell, Ber. 1900, 33, 2644). On heating with diacetylhydrazine, aceto-*o*-toluidide yields 1-*o*-tolyl-2,5-dimethyl-1:3:4-triazole (Pellizzari and Alciatore, Atti R. Accad. Lincei, 1901 [v.] 10, 444).

***N*-Chloro-derivative**, $CH_3C_6H_4NClCOCH_3$, from aceto-*o*-toluidide and potassium hypochlorite at the ordinary temperature. Prisms or plates, m.p. 43°. At 160°, or when a drop of sulphuric acid is added to its solution in acetic acid, 5-chloro-aceto-*o*-toluidide is formed (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790).

***N*-Bromo-derivative**; formed by the action of potassium hypobromite on a suspension of the acetyl-derivative in sodium bicarbonate solution at 0°. Yellow, four-sided plates, m.p. 100°.

(On keeping at the ordinary temperature for a few seconds, it is transformed into 5-bromoaceto-*o*-toluidide (Chattaway and Orton).

Chloroacetyl-derivative



by the action of chloroacetyl chloride on a well-cooled solution of *o*-toluidine in benzene (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 299; cf. Bischoff and Walden, Ann. 1894, 279, 62; Grothe, Archiv. der. Pharmacie, 1899, 238, 588). Slender needles, m.p. 111°–112°. For the corresponding bromo-, dichloro-, tri-chloro-, and thioacetyl-derivatives, see Rugheimer and Hoffmann, Ber. 1893, 18, 2987; Cloke, Ann. Chim. 1886, (6) 9, 215; Abenius and Widman, *l.c.*; Wallach, Ber. 1890, 13, 529; 1893, 16, 147).

Propionyl-derivative; from *o*-toluidine and propionic acid (Pictet and Duparc, Ber. 1887, 20, 3421). Needles, m.p. 87°, b.p. 299°/730 mm. Oxidised by potassium permanganate to propionyl-*o*-amino-benzoic acid.

Benzoyl-derivative; long broad needles, m.p. 131° (Gudeman, Ber. 1888, 21, 2553) or 143° (Brückner, Ann. 1880, 205, 130). Phosphorus pentachloride yields $C_8H_7N=CClC_6H_5$ (Just, Ber. 1886, 19, 982).

Oxalyl-derivative; plates, m.p. 131° (Bladis, Bull. Soc. chim. 1884, (2) 41, 130).

Phthalyl-derivative; needles, m.p. 165°, b.p. about 360° (Fröhlich, Ber. 1894, 17, 2679).

Diacetyl-derivative; by heating 1 part of aceto-*o*-toluidide with 1 part of acetyl chloride at 170°–190° (Kay, Ber. 1893, 26, 2885); from the monoacetyl-compound and acetic anhydride at 200°–205° (Bistrzycki and Ullrich, Ber. 1894, 27, 81). Oil (Kay). *crystalline m.m.*

Ber. 1896, 28, 1065; Clayton, Ber. 1895, 28, 1665; Sudborough, Chem. Soc. Trans. 1901, 79, 537).

4-Chloro-o-toluidine; by reduction of 4-chloro-2-nitrotoluene (Goldschmidt and Hönig, Ber. 1886, 19, 2441; Cohn, Monatsh. 1901, 22, 473; cf. Engelbrecht, Ber. 1874, 7, 797); from 2:4-dinitrotoluene (Beilstein and Kuhlberg, Ann. 1871, 158, 337). M.p. 21°-22°, b.p. 237°/722 mm. (G. and H.). B'HCl, needles; (B'HCl), PtCl₄ + 2H₂O, slender yellow needles.

Acetyl-derivative, leaflets, m.p. 139°-140° (E.) or 130°-131° (G. and H.). Oxidised by permanganate in presence of magnesium sulphate to 4-chloro-2-acetylamino-benzoic acid (Cohn).

5-Chloro-o-toluidine; by chlorination of aceto-o-toluidide followed by hydrolysis (Lellmann and Klotz, Ann. 1885, 231, 317); by the action of sulphuryl chloride on aceto-o-toluidide in carbon disulphide solution followed by hydrolysis with hydrochloric acid (Wynne, Chem. Soc. Trans. 1892, 61, 1045). The same (?) chlorotoluidine is obtained together with o-toluidine by reducing o-nitrotoluene with tin and hydrochloric acid (Beilstein and Kuhlberg, Ann. 1870, 156, 81). Thin plates, m.p. 29°-30° (W.; B. and K.; L. and K.), b.p. 241° (B. and K.), 236°-238°/730 mm. (L. and K.), or 246°/746 mm. (W.). B'HCl, small tables; B'HNO₃, leaflets.

Acetyl-derivative; by chlorination of aceto-o-toluidide (L. and K.); by the action of an aqueous solution of bleaching powder on an ice-cold solution of aceto-o-toluidide in diluted acetic acid solution (Claus and Stapelberg, Ann. 1893, 274, 286; cf. Chattaway and Orton, l.c., and Cohen and Dakin, *ibid.* 1902, 81, 1329); or by chlorination using sodium chlorate and hydrochloric acid (Reverdin and Crépeux, Ber. 1900, 33, 2497). Small slender needles, m.p. 129°-140° (W.; C. and O.). **N-Chloro-derivative**; four or six-sided prisms, m.p. 66°. On heating a solution in acetic acid 3:5-dichloroaceto-o-toluidide is formed (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790).

6-Chloro-o-toluidine; 6-nitro-o-toluidine is converted into 6-chloro-2-nitrotoluene and the latter is reduced (Reverdin and Crépeux; cf. Wynne and Groves; Nölting; Cohn). Liquid at the ordinary temperature, m.p. 2-8°, and darkens rapidly in the air (Wibaut, Rec. trav. chim. 1913, 32, 244), b.p. 242°-244°. B'HCl, silvery leaflets, decomposing at 250°-252°; H₂SO₄, silvery needles, decomposing at 250°-252°.

Acetyl-derivative; needles, m.p. 156° (Wibaut), 157°-159° (Janson, D. R. P. 107505 of 1898; Cohn, Monatsh. 1901, 22, 473); (Hönig, Ber. 1877, 20, 2417 gave 136°). **Benzoyl-derivative**; m.p. 170°-171° (Wibaut; Cohn) or 173° (N.).

3-Chloro-5-bromo-o-toluidine; by bromination of aceto-o-toluidide, followed by chlorination and hydrolysis. Colourless needles, m.p. 60° (Cohen and Murray, Chem. Soc. Trans. 1915, 101, 847).

Acetyl-derivative; m.p. 171°; **diacetyl-derivative**; m.p. 90-5° (C. and M.).

5-Chloro-3-bromo-o-toluidine; by reducing 5-chloro-3-bromo-2-nitrotoluene with tin and hydrochloric acid; from aceto-o-toluidide by successive chlorination, hydrolysis, and bromine.

Acetyl-derivative; colourless needles, m.p. 187°; **diacetyl-derivative**, m.p. 85° (C. and M.).

5(1)-Iodoaceto-o-toluidide; by treating aceto-o-toluidide with iodine monochloride in glacial acetic acid. It melts at 169-5° and yields a **dichloride**, which decomposes at 109°, and an **iodoso-derivative** (Willgerodt and Heusner, Ber. 1907, 40, 4077).

3:5-Dichloro-o-toluidine; by chlorination of aceto-o-toluidide, followed by hydrolysis (Claus and Stapelberg, Ann. 1893, 274, 291); readily obtained by Chattaway and Orton's method (above) (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1329). Glistening needles, m.p. 53° (C. and S.).

Acetyl-derivative; needles or columns, m.p. 186°. **N-chloro-derivative**, four-sided prisms, m.p. 78° (Chattaway and Orton l.c.).

4:5-Dichloro-o-toluidine; by reducing 3:4-dichloro-6-nitrotoluene with stannous chloride. Plates with a silky lustre, m.p. 100°-101° (Cohen and Dakin).

4:6-Dichloro-o-toluidine (?); by reducing dichloronitrotoluene (Wroblewsky, Ann. 1873, 168, 213). Leaflets, m.p. 88°, b.p. 259°. Does not form salts.

2:4-Dichlorotoluidine (?); by reducing β-dichloronitrotoluene. Plates, m.p. 87° (Seelig, Ann. 1887, 237, 103).

2:3:4-Trichloro-o-toluidine (?); by reduction of 2:3:4-trichloronitrotoluene (?) with stannous chloride and hydrochloric acid. Small needles, m.p. 105° (Seelig, Ann. 1887, 237, 142).

3:4:6-Trichloro-o-toluidine (?); by reduction of trichloronitrotoluene with tin and hydrochloric acid (Schultz, Ann. 1877, 187, 278). Needles, m.p. 91° (Schultz) or 94°-95° (Seelig, Ann. 1887, 237, 141; Ber. 1885, 18, 423). Becomes rose-coloured on keeping.

Acetyl-derivative; m.p. 191°.

Benzoyl-derivative; m.p. 213° (Schultz).

3-Bromo-o-toluidine; by reduction of 3-bromo-2-nitrotoluene (Neville and Winther, Ber. 1880, 13, 1945; Chem. Soc. Trans. 1880, 37, 630; cf. Wynne, *ibid.* 1892, 61, 1036, note). Oil. With bromine water it yields 3:5-dibromo-o-toluidine.

4-Bromo-o-toluidine; by reduction of 4-bromo-2-nitrotoluene (Körner, Zeit. f. Chem. 1889, (2) 5, 636; Hübner and Wallach, Ann. 1870, 154, 298; Hübner and Roos, Ber. 1873, 6, 799; Wroblewsky, Ann. 1873, 168, 77; Neville and Winther, Chem. Soc. Trans. 1880, 37, 442); from dinitrotoluene by conversion into 2-nitro-p-toluidine, replacement of the amino-group by bromine and reduction of the nitro-group (Heinemann, Ann. 1871, 158, 340). Plates, m.p. 32° (H. and R.), b.p. 253°-257° with partial decomposition. B'HCl, six-sided rhombic plates (H. and R.); B'HNO₃, long rhombic tables (W.; H.); B₂H₂SO₄, plates.

5-Bromo-o-toluidine; by successive bromination and hydrolysis of aceto-o-toluidide (Wroblewsky, Ann. 1873, 168, 182); by reduction of 5-bromo-2-nitrotoluene (Graw, Ann. 1875, 177, 249; Ber. 1875, 8, 865). Rhombic plates, m.p. 59-5° (Alt, Ann. 1882, 252, 321) or 56° (Wroblewsky; Niemcewicz, Ber. 1882, 35, 889; Cohen and Dakin, Chem. Soc. Trans. 1915, 105, 811; cf. Neville and Winther, l.c.), b.p. 245°. B'HCl, needles; B₂H₂SO₄, nearly square plates.

TOLUENE.

m.p. 183°; $B_2H_3SO_4 + 2H_2O$ (Alt); *oxalate*, needles, (G.).

Acetyl-derivative; by bromination of aceto-*o*-toluidide (W.; A.; N.); quantitatively by treating 5-iodoaceto-*o*-toluidide with bromine in chloroform solution (Malleis and Meyer, J. Amer. Chem. Soc. 1913, 35, 970); by the action of hydrobromic and nitric acids on aceto-*o*-toluidide (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20). Long needles, m.p. 156°–157° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 511). For compounds with sodium and potassium hydroxides, see Cohen and Brittain (*ibid.* 1898, 73, 161). *N-Bromo-derivative*; yellow rectangular plates, m.p. 91°. On heating with water at 100° it yields 3:5-dibromo-aceto-*o*-toluidide (Chattaway and Orton, *ibid.* 1900, 77, 794).

6-Bromo-o-toluidine; by reduction of 6-bromo-2-nitrotoluene with tin, stannous chloride, and hydrochloric acid (Friedländer, Bruckner and Deutsch, Ann. 1912, 388, 23). Yellow oil, b.p. 253°–255° (Nölting, Ber. 1904, 37, 1015).

Sulphate; m.p. 256° (N.).

Acetyl-derivative; white needles, m.p. 158° (N.), or 159°–161° (Cohen and Dutt, *l.c.*; Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627) or 163° (F., B. and D.). It is oxidised by potassium permanganate at 80° in the presence of magnesium sulphate to bromoacetylanthranilic acid, m.p. 224°.

3:5-Dibromo-o-toluidine; by passing bromine vapour into a solution of *o*-toluidine hydrochloride (Wroblewsky, Ann. 1873, 168, 187); by boiling bromoacetodibromo-*o*-toluidide with excess of alcoholic potassium hydroxide (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 288); by dibromination of *o*-toluidine and by the action of bromine on *o*-toluidine 5-sulphonic acid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429, 629; cf. Wynne, *ibid.* 1892, 61, 1038). Needles, m.p. 45°–46° (N. and W.; Cohen and Dutt), 50° (W.; Möhlau and Öhmichen, J. pr. Chem. 1881, (2) 24, 478), volatile with steam. It forms unstable compounds with strong acids.

Compounds with mercuric chloride, with zinc chloride, and with the chloride and bromide of cadmium are described by Hann and Spencer (J. Washington Acad. Sci. 1925, 15, 163).

($BHCl$), $PtCl_4$, yellow needles (A. and W.), $+1\frac{1}{2}H_2O$ (Claus and Immel, Ann. 1891, 265, 70).

Acetyl-derivative; needles, m.p. 205° (Chattaway and Orton, Ber. 1900, 33, 2399).

N-Bromo-derivative; plates, m.p. 120° (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 794).

Bromoacetyl-derivative; slender needles, m.p. 207° (A. and W.).

Diacyl-derivative; slender needles, m.p. 88° (A. and W.).

4:5-Dibromo-o-toluidine; by reduction of 4:5-dibromo-2-nitrotoluene. It melts at 96·8°–98° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 439; Cohen and Dutt, *ibid.* 1914, 105, 515; cf. Wroblewsky, Ann. 1873, 168, 184).

5:6-Dibromo-o-toluidine; by bromination of 6-bromoaceto-*o*-toluidide, followed by hydrolysis. It melts at 58°.

Acetyl-derivative; m.p. 165·5°–166·5° (Cohen and Dutt, *l.c.*).

Tribromo-o-toluidine; m.p. 105°–106°, is described by Gerver (Ann. 1873, 169, 379) as

being obtained by the action of 3 mols. of bromine on *o*-toluidine, and he states further that 1 mol. of bromine and a dilute alcoholic solution of *o*-toluidine yields a mixture of di- and tribromotoluidines, m.p. 85°–89°. Neville and Winther (Chem. Soc. Trans. 1880, 37, 438) could not prepare any higher derivative than a dibromotoluidine, however, and state that Gerver's *o*-toluidine possibly contained aniline.

3:5:6-Tribromo-o-toluidine; by reduction of 3:5:6-tribromo-2-nitrotoluene with iron powder and acetic acid; by bromination of 6-bromo-*o*-toluidine (Blanksma, Chem. Weekblad, 1914, 11, 185). Colourless crystals, m.p. 87°.

Acetyl-derivative; colourless crystals, m.p. 218° (B.).

Tribromotoluidine; from *p*-bromotoluene *o*-sulphonic acid by nitration, reduction, and bromination (Schäfer, Ann. 1874, 174, 362; Ber. 1874, 7, 1355). M.p. 72°.

4-Iodo-o-toluidine; by reduction of 4-iodo-2-nitrotoluene (Heinemann, Ann. 1871, 158, 338). Needles, m.p. 48°–49°, b.p. 273° (decomp.). $BHNO_3$, leaflets.

5-Iodo-o-toluidine; reduction of 3-iodo-6-nitrotoluene with ferrous sulphate and ammonia in aqueous solution at 66°–70° (Artmann, Monatsh. 1905, 26, 1091); by the action of iodine chloride on aceto-*o*-toluidide followed by hydrolysis (Fichter and Phillip, J. pr. Chem. 1906, (2) 74, 297); by the action of iodine on *o*-toluidine (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 498); and by trituration of *o*-toluidine hydrochloride with iodine and calcium carbonate, the yield being 98 p.c. (Hann and Berliner, J. Amer. Chem. Soc. 1925, 47, 1709). Long white needles, m.p. 91°–92° (A.), or short, colourless crystals, m.p. 88° (F. and P.), or 87·2° (H. and B.).

$BHCl$, short white needles, m.p. 214°; $BHNO_3$, slender tetragonal scales. The salts are dissociated by water. B_2HgCl_2 , m.p. 134·5°.

Acetyl-derivative; slender matted needles, m.p. 162°–163° (A.), 168° (F. and P.), 169° (W. and L.), or 176° (Malleis and Meyer, J. Amer. Chem. Soc. 1913, 35, 970). Oxidised by potassium permanganate to 5-iodo-*o*-acetylaminobenzoic acid, m.p. 235° (decomp.) (W. and L.).

Benzoyl-derivative; colourless needles, m.p. 184° (W. and L.).

6-Iodo-o-toluidine; obtained by reducing 2-iodo-6-nitrotoluene, is a liquid. $BHCl$, plates (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627), m.p. 254° (decomp.) (Nölting, Ber. 1904, 37, 1015).

Acetyl-derivative; white needles, m.p. 166° (N.).

3:6-Di-iodo-o-toluidine; by reduction of 2:5-di-iodo-6-nitrotoluene. Colourless needles, m.p. 86° (Wheeler and Brautlecht, Amer. Chem. J. 1910, 44, 126).

4:5-Di-iodo-o-toluidine; by the action of iodine chloride on *p*-iodo-*o*-toluidine. Stout needles or long prisms (Wheeler and Brautlecht, *ibid.* 1910, 44, 493).

3:5-Dibromo-4-iodo-o-toluidine; by reduction of dibromo-iodonitrotoluene (m.p. 69°) (Wroblewsky, Ann. 1878, 192, 210). Needles, m.p. 84°. On treatment with sodium amalgam it yields *o*-toluidine.

Acetyl-derivative; small needles, m.p. 121° (W.).

5-Nitroso-*o*-toluidine; by heating a mixture of 1 part of 5-nitroso-*o*-cresol, 5 parts of ammonium chloride, and 15 parts of dry ammonium acetate at 100° (Mehne, Ber. 1888, 21, 731). Small green needles with a bluish lustre, m.p. 115°–116° with slight detonation. On heating with sodium hydroxide it yields nitrosocresol and ammonia, and with hydroxylamine it is transformed into toluquinonedioxime.

3-Nitro-*o*-toluidine; together with the 5-nitro-isomeride by nitration of aceto-*o*-toluidide, followed by hydrolysis (Beilstein and Kuhlberg, Ann. 1871, 158, 345; Lellmann and Wurthner, *ibid.* 1885, 228, 240; Reverdin and Crépieux, Ber. 1900, 33, 2498; 1902, 35, 1439; Meisenheimer and Hesse, *ibid.* 1919, 52, 1161; Gabriel and Thieme, *ibid.* 1079; Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1127). Also by heating oxalo-*o*-toluidine on the water-bath with concentrated sulphuric acid until water-soluble, cooling to 50° and nitrating slowly with a mixture of nitric acid (D 1.52) and sulphuric acid, keeping the temperature below 50°. The product, after keeping for some hours and diluting with water, is heated at 140° until solution is complete, and finally at 160° for 50 minutes. This is then considerably diluted and steam distilled (Hadfield and Kenner, Chem. Soc. Proc. 1914, 30, 253). By treating 2:3-dinitrotoluene with 2.5N methyl alcoholic ammonia under pressure at 150°–160° for 15 hours (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 856); from 3-nitro-*o*-toluidine 5-sulphonic acid by eliminating the sulphonic group (Gnehm and Blumer, Ann. 1898, 304, 105; Nietzki and Pollini, Ber. 1890, 23, 138); together with the 5-nitro-isomeride by the transformation of *o*-toluene-nitroamine (Bamberger and Stingelin, Ber. 1897, 30, 1259).

Orange-yellow prisms, m.p. 97° (K. and P.; Zincke and Schwarz, Ann. 1899, 307, 44) or 95° (Wibaut, Rec. trav. chim. 1913, 32, 244; R. and C.).

Acetyl-derivative; large shining plates or prisms, m.p. 158° (L. and W.; Körner and Contardi, Atti R. Accad. Lincei, 1915, (v.) 24, i. 888).

4-Nitro-*o*-toluidine; together with the 6-nitro-derivative by nitration of phthalyl-*o*-toluidide, followed by hydrolysis (Städel, Ann. 1884, 225, 385); together with 2-nitro-*p*-toluidine by treating 2:4-dinitrotoluene with warm alcoholic ammonium sulphide (Graeff, Ann. 1885, 229, 343) or alone by reduction with stannous chloride and alcoholic hydrochloric acid (Anschütz, and Heussler, Ber. 1886, 19, 2161); by warming 2:4-tolylenediamine with an aqueous solution of sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3085); by a modification of the method of Green and Lawson (Chem. Soc. Trans. 1891, 59, 1013) by adding powdered potassium nitrate to a solution of *o*-toluidine in concentrated sulphuric acid cooled to –5°, a small amount of the 6-nitro-isomeride being formed simultaneously (Cohen and Dakin, *ibid.* 1902, 31, 1333); by heating 4-nitro-5-amino-*m*-toluic acid or its acetyl-derivative with concentrated sulphuric acid (Errera and Maltre, Gazz. chim. ital. 1906, 36, ii. 370); in 75 p.c. yield, together with 2.5 p.c. of 6-nitro-*o*-toluidine, by nitrating *o*-tolu-

idine in concentrated sulphuric acid (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1539) with mixed acids (Brady and Williams, *ibid.* 1920, 117, 1138). The latter method is much simpler than that of Nölting and Collin (Ber. 1884, 17, 265). Monoclinic prisms, m.p. 107° (N. and C.), 109° (S.), 104°–105° (A. and H.); cf. Jäger, Z. Krist. 1903, 89, and Willgerodt and Kok, Ber. 1908, 41, 2077.

B'HCl, white needles, m.p. 230° (Willgerodt and Kok); B'HBBr, small lustrous pale red crystals (Staden, J. pr. Chem. 1902, (2) 65, 249); B₂H₄SO₄, plates, decomposed by water.

Nitrous acid yields 4-nitro-*o*-cresol and nitro-indazole, whilst with sodium amalgam it yields azoxytoluidine.

Formyl-derivative, small yellow prisms, m.p. 178°–179° (Geigy & Co., U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

Acetyl-derivative; yellowish-white needles, m.p. 150°–151° (Nölting and Collin, *l.c.* 269).

5-Nitro-*o*-toluidine; by nitration of toluene *p*-sulphonyl-*o*-toluidide (Reverdin and Crépieux, Bull. Soc. chim. 1902, 27, 742); by nitration of aceto-*o*-toluidide, followed by hydrolysis (see the 3-nitro-derivative); as a by-product of the action of nitric anhydride on *o*-toluidine (Bamberger and Hoff, Ann. 1900, 311, 95); in low yield by heating 2:5-dinitrotoluene with alcoholic ammonia at 150° for 15 hours (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 859). Small citron-yellow needles, m.p. 127° (K. and P.) or 130° (Wibaut, Rec. trav. chim. 1913, 32, 244; Jäger, *l.c.*; Reverdin and Crépieux, Ber. 1900, 33, 2498).

Acetyl-derivative; short white needles, m.p. 201.6° (Körner and Contardi, Atti R. Accad. Lincei, 1915, (v.) 24, i. 888).

6-Nitro-*o*-toluidine; obtained in 80 p.c. yield by the gradual addition of a 15 p.c. ammonium sulphide solution to 2:6-dinitrotoluene in boiling alcohol, followed by complete extraction of the product with dilute hydrochloric acid (Cohen and Marshall, Chem. Soc. Trans. 1904, 85, 527; Ullmann, Ber. 1884, 17, 1957; Bernthsen, Ber. 1882, 15, 3018; Cunerth, Ann. 1874, 172, 223); in small quantities together with the 4-nitro-isomeride by nitrating *o*-toluidine in presence of an excess of sulphuric acid (Green and Lawson, Chem. Soc. Trans. 1891, 59, 1014). For separation from 2-nitro-*p*-toluidine, see Bernthsen (*l.c.*). Thin rhombic leaflets (Jäger, Z. Kristall. 1903, 38, 89) or long yellow needles, m.p. 91.5° (U.). B'HCl, long flat prisms; B'HBBr, yellowish leaflets or long thin needles, decomposed by water; B'HI, rhombohedra or flat prisms (Tatschaloff, J. pr. Chem. 1902, (2) 65, 239).

Acetyl-derivative; prisms, m.p. 157.5°–158° (U.), m.p. 160° (Cohen and Hodsman, Chem. Soc. Trans. 1907, 91, 975), or colourless needles, m.p. 163°; *benzyl-derivative*, m.p. 167°–167.5° (U.), or 145°–146° (C.).

3:4-Dinitro-*o*-toluidine; as main product, together with 4:5-dinitro-*o*-toluidine, by adding a sulphuric acid solution of 4-nitroaceto-*o*-toluidide to nitric acid (D. 1.5) cooled in ice, followed by hydrolysis by heating for 4–5 hours on the water-bath with dilute sulphuric acid (1 part acid; 2 parts water) (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1138; Morgan and Glover, *ibid.* 1921, 119, 1739). Lustrous, yellowish-brown needles, m.n. 131°–131.5°.

Acetyl-derivative; yellowish-white needles, m.p. 186° (M. and G.).

3 : 5-*Dinitro-o-toluidine*; in small quantity by nitrating toluene *p*-sulphonyl-*o*-toluidide (Reverdin and Crépieux, Bull. Soc. chim. 1902, (3) 27, 742); by heating dinitro-*o*-cresol and its ethers with alcoholic ammonia (Städel, Ann. 1883, 217, 183, 203; Ber. 1881, 14, 900; van Romburgh, Rec. trav. chim. 1884, 3, 398; Barr, Ber. 1888, 21, 1543); by transformation of 5-nitro-*o*-toluene nitroamine (Bamberger and Seitz, Ber. 1897, 30, 1255; Bamberger and Hoff, Ann. 1900, 311, 111); in upwards of 95 p.c. yield by the action of liquid ammonia, methyl or ethyl alcoholic ammonia on 2-chloro-3 : 5-dinitrotoluene (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 790).

Yellow columns or long tables, m.p. 208° or 209°–210° (H.), 211° (B. and S.), 213° (M. and D.).

Acetyl-derivative; slender white needles, m.p. 205·2° (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, i. 888. See also Reverdin and Crépieux, Ber. 1902, 35, 1439).

3 : 6-*Dinitro-o-toluidine* (see 5 : 6-dinitro-*o*-toluidine). Brilliant orange-yellow prisms, m.p. 151°.

Acetyl-derivative; pale yellow microscopic prisms, m.p. 209° (Brady and Taylor; cf. Körner and Contardi).

4 : 5-*Dinitro-o-toluidine* (see 3 : 4-dinitro-*o*-toluidine). Yellow needles, m.p. 191°–191·5°.

Acetyl-derivative; colourless needles, m.p. 180° (Morgan and Glover; Brady and Williams).

4 : 6-*Dinitro-o-toluidine*; together with 2 : 6-dinitro-*p*-toluidine by reducing 2 : 4 : 6-trinitrotoluene with ammonium hydrosulphide (Holleman and Boeseken, Rec. trav. chim. 1897, 16, 426) or by reducing in hydrochloric acid solution in presence of cupric chloride at a copper cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487); together with 2 : 6-dinitrotolyl-*p*-hydroxylamine by reducing 2 : 4 : 6-trinitrotoluene in cold alcoholic ammoniacal solution with hydrogen sulphide (Anschütz and Zimmermann, Ber. 1915, 48, 152). It melts at 155° (H. and B.; A. and Z.) or 135° (B. and E.). On diazotisation it is converted into 2 : 4-dinitrotoluene and 2 : 4-dinitroindazole (B. and E.).

Acetyl-derivative; white needles, m.p. 224° (B. and E.).

5 : 6-*Dinitro-o-toluidine*; formed together with 3 : 6-dinitro-*o*-toluidine by adding 6-nitroaceto-*o*-toluidide to a mixture of sulphuric acid and nitric acid (D 1·5) at 4°–7°, and allowing the temperature to rise to 12°, followed by hydrolysis with concentrated sulphuric acid at 100°. The bases are separated by conversion into the acetyl-derivatives or by crystallisation from glacial acetic acid and sieving the crystals (Brady and Taylor, Chem. Soc. Trans. 1920, 117, 876). Deep yellow needles, m.p. 216° (B. and T.).

Acetyl-derivative; large white crystals, m.p. 180° (B. and T.).

3-*Chloro-5-nitro-o-toluidine*; by chlorination of 5-nitro-*o*-toluidine. It melts at 168° (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151).

3-*Chloro-6-nitro-o-toluidine*; apparently formed together with 5-chloro-6-nitro-*o*-toluidine by heating 6-nitrotolyl-*o*-hydroxylamine with concentrated hydrochloric acid (Brand and Zeller, Ber. 1907, 40, 3324).

5-*Chloro-3-nitro-o-toluidine*; in poor yield together with 5-chloro-4-nitro-*o*-toluidine by dissolving 1 part of 5-chloro-2-toluidine nitrate in 25 parts of nitric acid (66 p.c.) and keeping for 6 hours. On pouring into water only the 4-nitro-derivative separates (Claus and Stapelberg, Ann. 1893, 274, 295). Yellow plates, m.p. 118°–119° (C. and S.), or long orange-yellow needles, m.p. 129°–130° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

Acetyl-derivative; in excellent yield by nitrating 5-chloroaceto-*o*-toluidide in glacial acetic acid at 15°–20° (C. and D.). Glistening needles, m.p. 187° (C. and S.), or prismatic needles, m.p. 197°–198° (C. and D.).

5-*Chloro-4-nitro-o-toluidine*; see 5-chloro-3-nitro-*o*-toluidine (cf. Reverdin and Crépieux, Ber. 1900, 33, 2505). Yellow columns, m.p. 128° (C. and S.), or 124° (Wibaut, Rec. trav. chim. 1913, 32, 244), 129°–130° (C. and D.).

5-*Chloro-6-nitro-o-toluidine*; by heating 6-nitrotolyl-*o*-hydroxylamine (Brand and Zöller, l.c.); by chlorination of 6-nitroaceto-*o*-toluidide in glacial acetic acid, followed by hydrolysis with hydrochloric acid in a sealed tube (Cohen and Hodsman, Chem. Soc. Trans. 1907, 91, 975). Yellow needles, m.p. 95°–96°.

Acetyl-derivative; m.p. 158°–160° (B. and Z.), or 153° (C. and H.); *benzoyl-derivative*; m.p. 212°–213° (C. and H.).

6-*Chloro-3-nitro-o-toluidine*; obtained quantitatively by the action of liquefied ammonia, or saturated alcoholic ammonia, on 2-chloro-5 : 6-dinitrotoluene. Pale amber refractive prisms with pyramidal ends, m.p. 151·5° (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 787).

3(?) : 5-*Dichloro-6-nitro-o-toluidine*; by chlorination of 6-nitroaceto-*o*-toluidide in glacial acetic acid for 5 hours at 100°. It melts at 195°–197° (Cohen and Hodsman, l.c.).

(α)-*Trichloronitrotoluidine*; by the action of alcoholic ammonia on trichlorodinitrotoluene (m.p. 227°). Orange-yellow needles, m.p. 191° (Seelig, Ber. 1885, 18, 423; Ann. 1887, 237, 140).

(β)-*Trichloronitrotoluidine*; in a similar manner to the α -compound from trichlorodinitrotoluene (m.p. 141°). Orange-red needles, m.p. 192° (Seelig).

3-*Bromo-5-nitro-o-toluidine*; by bromination of 5-nitro-*o*-toluidine (Neville and Winther, Ber. 1880, 13, 964; Chem. Soc. Trans. 1880, 37, 431; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 572). It melts at 180·3°–181·3°.

5-*Bromo-3-nitro-o-toluidine*; by successive bromination, nitration, and hydrolysis of aceto-*o*-toluidide (Wroblewsky, Ann. 1878, 192, 206; Neville and Winther, Ber. 1880, 13, 969; Chem. Soc. Trans. 1880, 37, 436, 448). Orange prisms, m.p. 139° (W.), or 143° (N. and W.).

Acetyl-derivative; by treating 5-bromoaceto-*o*-toluidide with 4 parts of nitric acid (D 1·48) below 25°. Needles, m.p. 205° (Niementowski, Ber. 1892, 25, 869; Claus and Beck, Ann. 1892, 269, 219).

5-*Bromo-4-nitro-o-toluidine*; by nitration of 5-bromo-*o*-toluidine in sulphuric acid with nitric acid (D 1·42) and sulphuric acid below 3°. Yellow crystals, m.p. 118° (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 949).

6-*Bromo-3-nitro-o-toluidine*; by nitration and hydrolysis of 6-bromoaceto-*o*-toluidide

(Blanksma, Chem. Weekblad, 1912, 9, 968). Orange-yellow crystals, m.p. 144° (B.).

Acetyl-derivative; yellow crystals, m.p. 199° (B.).

3:5-Dibromo-4-nitro-o-toluidine; by bromination of 4-nitro-o-toluidine. Yellow crystals, m.p. 104°.

Acetyl-derivative; colourless crystals, m.p. 201°; *diacetyl-derivative*; m.p. 159° (Blanksma, Chem. Weekblad, 1909, 6, 717; Morgan and Clayton, *l.c.* 951). It shows a remarkable stability to diazotising agents, which leave it practically unaffected.

3:5-Dibromo-6-nitro-o-toluidine; by bromination of 6-nitro-o-toluidine. It melts at 105° (Blanksma, Chem. Weekblad, 1914, 11, 185).

6-Bromo-3:5-dinitro-o-toluidine; by heating 2:6-dibromo-3:5-dinitrotoluene with alcoholic ammonia at 100°. Yellow crystals, m.p. 200°.

Acetyl-derivative; colourless crystals, m.p. above 300° (Blanksma, *ibid.* 1912, 9, 968).

5-Bromo-3:6(1)-dinitro-o-toluidine; *acetyl-derivative*; by treating 1 part of 5-bromo-aceto-o-toluidide with a mixture of 1 part of sodium nitrate and 20 parts of sulphuric acid. Pale yellow hair-like needles, m.p. 244° (decomp.) (Niementowski, Ber. 1892, 25, 870).

3:5-Dibromo-4:6-dinitro-o-toluidine; *acetyl-derivative*; by the action of nitric acid (D 1.52) and sulphuric acid on 3:5-dibromo-4-nitro-aceto-o-toluidide. White crystals, m.p. 280° (Blanksma, Chem. Weekblad, 1909, 6, 717).

3:5:6-Tribromo-4-nitro-o-toluidine; by nitration and hydrolysis of 3:5:6-tribromoaceto-o-toluidide. Light brown crystals, m.p. 203°.

Acetyl-derivative; colourless crystals, m.p. 275° (Blanksma, Chem. Weekblad, 1914, 11, 185).

3-Iodo-5-nitro-o-toluidine; by the action of iodine chloride on 5-nitro-o-toluidine in glacial acetic acid. Long brown prisms, m.p. 173° (Wheeler, Brautlecht and Hoffman, Amer. Chem. J. 1910, 44, 493).

5-Iodo-3-nitro-o-toluidine; by the action of iodine chloride on 3-nitro-o-toluidine in glacial acetic acid. Orange needles, m.p. 135° (Wheeler, &c.).

5-Iodo-4-nitro-o-toluidine; similarly from 4-nitro-o-toluidine. Bright yellow prisms, m.p. 109° (Wheeler, &c.).

5-Iodo-6-nitro-o-toluidine; by warming equal weights of 6-nitro-o-toluidine and iodine for several hours with ether, water, and calcium carbonate. Yellow prisms, m.p. 85° (Wheeler, &c.).

Methyl-o-toluidine; by reduction of nitroso-methyl-o-toluidine with tin and hydrochloric acid (Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279); by heating o-tolylglycine at 200°-210° (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 303); in a yield of 46 p.c. by methylation of o-toluidine hydrobromide or hydroiodide with methyl alcohol at 150° (Reinhardt and Staedel, Ber. 1883, 16, 29) or with dimethyl sulphate (Ullmann, Ann. 1903, 327, 104; Gnehm and Blumer). Colourless oil, b.p. 207°-208°; D_{20}^{20} 0.973; $B^{\circ}H.PtCl_6$ (A. and W.); $B^{\circ}HCl$, prisms (Geigly and Blumer, Ann. 1899, 304, 96); $B^{\circ}O.H_2O$, leaflets (G. and B.); *picrate*, prisms (G. and B.).

For the manufacture of safranine and azine dye from methyl-o-toluidine, see Bayer & Co.,

Eng. Pat. 6176 of 1895; Fr. Pat. 245641; D. R. P. 90256 of 1895; and M. L. B., D. R. P. 80768 of 1894; Weinberg, Ber. 1893, 26, 307; Bernthsen, *ibid.* 992.

Acetyl-derivative; m.p. 55°-56°, b.p. 260° (M., R. and N.), or 250°-251° (R. and S.).

Nitrosoamine; oil. Transformed by alcoholic hydrochloric acid into 5-nitroso-methyl-o-toluidine, green plates, m.p. 151°. With boiling aqueous sodium hydroxide it yields nitroso-o-cresol and methylamine. It is oxidised by potassium permanganate to nitromethyltoluidine, greenish-yellow needles, m.p. 134° (Kock, Ann. 1888, 243, 308).

4-Chloromethyl-o-toluidine; by methylating 4-chloro-o-toluidine (Störmer and Hoffmann, Ber. 1898, 31, 2532). Liquid, b.p. 248.5°-249.5°/760 mm., D_{20}^{20} 1.138.

Nitrosoamine; oil. D_{20}^{20} 1.226 (S. and H.).

5-Chloromethyl-o-toluidine; oil, b.p. 245°-246°/740 mm. (Geigy & Co., D. R. P. 105103 of 1898).

Dichloromethyl-o-toluidine; by heating dichloro-o-tolylglycine above its melting-point Hentschel, J. pr. Chem. 1899, (2) 60, 83). Oil, b.p. 258°-259°; $B^{\circ}H.PtCl_6$, slender yellow needles (H.).

3-Nitromethyl-o-toluidine; together with 5-nitromethyl-o-toluidine by the transformation of the N-methylester of toluene o-nitroamine (Bamberger and Stingelin, Ber. 1897, 30, 1259). Yellowish-red oil. According to Gnehm and Blumer (Ann. 1899, 304, 103) when methyl-o-toluidine is nitrated a mixture of 4-nitromethyl-o-toluidine and a product, m.p. 48°, is obtained. This latter is stated to be possibly the 3-nitro-derivative.

4-Nitromethyl-o-toluidine; by boiling its acetyl-derivative with concentrated hydrochloric acid (Gnehm and Blumer, *l.c.*); by nitration of methyl-o-toluidine; by methylation of 4-nitro-o-toluidine. Red leaflets or yellow prisms, m.p. 107.5°.

$B^{\circ}HCl$, leaflets decomposed by water; *picrate*, compact red prisms; *nitrosoamine*, pale yellow needles, m.p. 95°.

Acetyl-derivative; m.p. 119°.

5-Nitromethyl-o-toluidine; by oxidation of a dilute solution of 5-nitroso-methyl-o-toluidine with potassium permanganate (Kock, Ann. 1888, 243, 309); together with 5-nitrodimethyl-o-toluidine by methylating 5-nitro-o-toluidine. The products are separated by acetylation and distillation with steam (Bernthsen, Ber. 1892, 25, 3131); together with the 3-nitro-isomeride by the method of Bamberger and Stingelin (*l.c.*). Yellow tables, m.p. 137° (B.). It does not form a sulphate with sulphuric acid.

Nitrosoamine; oil which crystallises on keeping, m.p. 65° (B.).

Acetyl-derivative; rhombohedra-like crystals, m.p. 97° (B.).

6-Chloro-3-nitromethyl-o-toluidine; by the action of methylamine on 2-chloro-5:6-dinitrotoluene in alcoholic solution; by heating 6-chloro-3-nitro-o-toluidine with 1 part of methyl sulphate and 2 parts of toluene for 2 hours at 11 (Morgan and Jones, Chem. Soc. Trans. 1901, 119, 190). Orange-coloured acicular prisms, m.p. 84°-87°.

Nitrosoamine, pale yellow prismatic needles, m.p. 86°-87° (M. and J.).

3(1)-Nitro-4-chloromethyl-o-toluidine; by the

action of concentrated hydrochloric acid on its nitrosoamine (Störmer and Hoffmann, Ber. 1896, 31, 2533). Bright yellow needles, m.p. 185°-186°; nitrosoamine; yellowish-white plates, m.p. 80.5°-81.5° (S. and H.).

4-Nitrobromomethyl-o-toluidine; by bromination of 4-nitromethyl-o-toluidine in glacial acetic acid with cooling. Yellowish-brown needles, m.p. 133° (Gnehm and Blumer, Ann. 1899, 304, 103).

3:5-Dinitromethyl-o-toluidine; by the transformation of the N-methyl ester of 5-nitro-o-toluene nitroamine (Bamberger and Seitz, Ber. 1897, 30, 1255). M.p. 128°.

Nitrosoamine; yellowish rhombohedra, m.p. 94°-95° (S. and H.).

3:5-Dinitrotolyl-o-methylnitroamine; by boiling dimethyl-o-toluidine with nitric acid (D 1.48-1.5). Pale yellow crystals, m.p. 119°-120°. Decomposed by heating with 5 p.c. potassium hydroxide into methylamine and 3:5-dinitro-o-cresol, and on reduction with tin and hydrochloric acid it yields the corresponding monomethyl triamine (Romburgh, Rec. trav. chim. 1884, 3, 396).

Dimethyl-o-toluidine; by heating o-toluidine with methyl iodide (Clarke, Amer. Chem. J. 1905, 33, 496); by distilling trimethyl-o-toluidine hydrate (Thomsen, Ber. 1877, 10, 1586; Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279); in 93 p.c. yield by methylating o-toluidine hydrobromide or hydriodide with a little more than 2 equivalents of methyl alcohol for 8 hours at 150° (Reinhardt and Stadel, Ber. 1883, 16, 29). Liquid, b.p. 184.8°; D_4^{20} 0.9286 (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 623), or b.p. 185.5°; D_4^{25} 0.9417, D_{15}^{25} 0.9333, D_{25}^{25} 0.9268 (Perkin, Chem. Soc. Trans. 1896, 69, 1211); magnetic rotatory power at 15.3° 18.61 (P.); refractive power, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218). It does not condense with formaldehyde in presence of hydrochloric acid (Cohn, Chem. Zeit. 1900, 24, 564). $B'_2H_2PtCl_6$, white needles;



yellow unstable crystals (Wurster and Roser, Ber. 1879, 12, 1826); oxide, $CH_3C_6H_4N(CH_3)_2O$, is formed together with other products by prolonged action of hydrogen peroxide on dimethyl-o-toluidine. The oxide forms a picrate, long greenish-yellow needles, m.p. 145.5°-146.5° (Bamberger and Tschirner, Ber. 1890, 32, 354).

Bromodimethyl-o-toluidine; by brominating dimethyl-o-toluidine in acetic acid; by heating bromo-o-toluidine with methyl alcohol and hydrochloric acid at 180°-200° (Michler and Sampaio, Ber. 1881, 14, 2172). Liquid, b.p. 244°-245°, volatile with steam.

4-Nitrodimethyl-o-toluidine; nitration of dimethyl-o-toluidine with mixed acids at 0° (Gnehm and Blumer, Ann. 1899, 304, 107; Rohde, Zeitsch. f. Elektrochem. 1901, 7, 329); by methylation of 4-nitro-o-toluidine (G. and B.; Staden, J. pr. Chem. 1902, (2) 65, 249). Golden leaflets or rods, m.p. 14° (S.), formerly described as a yellow oil, b.p. 280° (decomp.). $B'HI$, yellow leaflets, m.p. 192°.

5-Nitrodimethyl-o-toluidine; together with 5-nitromethyl-o-toluidine by methylating 5-nitro-o-toluidine (Bernthsen, Ber. 1892, 25, 3133; cf. Haibach, J. pr. Chem. 1902, (2) 65,

242). Dark red flat rhombic pyramids, m.p. 48°-50° (H.), or small tables or needles, m.p. 47.5° (B.).

6-Nitrodimethyl-o-toluidine; by heating 6-nitro-o-toluidine hydrobromide with methyl alcohol for 6-10 hours at 100°-110°. Transparent golden crystals, m.p. 25°-25.5°, b.p. 191°-192°/9.5-10 mm. (von Tschaloff, J. pr. Chem. 1902, (2) 65, 239). $B'HI$, greyish-brown leaflets (T.).

Ethyl-o-toluidine; in 54 p.c. yield by heating o-toluidine hydrobromide or hydriodide with 5 p.c. excess of ethyl alcohol at 150° for 8 hours (Reinhardt and Stadel, Ber. 1883, 16, 31); by electrolytic reduction of aceto-o-toluidine in sulphuric acid solution (Baillie and Tafel, Ber. 1899, 32, 73; Vorländer, *ibid.* 1901, 34, 1462). Liquid, b.p. 213°-214° (R. and S.), or 204°-206° (Norton, Amer. Chem. J. 1885, 7, 118), or 214°-216°/737 mm. (B. and T.); D_{15}^{25} 0.9534 (N.).

Acetyl-derivative; b.p. 254°-256° (R. and S.); nitrosoamine; oil, volatile with steam (N.).

5-Chloroethyl-o-toluidine; oil, b.p. 252°-253°/760 mm. (Geigy & Co., D. R. P. 105103 of 1898).

5-Nitrosoethyl-o-toluidine; by keeping a mixture of ethyltolyl-o-nitrosoamine and absolute alcoholic hydrochloric acid (O. Fischer and Hepp, Ber. 1886, 19, 2994); by the action of sodium nitrite upon a solution of ethyl-o-toluidine in hydrochloric acid (O. Fischer, Ann. 1895, 286, 163; Weinberg, Ber. 1892, 25, 1610). Green leaflets with a blue shimmer, m.p. 140°.

4-Nitroethyl-o-toluidine; by nitration of thyl-o-toluidine with mixed acids at a low temperature (MacCullum, Chem. Soc. Trans. 1895, 67, 247). Light red needles, m.p. 81°-82°.

Nitrosoamine; m.p. 56°. When treated with zinc chloride or sulphuric acid the ethyl-amino-compound is regenerated (M.).

Acetyl-derivative; tables, m.p. 90° (M.).

5-Nitroethyl-o-toluidine; together with a little of the diethyl-derivative by heating 5-nitro-o-toluidine with ethyl iodide, alcohol and sodium hydroxide. The two bases are separated by crystallisation from a little hot alcohol and acetylation. Large dark yellow plates, m.p. 96° (Bernthsen, Ber. 1892, 25, 3137).

Acetyl-derivative; tables or prisms, m.p. 96°-97° (B.).

4-Nitrobromoethyl-o-toluidine; by brominating 4-nitroethyl-o-toluidine in acetic acid. Needles, m.p. 114°; $B'HI$, m.p. 194°-195° (decomp.) (MacCullum, *l.c.*).

Diethyl-o-toluidine; in 70 p.c. yield by ethylating ethyl-o-toluidine with ethyl iodide at 100° (Norton, Amer. Chem. J. 1885, 7, 119), or in 90 p.c. yield by ethylating o-toluidine hydrobromide or hydriodide with ethyl alcohol at 150° for 8 hours (Reinhardt and Stadel, Ber. 1883, 16, 29). Oil, b.p. 208°-209°/755 mm. (R. and S.), or 210°/738 mm. (van Romburgh, Rec. trav. chim. 1884, 3, 402). $B'HI + H_2O$, prisms, m.p. 72°-73° (N.).

When warmed with fuming nitric acid it yields a dinitrotolyl-o-ethylnitroamine, crystals, m.p. 71°-72° (v. R.), and when treated in acid solution with iodine and potassium iodide, it yields a hydrogen iodide periodide, $C_{11}H_{11}NHII$, steel-blue crystalline precipitate or dark brown

prisms, m.p. 109° (Samtleben, Ber. 1896, 31, 1145).

5-Nitroethyl-o-toluidine; see 5-nitroethyl-o-toluidine. Oil, readily soluble in dilute sulphuric acid (Bernthsen, Ber. 1892, 25, 3137).

Phenyl-o-toluidine; together with diphenylamine and ditolylamine, by heating o-toluidine with aniline hydrochloride at 280° (Girard and Willm, Bull. Soc. chim. 1876, (1) 25, 248) or by heating a mixture of 1 part of bromobenzene with 3 parts of o-toluidine and 8 parts of soda lime for 8 hours at 390° (Merz and Paschko-wesky, J. pr. Chem. 1893, (2) 48, 461). M.p. 41°, b.p. 305°/727.5 mm. (Graebe, Ann. 1887, 238, 363). It forms a violet-blue coloration with nitric acid.

6-Chloro-3-nitrophenyl-o-toluidine; by heating 2-chloro-5:6-dinitrotoluene with alcoholic aniline for several weeks; in 75 p.c. yield by heating 2-chloro-5-nitro-o-toluidine for 10 hours under a reflux with bromobenzene in presence of nitrobenzene, potassium carbonate, and cuprous iodide. Rhomboidal plates, m.p. 108°-109°.

Nitrosoamine, yellow prisms, m.p. 91° (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190).

2:4-Dinitrophenyl-o-toluidine; from chloro-2:4-dinitrobenzene and o-toluidine. M.p. 101°-102° (Leymann, Ber. 1882, 15, 1236), or 123° (M. L. B., Eng. Pat. 17639 of 1895; Fr. Pat. 250460; D. B. P. 85388 of 1895), or 120° (Reitzenstein, J. pr. Chem. 1903, (2) 68, 251).

3:5-Dinitrophenyl-o-toluidine; from 2-chloro-3:5-dinitrotoluene and aniline. Red leaflets, m.p. 169° (Nietzki and Rehe, Ber. 1892, 25, 3007).

Di-o-tolylamine (see phenyl-o-toluidine, Girard and Willm); by heating o-cresol, ammonium-zinc chloride, and ammonium chloride at 330°-340° (Merz and Müller, Ber. 1887, 20, 547). Liquid, b.p. 312°/727.5 mm. (Graebe).

Anhydroformaldehyde-o-toluidine; from formaldehyde and o-toluidine. Oil (Wellington and Tollens, Ber. 1885, 18, 3307), or lustrous plates, m.p. about 100° (Eberhardt and Welter, Ber. 1894, 27, 1808).

Methylene-di-o-tolyl-diimide; by heating a mixture of o-toluidine, formaldehyde, potassium hydroxide, and alcohol at 100° (Eberhardt and Welter, l.c.); or by the action of formaldehyde on an aqueous solution of o-toluidine (Eibner, Ann. 1898, 302, 349).

Prismatic needles, m.p. 52° (E. and W.). On heating with aniline hydrochloride it yields diaminoditolylmethane, and by boiling with alcohol it yields anhydroformaldehyde-o-toluidine (E. and W.).

The condensation of formaldehyde with o-toluidine in presence of concentrated sulphuric and acetic acids (cf. J. Russ. Phys. Chem. Soc. 1904, 36, 1126) yields as sole product 6-amino-5-methylbenzo-cyclo-butadiene (Nastukoff and Kroneberg, *ibid.* 1912, 44, 1200; cf. Kroneberg, *ibid.* 1914, 48, 306).

It is also stated that when 4 mols. of o-toluidine and 1 mol. of methylene chloride are heated for 7 hours at 110°-115°, two methylene-di-o-toluidines are formed.

The liquid compound is a thick oil, b.p. above 350° (decamp.); B_2H_6 , $PtCl_4$, is amorphous.

The solid compound forms small trimetric crystals, m.p. 128°, yielding a crystalline di-

hydrochloride, dihydrobromide, sulphate, and dioxalate (Grünhagen, Ann. 1890, 256, 303).

Tolyl-o-hydroxylamine; by reducing o-nitrotoluene with zinc dust and 66 p.c. alcohol in the presence of calcium chloride and sufficient ether to keep the temperature at about 65° (Bretschneider, J. pr. Chem. 1897, (2) 55, 293); by electrolytic reduction of o-nitrotoluene in dilute acetic acid (Haber, Zeitsch. Elektrochem. 1898, 5, 77); by oxidising o-toluidine with a persulphate in presence of ether and in contact with ice (Bamberger and Tschirner, Ber. 1899, 32, 1677). It solidifies to a resin in a mixture of solid carbon dioxide and ether and is readily oxidised to o-nitrosotoluene. On mixing with thionyl-aniline in benzene solution it yields o-toluidine phenyl sulphonamate, m.p. 206°, and azo-o-toluene (Michaelis and Petou, Ber. 1898, 31, 984). The action of methyl alcohol, ethyl alcohol and sulphuric acid, dilute sulphuric acid, dilute and concentrated hydrochloric acid on o-, m-, and p-tolylhydroxylamine under various conditions is described by Bamberger (Ann. 1921, 424, 233, 297).

6-Nitrotolyl-o-hydroxylamine; obtained in 50-60 p.c. yield when 2:6-dinitrotoluene is reduced electrolytically in presence of sodium acetate, acetic acid and alcohol (Brand and Zöller, Ber. 1907, 40, 3324). It exists in three modifications, two stable and one unstable, which are interconvertible by inoculation of their solutions in benzene. The stable yellow form has m.p. 117°-117.5°, the stable colourless form becomes yellow at 105° and melts at 117°-117.5° (Brand, Ber. 1911, 44, 2045).

With aqueous sodium hydroxide it yields mainly 2:2'-dinitro-6:6'-azoxytoluene, and when heated dinitrosotoluene is formed. When oxidised with ferric chloride and sodium acetate in aqueous solution 2-nitro-6-nitrosotoluene, colourless needles, m.p. 117°, is obtained, whilst with concentrated sulphuric acid it yields 2-nitro-6-amino-3-hydroxytoluene, and when heated with concentrated hydrochloric acid 3-chloro-2-nitro-6-aminotoluene, together with a small amount of the isomeric 5-chloro-2-nitro-6-aminotoluene, is produced (Brand and Zöller, l.c.).

4:6-Dinitrotolyl-o-hydroxylamine; together with 2:6-dinitrotolyl-p-hydroxylamine by reducing 2:4:6-trinitrotoluene in almost neutral solution at a silver cathode. Light yellow crystals, m.p. 109° (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; Ber. 1916, 49, 673).

m-Toluidine; by reduction of m-nitrotoluene (Beilstein and Kuhlberg, Ann. 1870, 155, 9; 1870, 156, 66); from p-toluidine by successive acetylation, nitration, hydrolysis, elimination of the amino-group, and reduction (Lorenz, Ber. 1874, 7, 448); by heating m-cresol with ammonium-zinc bromide and ammonium bromide at 330°-340° (Merz and Müller, Ber. 1887, 20, 548); by reducing m-nitrobenzylidene chloride with zinc in presence of alcohol and hydrochloric acid below 12° (Krich, Ber. 1892, 15, 2011; Widman, *ibid.* 1890, 13, 677; Herz, *ibid.* 1895, 18, 3396; Steiner and Vienne, Bull. Soc. chim. 1895, 35, 429; Widman, *ibid.* 1891, (2) 36, from m-nitrotoluenes by passing its vapour mixed with hydrogen over heated reduced copper or nickel (Bamberger and

Bamberger, *Chem. Zentr.* 1901, 122, 277).

Colourless oil, b.p. 203.3° (Kahlbaum, *Zeitsch. physikal. Chem.* 1898, 26, 621, 648), 202°-205° (M. and M.; Lorenz, *Ann.* 1874, 172, 190), 199°-202° (Buckha and Schachtebeck, *Ber.* 1889, 22, 840), 199°-199.5° (Schraube and Romig, *ibid.* 1893, 26, 579); D_{40}^{20} 0.98912 (Kahlbaum), D_{40}^{20} 1.0041, D_{15}^{25} 0.9961, D_{25}^{25} 0.990 (Perkin, *Chem. Soc. Trans.* 1896, 69, 1245; cf. Neubeck, *Zeitsch. physikal. Chem.* 1887, 1, 658); magnetic rotatory power at 15° 16.21 (P.); refractive power, see Brühl (*Zeitsch. physikal. Chem.* 1895, 16, 216); molecular heat of combustion at constant volume, 964.6 Cal.; at constant pressure, 965.6 Cal. (Petit, *Ann. Chim.* 1889, [6] 18, 154).

Its solution in diluted sulphuric acid is coloured yellow-brown by chromic acid and sulphuric acid, and dark red by nitric acid. When *m*-toluidine is dissolved in ether and an equal volume of water is added, followed by a few drops of calcium hypochlorite solution, the aqueous layer is coloured brownish-yellow, and the ethereal layer reddish (Lorenz, *Ann.* 1874, 172, 180).

It resembles the *o*-compound in many of its properties, but may be distinguished from the latter by its acetyl-derivative, m.p. 65.5° (aceto-*o*-toluidide melts at 110°). It may be detected and also estimated by conversion into the dimethyl-derivative, which, unlike the corresponding *o*- and *p*-compounds, readily yields a nitroso-derivative as a yellow crystalline precipitate when treated with nitrous acid (Wurster and Riedel, *Ber.* 1879, 12, 1796).

When hydrogenated in the presence of reduced nickel it yields *m*-methyl cyclohexylamine, together with the corresponding secondary and tertiary bases (Sabatier and Senderens, *Bull. Soc. chim.* 1904, (3) 31, 709). It reacts with diphenylthiocarbamide in presence of lead hydroxide to yield diphenyl-*m*-tolyl-guanidine (Alway and Viele, *Amer. Chem. J.* 1902, 28, 294); with benzylidene-acetyl-acetone to yield β -toluidinebenzyl-acetyl-acetone (Ruhemann and Watson, *Chem. Soc. Trans.* 1904, 85, 1170); with methylene di-iodide to yield di-*m*-tolyl-methylenediamine (Senier and Goodwin, *ibid.* 1902, 81, 280); with chloroacetylurethane to yield β -*m*-tolylhydantoin (Frerichs and Breustedt, *J. pr. Chem.* 1902, (2) 66, 231), and with benzaldehyde cyanhydrin to yield *m*-tolylamino-benzyl cyanide (Sachs and Goldmann, *Ber.* 1902, 35, 3319). Coupling with diazo-compounds has been studied by Mehner (*J. pr. Chem.* 1902, (2) 66, 401). The action of dichloroacetic acid on *m*-toluidine has been studied by Heller (*Ann.* 1908, 358, 349).

It is only employed to a limited extent technically in the production of dyestuffs (M. L. B., *Eng. Pat.* 5119 of 1897; *Fr. Pat.* 264579; *D. R. P.* 93499 of 1896; *Eng. Pat.* 14937 of 1908; *U.S. Pat.* 913940; *D. R. P.* 219210 of 1907; Monnet, Reverdin and Nölting, *Ber.* 1879, 12, 445; Rosenstiehl and Gerber, *Compt. rend.* 1882, 94, 1319; 95, 238).

For a new sensitive indicator from *m*-toluidine see Träger and Hille (*J. pr. Chem.* 1903, (2) 68, 297).

Salts (see Lorenz); $B'HCl$, leaflets, m.p. 228°, b.p. 247.8°/728 mm. or 249.8°/760 mm. (Ullmann, *Ber.* 1898, 31, 1699); $B'HNO_2$, large

rhombic tables; $B'H_2SO_4$, needles; $B'C_2H_5O_2$, unstable leaflets; $B'_2(C_2H_5O)_2$; $B'_2C_2H_5O_2$ (Eisenberg, *Ann.* 1880, 205, 270); $B'_2H_2PtCl_6$, yellow slender needles (Widman); $B'HBI_2$ (Kraut, *Ann.* 1881, 210, 323); $B'_2H_2ZnCl_4$, needles (Base, *Amer. Chem. J.* 1898, 20, 654); $B'_2H_2ZnCl_4$, needles (B.); $B'HCl_2HgCl_4$, tables (Swan, *Amer. Chem. J.* 1898, 20, 624); $B'HCl-HgCl_4$, tables (Swan); ($B'HCl$), $HgCl_4$, leaflets (Swan); $B'HSnCl_4 + \frac{1}{2}H_2O$, silver leaflets (Slagle, *Amer. Chem. J.* 1898, 20, 642); $B'_2H_2SnCl_4 + H_2O$, monoclinic tables (Slagle); $B'_2H_2SbCl_5 + H_2O$ (Higbee, *Amer. Chem. J.* 1900, 23, 150); $B'_2H_2SbCl_5$, rhombic tables (H.); $B'_2H_2ZnBr_4 + 4H_2O$, prisms (B.); $B'_2H_2ZnBr_4$, needles and prisms (B.); $B'_2H_2SbBr_4 + H_2O$ (H.); $B'_2H_2SbI_4$ (H.); $B'_2H_2SnCl_4$, pearly white plates, m.p. 76° (Druce, *Chem. News*, 1919, 119, 272); $B'_2H_2SnCl_4$, pale pink, nacreous plates, m.p. 284° (D.); *picrate*, striated monoclinic crystals, decomposing when heated above 180° (Jerusalem, *Chem. Soc. Trans.* 1909, 95, 1284).

Formyl-derivative; liquid at -18°, b.p. 278°/724 mm. (Niementowski, *Ber.* 1887, 20, 1892). Decomposes on long boiling, forming methane ditolylamidine, $CH(NC_2H_5)_2NHC_2H_5$, needles or plates, m.p. 123°.

Acetyl-derivative; long needles, m.p. 65.5°, b.p. 203° (Beilstein and Kuhlberg; Morgan and Micklethwait, *Chem. Soc. Trans.* 1913, 103, 1400); **benzoyl-derivative**; m.p. 125° (Just, *Ber.* 1886, 19, 983).

Chloroacetyl-derivative; m.p. 141°. On fusion with potassium hydroxide it is converted into 5:5'-dimethylindigotin (Kuhara and Chikashigé, *Amer. Chem. J.* 1902, 27, 1).

Dichloroacetyl-derivative; plates which sublime, m.p. 98°-100° (Rugheimer and Hoffmann, *Ber.* 1885, 18, 2988).

2-Chloro-*m*-toluidine; by reducing 2-chloro-3-nitrotoluene (Wynne and Greeves, *Chem. Soc. Proc.* 1895, 11, 151; *Chem. Soc. Trans.* 1895, 67, 1548; cf. Cohen and Dakin, *ibid.* 1901, 79, 1128); by the action of hydrochloric acid on *m*-tolylhydroxylamine (Bamberger, *Ber.* 1902, 35, 3697). M.p. 6.6° (Wibaut, *Rec. trav. chim.* 1913, 32, 244), b.p. 228°-229° (W. and G.), and is volatile with steam.

Acetyl-derivative; needles, m.p. 132°-133° (W. and G.; W.), or 133°-134° (Bamberger, Ter-Sarkissjanz and de Werra, *Ber.* 1905, 35, 3697, 3711), or 126°-128° (Cohen and Dakin, *l.c.* 1321); **benzoyl-derivative**; needles, m.p. 125° (W.).

4-Chloro-*m*-toluidine; by the action of hydrochloric acid on *m*-tolylhydroxylamine (Bamberger); reduction of 4-chloro-3-nitrotoluene (Goldschmidt and Hönig, *Ber.* 1886, 19, 2443; Gattermann and Kaiser, *Ber.* 1885, 18, 2601; cf. Engelbrecht, *ibid.* 1874, 7, 797; Claus, *J. pr. Chem.* 1892, (2) 48, 29). Thin very volatile colourless leaflets, m.p. 29°-30° or 32°, b.p. 230°/758 mm. (G. and K.; C.).

$B'HCl$, needles, partially dissociated in water (G. and K.).

Acetyl-derivative; long silky needles, m.p. 96°-97° (G. and K.; G. and H.; E.), or 124° (C.).

5-Chloro-*m*-toluidine; by reduction of 5-chloro-3-nitrotoluene (Hönl, *Ber.* 1887, 20, 2419). Liquid, b.p. 242°/730 mm., volatile with steam.

BHCl, small needles; **BHNO₃**, m.p. 198° (decomp.) (H.).

Acetyl-derivative; needles, m.p. 146° (H.) or 151° (W. and G.).

6-Chloro-m-toluidine; by the action of hydrochloric acid on *m*-tolylhydroxylamine (Bamberger); by the method of Chattaway and Orton (Chem. Soc. Trans. 1901, 79, 461); by reducing 6-chloro-3-nitrotoluene (Henry and Radziszewski, Ber. 1869, 2, 308, 599; Wroblewsky, Ann. 1873, 168, 206; Goldschmidt and Hönig, Ber. 1886, 19, 2443; 1887, 20, 199; Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1544); by reducing *m*-nitrotoluene with zinc and hydrochloric acid (Kock, Ber. 1887, 20, 1567). Tables, m.p. 83.5°–84.1° (Bamberger, Ter-Sarkissjanz and de Werra; Reverdin and Crépieux, Ber. 1900, 33, 2503; Chattaway and Orton).

BHCl, long slender needles; **BHNO₃**, long broad needles, m.p. 164°; **B₂H₄SO₄**.

Acetyl-derivative; colourless plates, m.p. 89° (G. and H.), 91.2°–91.7° (B., T-S. and de W.), 92° (M. and C.).

2:5-Dichloro-m-toluidine; by reduction of 2:5-dichloro-3-nitrotoluene (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330). It melts at 69°–70°.

2:6-Dichloro-m-toluidine; by chlorination of 2-chloro-aceto-*m*-toluidide followed by hydrolysis with hydrochloric acid at 130° (Cohen and Dakin), or by reduction of 2:6-dichloro-3-nitrotoluene, followed by distillation with steam (C. and D., l.c. 1346). Colourless needles, m.p. 59°–60°.

Acetyl-derivative; long needles, m.p. 120°–122° (C. and D.); *benzenesulphonyl-derivative*, m.p. 114° (Raper, Cohen and Thomson, *ibid.* 1901, 85, 371).

4:5-Dichloro-m-toluidine; by reducing 3-nitro-4:5-dichlorotoluene; *acetyl-derivative*, needles, m.p. 158°–159° (Cohen and Dakin, l.c. 1338).

4:6-Dichloro-m-toluidine; by chlorination of aceto-*m*-toluidide in glacial acetic acid with sodium chlorate and hydrochloric acid, followed by hydrolysis (Reverdin and Crépieux, l.c.); by reduction of 2:4-dichloro-5-nitrotoluene (Cohen and Dakin, l.c.). Crystals, m.p. 85°, volatile with steam (*cf.* Seelig, Ann. 1887, 237, 163).

Acetyl-derivative; as above (R. and C.); by the action of bleaching powder on aceto-*m*-toluidide in glacial acetic acid (C. and D., l.c. 1332). Colourless needles, m.p. 156°–157° (R. and C.; C. and D.).

5:6-Dichloro-m-toluidine; by reducing 2:3-dichloro-5-nitrotoluene. Needles, m.p. 88°, b.p. 292° (Wynne and Greeves, l.c.).

Acetyl-derivative, m.p. 187° (W. and S.).

2:4:6-Trichloro-m-toluidine; by chlorination of aceto-*m*-toluidide in acetic acid and hydrochloric acids with sodium chlorate at 15°–25°, followed by hydrolysis of the acetyl-derivative with 50 p.c. sulphuric acid (Cohen and Dakin, l.c. 1336; Reverdin and Crépieux). Glistening white needles, volatile with steam, m.p. 77°–78° (C. and D.).

Acetyl-derivative; m.p. 181° (R. and C.).

2:5:6-Trichloro-m-toluidine; by nitration and reduction of 2:3:6-trichlorotoluene. It melts at 85°–87° (Cohen and Dakin, Chem. Soc. Trans. 1901, 85, 1281).

4-Bromo-m-toluidine; by reduction of 4-bromo-3-nitrotoluene (Nevile and Winther, Chem. Soc. Trans. 1880, 37, 442; Ber. 1880, 13, 972; Claus, J. pr. Chem. 1892, (2) 46, 25; Wroblewsky, Ann. 1873, 168, 77; Hübner and Roos, Ber. 1873, 6, 800). Prisms, m.p. 30.6°–32° (N. and W.), 35° (C.); 67° (W.), 75° (H. and R.). The higher melting-point compounds are impure.

Acetyl-derivative; m.p. 113.7°–114.6° (N. and W.), 164° (C.).

5-Bromo-m-toluidine; by reducing 5-bromo-3-nitrotoluene (Wroblewsky, Ann. 1878, 192, 203). It crystallises with difficulty, m.p. 35.6°–36°, b.p. 255°–260°; D₁₅ 1.442 (W.); Nevile and Winther, Ber. 1880, 13, 964; Chem. Soc. Trans. 1880, 37, 429). **BHCl**, tables; **BHNO₃**, long needles; **B₂H₄SO₄**, tables.

Acetyl-derivative; m.p. 167°–168° (N. and W.).

6-Bromo-m-toluidine; by brominating aceto-*m*-toluidide, followed by hydrolysis of the product with alcoholic potash (Wroblewsky, Ann. 1873, 168, 172); by reducing 6-bromo-3-nitrotoluene (Nevile and Winther, l.c.). Crystals, m.p. 78.4°–78.8°, b.p. 240° (N. and W.). **BHNO₃**, prisms.

It is probable that the product, described as a liquid and obtained by Hübner and Roos (Ber. 1873, 6, 801) by the reduction of nitrated *o*-bromotoluene is identical with this amine. **BHCl**, small rhombic tables; **BHNO₃**, small rhombic tables; **B₂H₄SO₄**, very slightly soluble in water.

2:5-Dibromo-m-toluidine; by reduction of 2:5-dibromo-3-nitrotoluene. M.p. 72.4°–73.1° (Nevile and Winther, l.c.).

Acetyl-derivative; m.p. 144°–145° (N. and W.).

2:6-Dibromo-m-toluidine; this compound is stated by Wroblewsky to be formed by the action of 2 mols. of bromine on aceto-*m*-toluidide, followed by hydrolysis, and is described as melting at 92.5°. Nevile and Winther (Chem. Soc. Trans. 1880, 37, 439) found that under these conditions a mixture of a monobromotoluidine, m.p. 76°–77°, 4:6-dibromo-*m*-toluidine, 2:6-dibromo-*m*-toluidine, m.p. 33°–35°, and 2:4:6-tribromo-*m*-toluidine is formed.

4:5-Dibromo-m-toluidine; by reducing the corresponding dibromonitrotoluene (Nevile and Winther, l.c.; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 510). Long needles or flat prisms, m.p. 58°–59° (N. and W.).

Acetyl-derivative; m.p. 163.5°–164° (C. and D.).

4:6-Dibromo-m-toluidine; together with 2:6-dibromo-*m*-toluidine by brominating aceto-*m*-toluidide, separation being effected by crystallisation from alcohol in which the 2:6-*is* more soluble; by brominating 4-bromo-aceto-*m*-toluidide, followed by hydrolysis (Nevile and Winther, l.c.); by bromination of 6-bromoaceto-*m*-toluidide (Cohen and Dutt, l.c. 515); by reduction of 4:6-dibromo-3-nitrotoluene with tin and hydrochloric acid (Davies, Chem. Soc. Trans. 1901, 81, 872). Dull greyish radiating prisms, m.p. 74.5°–75° (D.).

Acetyl-derivative; white prisms or needles, m.p. 168°–168.6° (N. and W.), 168°–169° (C. and D.).

5:6-Dibromo-m-toluidine; by bromination and hydrolysis of 4-bromoaceto-

toluidide; by reduction of 5:6-dibromo-3-nitrotoluene (Neville and Winther, l.c.). It melts at 86.4° (N. and W.) or 83°-85° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 512).

Acetyl-derivative; m.p. 204°-205° (N. and W.).

2:4:6-Tribromo-*m*-toluidine; by the action of bromine vapour on *m*-toluidine hydrochloride; by bromination of aceto-*m*-toluidide, followed by hydrolysis (Wroblewski, Ann. 1873, 168, 195; Neville and Winther, Chem. Soc. Trans. 1880, 37, 440, 448).

Monoacetyl-derivative; colourless crystals m.p. 205°.

Diacetyl-derivative; colourless crystals, m.p. 103° (Blanksma, Chem. Weekblad, 1909, 6, 717).

2:5:6-Tribromo-*m*-toluidine; by brominating 2:5-dibromoaceto-*m*-toluidide, followed by hydrolysis (Neville and Winther). It melts at 93°-94°.

Acetyl-derivative; m.p. 179°-181° (N. and W.).

4:5:6-Tribromo-*m*-toluidine; by successive bromination and hydrolysis of 4:5-dibromoaceto-*m*-toluidide (N. and W.). It melts at 96°-96.8°.

Acetyl-derivative; m.p. 171°-173° (N. and W.).

Tribromo-*toluidine*; from *o*-bromotoluene *m*-sulphonic acid, by nitration, reduction and bromination (Schäfer, Ann. 1874, 174, 362; Ber. 1874, 7, 1355). M.p. 82°.

Tetra-bromo-*m*-toluidine; by brominating 5-bromo-*m*-toluidine (Neville and Winther, Ber. 1880, 13, 975; Chem. Soc. Trans. 1880, 37, 449); or 4:5-dibromo-*m*-toluidine (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 510). White needles, m.p. 223°-224° (N. and W.).

6-Chloro-2:4-dibromo-*m*-toluidine; by brominating an aqueous solution of 6-chloro-*m*-toluidine 4-sulphonic acid (Davies, Chem. Soc. Trans. 1921, 119, 866). Long colourless needles, m.p. 99.5°, which on keeping become bright red. Insoluble in dilute hydrochloric acid and only slightly soluble in hot fuming hydrochloric acid.

2-Iodo-*m*-toluidine; by reducing 2-iodo-3-nitrotoluene with ferrous sulphate and ammonia (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441). Long flat prisms, m.p. 41°-42°.

Acetyl-derivative; m.p. 135°. On oxidation with potassium permanganate it yields 2-iodo-3-acetylaminobenzoic acid, m.p. 119° (Wh. and L.).

4-Iodo-*m*-toluidine; similarly from 4-iodo-3-nitrotoluene. It melts at 38°-38.5° (Wheeler and co-workers, *ibid.* 1910, 44, 126, 493), and not at 48° as stated by Willgerodt and Simonis (Ber. 1906, 39, 269). B'HCl, pale yellow needles; B'HNO₃, red needles; B'H₂SO₄ (Wi. and S.). *Acetyl-derivative*; m.p. 151° (W.), 145°-146° (Wi. and S.). On treatment with iodine chloride it yields 4:6-di-iodoaceto-*m*-toluidide.

Formyl-derivative; slender colourless needles, m.p. 129° (Wi. and S.).

5-Iodo-*m*-toluidine; by reducing 5-iodo-3-nitrotoluene (W.). Long colourless needles, m.p. 78°-78.5°.

Acetyl-derivative; m.p. 183° (W.).

An *iodo-*toluidine**; needles or leaflets, m.p. 188°-189° described by Hübner and Glassner (Ber. 1875, 8, 562), and is obtained from nitrated

p-iodotoluene. It forms a *hydrochloride*, needles; a *nitrate*, plates; and a *sulphate*, needles.

6-Iodo-*m*-toluidine; by reducing 6-iodo-3-nitrotoluene (Artmann, Monatsh. 1905, 26, 1091; Holleman, Rec. trav. chim. 1912, 31, 267). Colourless leaflets which decompose slowly on exposure to air, m.p. 98°-99° (A.), or m.p. 37°-39° (Wheeler, &c.), or m.p. 42° (H.). B'HCl, short needles; B'HNO₃, aggregates of slender needles (A.).

Acetyl-derivative; white needles, m.p. 132° (A.).

2:5-Di-iodo-*m*-toluidine; by reduction of 2:5-di-iodo-3-nitrotoluene (Wheeler, &c.). Pale brown prisms, m.p. 82°.

Acetyl-derivative; long colourless needles, m.p. 198°-199° (W.).

2:6-Di-iodo-*m*-toluidine; by the action of iodine chloride on 2-iodoaceto-*m*-toluidide, followed by hydrolysis (Wheeler, &c.). Colourless prisms, m.p. 88°.

Acetyl-derivative; colourless prisms, m.p. 171° (W.).

4:5-Di-iodo-*m*-toluidine; by reducing 4:5-di-iodo-3-nitrotoluene (Wheeler, &c., l.c.). Colourless slender needles, m.p. 66°-67°.

Acetyl-derivative; m.p. 183°-184° (W.).

4:6-Di-iodo-*m*-toluidine; by the action of iodine on 4-iodo-*m*-toluidine (Wheeler, &c.). Stout colourless needles, m.p. 73°-74°.

Acetyl-derivative; long colourless needles, m.p. 213° (W.).

5:6-Di-iodo-*m*-toluidine; by the action of ferrous sulphate and ammonia on 2:3-di-iodo-5-nitrotoluene (W.). Colourless crystals, volatile with steam, m.p. 106°.

Acetyl-derivative; m.p. 208° (W.).

2:4:6-Tri-iodo-*m*-toluidine; pale brown hair-like needles, m.p. 135°.

Acetyl-derivative; m.p. 265° (W.).

2:4:6-Tri-iodo-*m*-toluidine; together with 2:4:5:6-tetraiodo-*m*-toluidine by warming mixture of 2:5-di-iodo-*m*-toluidine with iodine, water, ether and calcium carbonate for 18 hours. Colourless needles, m.p. 119°-120° (W.).

4:5:6-Tri-iodo-*m*-toluidine; by warming a mixture of 5:6-di-iodo-*m*-toluidine, iodine, water, ether and calcium carbonate for several hours. Small needles, m.p. 122°.

Acetyl-derivative; colourless needles, m.p. 265° (decomp.) (W.).

2:4:5:6-Tetraiodo-*m*-toluidine; together with other products by iodination of 2:5- or 5:6-di-iodo-*m*-toluidine under similar conditions (W.). Small needles, m.p. 205° (W.).

6-Chloro-4-iodo-*m*-toluidine; by successive chlorination and hydrolysis of 4-iodoaceto-*m*-toluidide (Willgerodt and Simonis, Ber. 1906, 39, 269). Thin colourless plates, m.p. 65°; *oxalate*; large plates, m.p. 165°.

Acetyl-derivative; aggregates of small colourless needles, m.p. 196.5° (Wi. and S.).

6-Nitroso-*m*-toluidine; by heating 1 part of nitroso-*m*-cresol with 15 parts of dry ammonium acetate and 5 parts of ammonium chloride for 1 hour at 100° (Mehne, Ber. 1888, 21, 730). Steel-blue needles, m.p. 178°.

2-Nitro-*m*-toluidine; see also Lampricht, Ber. 1885, 18, 1402; Stadel and Kolb, Ann. 890, 259, 216; Nöling and Stoecklin, Ber. 891, 24, 564; together with small quantities

of 2-nitro-*o*-toluidine and 2,3-toluylenediamine by reduction of 2:3-dinitrotoluene suspended in alcoholic hydrochloric acid with stannous chloride and absolute alcohol at 7° and keeping the mixture for 12 hours. It forms deep red prisms, m.p. 107°–108° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052), and was formerly erroneously regarded as a dinitroazo-toluene (Kenner and Parkin, *ibid.* 1920, 117, 857). When 2:3-dinitrotoluene is reduced with hydrogen sulphide in alcoholic ammoniacal solution, Kenner and Parkin (*l.c.*) obtained a dinitroditolyl sulphide (most probably the 2:2':6:6'-compound) and a substance, m.p. 54°. 2-Nitro-*m*-toluidine is obtained also by heating 3-chloro-2-nitrotoluene with concentrated ammonia solution (D 0.880) at 200° for 8 hours.

Acetyl-derivative; transparent prisms, m.p. 126° (B. and K.) or 136° (L.).

4-Nitro-*m*-toluidine; from 4-nitro-*m*-tolyl-ethyl ether and ammonia (Städel and Kolb, Ann. 1890, 259, 224; Green and Rowe, Chem. Soc. Trans. 1913, 103, 898; Morgan and Scharff, Chem. Soc. Trans. 1914, 105, 121); by hydrolysis of the acetyl-derivative, obtained together with 6-nitroaceto-*m*-toluidide by nitrating aceto-*m*-toluidide with fuming nitric acid in glacial acetic acid (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333); from 4-nitro-2:5-toluylenediamine by the diazo-reaction (Morgan and Micklethwait, *ibid.* 1913, 103, 1399; Morgan and Scharff, *l.c.*); by heating 3:4-dinitrotoluene with 2.5/N-methyl alcoholic ammonia at 150° for 6 hours (Kenner and Parkin, *ibid.* 1920, 117, 858). Golden-yellow plates, or orange-yellow spicules, m.p. 109° (S. and K.), 110°–110.5° (C. and D.), or 112° (M. and M.).

Acetyl-derivative; yellow needles, m.p. 88°–89° (M. and M.) or 86°–87° (C. and D.); *benzoyl-derivative*; long yellow needles, melting indefinitely at 83° (M. and M.); *benzenesulphonyl-derivative*; prisms, m.p. 137°–138° (M. and S.).

5-Nitro-*m*-toluidine; in 80 p.c. yield by reducing 3:5-dinitrotoluene with alcoholic ammonium sulphide (Städel, Ann. 1883, 217, 199; Neville and Winther, Ber. 1882, 15, 2985; Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 529). Yellow or brownish-red needles, m.p. 98°–98.4° (N. and W.; Haibach). B'HBr, thin leaflets (Haibach, J. pr. Chem. 1902, (2) 65, 242).

Acetyl-derivative; white microcrystalline powder, m.p. 187° (B., D. and R.). If a solution of the acetyl-derivative in concentrated sulphuric acid is added to nitric acid, or if the solid compound be added to a mixture of nitric and sulphuric acids, 5:6-dinitroaceto-*m*-toluidide is the main product, but if the acetyl-compound is added directly to fuming nitric acid 4:5-dinitroaceto-*m*-toluidide preponderates (B., D. and R.).

6-Nitro-*m*-toluidine; by successive nitration and hydrolysis of aceto-*m*-toluidide (Beilstein and Kuhlberg, Ann. 1871, 158, 348), or together with the 4-nitro-isomeride when the nitration is effected in glacial acetic acid solution (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333; Cook and Brady, *ibid.* 1920, 117, 752); by heating 6-nitro-3-amino-*p*-toluic acid with hydrochloric acid at 150° (Filati and Cross, Gazz. chim. ital. 1882, 12, 204); by heating 6-nitro-3-amino-

ethyl ether with concentrated ammonia (D 0.9) at 140°–150° for 8 hours (Städel and Kolb, Ann. 1890, 259, 214); as chief product, together with the 4-nitro-isomeride, by nitrating *m*-toluidine dissolved in glacial acetic acid and sulphuric acid with nitric acid (63 p.c.) and sulphuric acid at 0°, the isomerides being separated by distilling with a current of steam (Nölting and Stoecklin, Ber. 1893, 26, 564; cf. Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1397; Kenner and Parkin, *ibid.* 1920, 117, 858). Long, slender, saffron-yellow needles, m.p. 138° (N. and S.), 138°–140° (M. and M.), 133°–134° (C. and D.), or 135°–138° (Cohen and Hodsman, *ibid.* 1907, 91, 976).

Acetyl-derivative; small rhombic cubes, m.p. 101°–102° (B. and K.), or massive red prisms, m.p. 103°–104° (C. and D.), or m.p. 109° (M. and M.). It is separated from 4-nitroaceto-*m*-toluidide by mechanical means, followed by crystallisation from alcohol (C. and D.), or by pouring the reaction product into water when the 6-nitro-isomeride separates, whilst the filtrate on keeping deposits 4-nitroaceto-*m*-toluidide (C. and B.).

2:4-Dinitro-*m*-toluidine; *acetyl-derivative*; colourless needles, m.p. 211°–212° (C. and B.).

2:6-Dinitro-*m*-toluidine; in 10–15 p.c. yield by the action of hydroxylamine hydrochloride on 2:6-dinitrotoluene in methyl alcoholic potassium hydroxide solution at 30°, and addition of much water to the resulting solution (Meisenheimer and Patzig, Ber. 1906, 39, 2533); by the action of 10 p.c. alcoholic ammonia on 3-bromo-2:6-dinitrotoluene (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339). Pale yellow prisms or needles, m.p. 133.8° (K. and C.) or 132.5° (M. and P.).

Acetyl-derivative; colourless plates or large prisms, m.p. 166° (K. and C.; C. and B.).

4:5-Dinitro-*m*-toluidine; see 5-nitro-*m*-toluidine. Large brownish-yellow needles, m.p. 131°.

Acetyl-derivative; fine white needles, m.p. 177° (B., D. and R.).

4:6-Dinitro-*m*-toluidine; by keeping a mixture of 3:4:6-trinitrotoluene and alcoholic ammonia for 1 day (Hepp, Ann. 1883, 215, 368); by heating *m*-bromo-4:6-dinitrotoluene with alcoholic ammonia (Bentley and Warren, Amer. Chem. J. 1890, 12, 2); by heating 4:6-dinitro-*m*-cresyl ethyl-ether with concentrated aqueous ammonia at 100° (Städel and Kolb, Ann. 1890, 259, 220); as the main product, together with a small quantity of 2:6-dinitro-*m*-toluidine, and very little, if any, 2:4-dinitro-*m*-toluidine, by gradual addition of aceto-*m*-toluidide to 10 times its weight of nitric acid (D 1.5) with thorough agitation, keeping the temperature below 25°, followed by hydrolysis. Occasionally 2:4:6-trinitro-*m*-toluidine is formed also (Cook and Brady, Chem. Soc. Trans. 1920, 117, 760); together with the 2:6-dinitro-isomeride by gradual addition of 6-nitroaceto-*m*-toluidide to an excess of nitric acid (D 1.5) below 25°, followed by hydrolysis (C. and B.). Small golden-yellow crystals, m.p. 192°–193° (H.) or 195° (S. and K.).

Acetyl-derivative; pale yellow needles, m.p. 103° (C. and B.).

3:5-Dinitro-*m*-toluidine; see 5-nitro-*m*-toluidine. Orange-yellow plates, m.p. 145°.

Acetyl-derivative; faintly yellow sandy powder, m.p. 172° (Brady, Day and Rolt).

2:4:6-Trinitro-*m*-toluidine; by the action of concentrated alcoholic ammonia on the ethyl-ether of 2:4:6-trinitro-*m*-cresol (Nölting and Salis, Ber. 1882, 15, 1864; Ann. Chim. 1885, (6) 4, 128; Städel and Kolb, Ann. 1890, 259, 222), or on *m*-bromo-trinitrotoluene (Bentley and Warren, Amer. Chem. J. 1890, 12, 5), or on 3-chloro-2:4:6-trinitrotoluene (Reverdin, Dresel and Deletra, Bull. Soc. chim. 1904, (3) 31, 631). Small crystals, m.p. 136° (S. and K.) or 126° (N. and S.).

Acetyl-derivative, microscopic white silky needles, m.p. 249° (decomp.) (Cook and Brady, Chem. Soc. Trans. 1920, 117, 752).

2-Chloro-4-nitro-*m*-toluidine; by keeping a solution of 2-chloro-3:4-dinitrotoluene in about 60 parts of absolute alcohol saturated with ammonia for 14 days (Morgan and Glover, Chem. Soc. Trans. 1921, 119, 1704). Golden-yellow needles, m.p. 105°. It yields a deep red coloration with alcoholic sodium hydroxide.

6-Chloro-4-nitro-*m*-toluidine; obtained together with 6-chloro-2-nitro-*m*-toluidine by successive nitration and hydrolysis of 6-chloro-aceto-*m*-toluidide (B. A. S. F., D. R. P. 226772 of 1908; Morgan and Challenor, Chem. Soc. Trans. 1921, 117, 1544), or together with 27 p.c. 6-chloro-3-nitro-*p*-toluidine, by the action of alcoholic ammonia on 2-chloro-4:5-dinitrotoluene. The latter mixture melts at 144°, and is not separated by repeated crystallisation from alcohol, petroleum or glacial acetic acid (Morgan and Drew, *ibid.* 1920, 117, 789; Morgan and Challenor, *l.c.*). Yellowish-brown prisms, m.p. 158°–159°.

2:4:5-Trichloro-6-nitro-*m*-toluidine; the *acetyl-derivative*, which does not melt below 200°, is obtained together with a *dichloro-6-nitroaceto-*m*-toluidide*, colourless needles, m.p. 181°–183°, by treating 6-nitroaceto-*m*-toluidide with aqueous sodium chlorate in presence of glacial acetic and concentrated hydrochloric acids (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333).

4:5:6-Trichloro-2-nitro-*m*-toluidine; by treating 4:5:6-trichlorodinitrotoluene with alcoholic ammonia at 80°–100°. It melts at 192° (Seelig, Ber. 1885, 18, 420).

6-Bromo-2-nitro-*m*-toluidine; see 6-bromo-4-nitro-*m*-toluidine. It melts at 102°–103° (Neville and Winther, Ber. 1880, 13, 972; Chem. Soc. Trans. 1880, 37, 444; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 513).

6-Bromo-4-nitro-*m*-toluidine; as main product together with the 2-nitro-isomeride by nitrating 4-bromoaceto-*m*-toluidide with sulphuric and nitric acids (N. and W.), or in presence of glacial acetic acid (C. and D.), followed by hydrolysis. Dark yellow or brown needles, m.p. 179°–181°.

Acetyl-derivative; m.p. 125°–125.5° (C. and D.).

5-Bromo-6-nitro-*m*-toluidine; by successive nitration and hydrolysis of 5-bromoaceto-*m*-toluidide (Neville and Winther, Ber. 1880, 13, 1945; Chem. Soc. Trans. 1880, 37, 630). It melts at 87°–88°.

2:6-Dibromo-4-nitro-*m*-toluidine; by bromination of 6-bromo-4-nitro-*m*-toluidine (N. and W.). Yellow needles, m.p. 130°–133° (C. and D.) or 124°–130° (N. and W.).

2:4:6-Tribromo-5-nitroaceto-*m*-toluidide; by nitrating 2:4:6-tribromoaceto-*m*-toluidide with nitric acid (D 152), followed by hydrolysis with concentrated sulphuric acid at 110° (Blankama, Chem. Weekblad, 1909, 6, 717). Pale yellow needles, m.p. 184°.

Acetyl-derivative; colourless needles, m.p. 261°; *diacetyl-derivative*; colourless crystals, m.p. 188° (B.).

Methyl-*m*-toluidine; by the action of dimethyl sulphate (Ullmann, Ann. 1903, 327, 104) or methyl iodide on *m*-toluidine. The product is freed from *m*-toluidine by treating the ethereal solution with dilute sulphuric acid and from the dimethyl-derivative by subsequent treatment with acetic anhydride (Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279). Liquid, b.p. 206°–207°.

Acetyl-derivative; m.p. 60°, b.p. about 250°.

4-Nitromethyl-*m*-toluidine; by the action of methylamine on the methyl-ether of 4-nitro-*m*-cresol. Brownish-yellow flat prisms, m.p. 83° (O. Fischer and Rigaud, Ber. 1902, 35, 1258).

6-Nitromethyl-*m*-toluidine; by the action of concentrated nitric acid on the nitrosoamine (Störmer and Hoffmann, Ber. 1898, 31, 2535). Yellowish-brown plates with a blue sheen, m.p. 92°–93°.

Nitrosoamine; yellowish plates, m.p. 73°–74°.

6-Chloro-4-nitromethyl-*m*-toluidine; by the action of dry methylamine on an absolute alcoholic solution of 6-chloro-4:5-dinitrotoluene; by heating 6-chloro-4-nitro-*m*-toluidine with methyl sulphate in toluene at 100° for 4 hours (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190). Long red acicular prisms, m.p. 126°–127°.

Nitrosoamine; yellow plates, m.p. 70°.

2:4:6-Trinitromethyl-*m*-toluidine; by the action of methylamine on the methyl-ether of 2:4:6-trinitro-*m*-cresol. It melts at 138° (Blanksma, Rec. trav. chim. 1902, 21, 327).

Dimethyl-*m*-toluidine; by the action of methyl iodide on *m*-toluidine or by distilling toluene trimethylammonium hydroxide (Monnet, Reverdin and Nölting). B.p. 215° (Wurster and Riedel, Ber. 1879, 12, 1797), 208° (Reinhardt and Städel, *ibid.* 1883, 16, 31). $B'_2H_4Fe(CN)_6 + 2H_2O$, white needles; $B'_2H_4Fe(CN)_6 + 1\frac{1}{2}H_2O$ (Wurster and Roser, *ibid.* 1879, 12, 1826).

Nitroso-derivative; green leaflets or long needles, m.p. 92°. Does not give Liebermann's nitroso-reaction. With aniline, *o*-toluidine, &c., it yields steel-blue double compounds. $B'HCl$, yellow or greenish-yellow needles; $B'_2H_4Fe(CN)_6 + H_2O$; $B'_2H_4Fe(CN)_6 + H_2O$ (Wurster and Roser).

Nitrodimethyl-*m*-toluidine; by oxidising the above nitroso-compound with potassium permanganate (Wurster and Riedel). Long yellow needles, m.p. 84°.

5-Nitrodimethyl-*m*-toluidine; blood-red, glistening rhombic tables or double pyramids, m.p. 52° (Jäger, Z. Kristall. 1903, 38, 89), or 48°–50° (Haibach, J. pr. Chem. 1902, (2) 65, 342).

Dinitrodimethyl-*m*-toluidine; by nitrating an acetic acid solution of dimethyl-*m*-toluidine (Wurster and Riedel). Yellow needles, m.p. 107°. When the nitration is carried out with nitric acid alone or in presence of sulphuric acid this compound is accompanied by an isomeride, small yellow crystals, m.p. 168°, which is less

soluble in alcohol than the former (Wurster and Riedel).

Bromodimethyl-m-toluidine; by brominating dimethyl-m-toluidine hydrochloride (Wurster and Riedel, Ber. 1878, 12, 1800). White leaflets, m.p. 98°, b.p. 276°. $B_2H_4Fe(CN)_6 + 4H_2O$; $B_2H_4Fe(CN)_6 + 4\frac{1}{2}H_2O$ (Wurster and Roser, l.c., 1825).

4-Nitroethyl-m-toluidine; by treating the ethyl-ether of 4-nitro-m-cresol with ethylamine at 165°–170°. It melts at 60° (Fischer and Rigaud, Ber. 1901, 34, 4202).

2:4:6-Trinitroethyl-m-toluidine; in a similar manner from 2:4:6-trinitro-m-cresol. It melts at 98°, and the nitroamine at 79° (Blanksma).

Diethyl-m-toluidine; b.p. 227°–228° (Reinhardt and Stadel, Ber. 1883, 16, 31).

Phenyl-m-toluidine; by strongly heating a mixture of 5-phenylamino-m-cresol with zinc dust (Zega and Buch, J. pr. Chem. 1886, (2) 33, 542). Reddish oil, b.p. 300°–305°. Its solution in sulphuric acid is coloured an intense green by nitric acid.

4-Nitrophenyl-m-toluidine; by heating 5-phenylamino-4-nitrotoluene 2-sulphonic acid with sulphuric acid (25 p.c.) at 145° for 4 hours (Schraube and Romig, Ber. 1893, 26, 581). Yellowish-red plates from alcohol or six-sided tables from ligroin, m.p. 110°.

Diphenyl-m-toluidine; by the interaction of m-chlorotoluene and potassium diphenylamine (Haussermann, Ber. 1901, 34, 38). It melts at 69°–70°.

6-Chloro-4-nitrophenyl-m-toluidine; by boiling 2-chloro-4:5-dinitrotoluene with aniline in alcoholic solution for 36 hours; in a yield of 50 p.c. from 6-chloro-4-nitro-m-toluidine by heating under a reflux with bromobenzene, potassium carbonate and cuprous iodide (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190). Rectangular pyramids, m.p. 95°–96°.

Nitrosoamine; yellow prisms, m.p. 95°–96°.

2-Chloro-4-nitrophenyl-m-toluidine; in a similar manner to the 6:4-isomide from 2-chloro-3:4-dinitrotoluene and 2-chloro-4-nitro-toluidine, respectively (M. and J.). Orange-red needles, m.p. 95°.

Di-m-tolylamine; by heating m-toluidine with its hydrochloride at 210°–240° (Cosack, Ber. 1880, 13, 1091); by heating m-cresol with ammonia, zinc chloride and ammonium chloride at 330°–340° (Merz and Müller, Ber. 1887, 20, 99). Liquid, b.p. 319°–320°, volatile with steam.

Acetyl-derivative; tables, m.p. 43° (C.).

Tolyl-m-hydroxylamine; plates, m.p. 68° (Bamberger, Ber. 1895, 28, 248). On oxidation yields m-azoxytoluene and m-nitrosotoluene.

Nitroso-derivative, $(CH_3)_2C_6H_3N(NO)OH$, as glistening needles, m.p. 54°–54.5° (B.). **Tolyl-m-hydroxylamine** when treated in the same way with formaldehyde or when acted upon by trimethane yields **methylene-N,N-di-tolyl-hydroxylamine**, $CH_3N(OH)C_6H_4CH_3$, plates, m.p. 118° (Bamberger and Tschirner, Ber. 1900, 33, 951, 959), and when added in a dry-divided condition to concentrated hydrochloric acid saturated at –8° to –10° with hydrogen chloride and the mixture allowed to remain in an ice chest for 7 days, the product consists of m-azoxytoluene, 3-amino-6-cresol, 4-chloro-m-toluidine, 2-chloro-m-toluidine, and

4-chloro-m-toluidine (Bamberger, Tar-Sarkis-janz and de Werra, Ber. 1902, 35, 3697; cf. Bamberger and de Werra, *ibid.* 3711). It reacts with thionyl aniline yielding m-toluidine phenylsulphonamide and benzene-azo-m-toluene (Michaelis and Petou, Ber. 1898, 31, 984).

p-Toluidine; see o-toluidine; by reduction of p-nitrotoluene (Muspratt and Hofmann, Ann. 1845, 54, 1; 1848, 66, 144; Noad, *ibid.* 1847, 63, 305; Miller, Zeit. f. Chem. 1864, 161; Sell, Chem. Soc. Trans. 1863, 16, 186); together with ditolyl oxide by heating p-cresol with ammoniacal zinc chloride at 300° (Buch, Ber. 1884, 17, 2637; Merz and Müller, *ibid.* 1887, 20, 545); by reduction of p-nitrobenzyl chloride with zinc dust (Rudolf, Jahresbericht, 1885, 2082; D. R. P. 34234 of 1885); by treating p-aminobenzyl alcohol with a solution of stannous chloride at 100° for $\frac{1}{2}$ hour (Thiele and Dimroth, Ann. 1899, 305, 121); by reduction of polymerised anhydro-p-aminobenzyl alcohol with zinc dust and hydrochloric acid (Kalle & Co., Eng. Pat. 1963 of 1895; Fr. Pat. 246918; D. R. P. 83544 of 1894); by the action of heat on the salts of methylaniline (Hofmann, Ber. 1872, 5, 720).

The conversion of methylaniline into p-toluidine hydrochloride has been studied by Beckmann and Correns (Ber. 1922, 55, 852), who showed that the main factor governing the change is the temperature, the addition of such salts as zinc chloride or aluminium chloride having little effect. p-Toluidine is also formed by the action of hydroxylamine on toluene in presence of aluminium or ferric chloride (Graebe, Ber. 1901, 34, 1778), and by heating hydrazo-p-toluene with alcohol at 120°–130° (Biehringer and Busch, Ber. 1903, 36, 339).

Commercial p-nitrotoluene usually contains some nitrobenzene and o-nitrotoluene, consequently the crude reduction product contains aniline and o-toluidine. The crude product may be first purified by distillation, freezing the fraction, b.p. 195°–205°, followed by crystallising the solid product from ligroin.

p-Toluidine crystallises from aqueous alcohol in leaflets, m.p. 45° (Städeler, J. pr. Chem. 1864, 425), or 42–77° (Mills, Phil. Mag. 1882, (5) 14, 27), 42–8° (Perkin, Chem. Soc. Trans. 1896, 69, 1245), b.p. 198° (Muspratt and Hofmann), or 200–4° (Hulett, Zeitsch. physikal. Chem. 1898, 28, 651, 657; Kahlbaum, *ibid.* 1898, 29, 621; cf. Neubeck, *ibid.* 1887, 1, 659), or 200–3° (P.); D_{50}^{20} 0.973, D_{70}^{20} 0.967 (P.), 1.046 (Räddorf, Ber. 1879, 12, 252); magnetic rotatory power at 50° 15.87 (P.); dissociation constant, $K = 20.6 \times 10^{-10}$ (Löwenherz, Zeitsch. physikal. Chem. 1898, 25, 394); refractive power, see Brühl (*ibid.* 1895, 16, 216), Eykman (Rec. trav. chim. 1893, 12, 278); cryoscopic behaviour, see Auwers (*ibid.* 1897, 23, 451), Ampela and Rinatoni (Gazz. chim. ital. 1897, 27, i. 43); heat of combustion at constant pressure, 958.6 Cal., heat of combustion at constant volume, 957.96 Cal. (Petit, Compt. rend. 1888, 107, 226; Ann. Chim. 1889, (6) 18, 152).

p-Toluidine may be separated from aniline by means of the oxalate (Brimmeyer, Zeit. f. Chem. 1865, (2) 1, 513), or by acetylation (Weith and Merz, Ber. 1893, 2, 433), or by means of formaldehyde (D. R. P. 87615 of 1895). A

and Tschirner, *ibid.* 1899, 32, 1677; Otto, Ann. Chim. 1898, (7) 13, 142). When heated with aqueous regia *p*-toluidine yields chlorotoluene; with hydrogen iodide toluene is produced; and when heated with a meta-derivative of nitrobenzene in the presence of hydrochloric acid, dyestuffs of the chrysaniline series are formed (D. R. P. 65985 of 1892; 78377, 79263, 79585, 79877, 81048 of 1894).

p-Toluidine heated with sulphur gives rise to the primuline bases (Green, Ber. 1889, 22, 968; Jacobson, *ibid.* 330; Gattermann, *ibid.* 422; Gattermann and Pfitzinger, *ibid.* 1063; Hunter, J. Soc. Chem. Ind. 1923, 42, 302 T). Heated with ethyl alcohol and zinc chloride *p*-toluidine forms 4-amino-1-methyl-3-ethylbenzene (Willgerodt and Brandt, J. pr. Chem. 1904, (2) 69, 433).

p-Toluidine condenses with bromo- and sulphonated methylaminoanthraquinones, &c., forming bluish-green dyes (Fr. Bayer & Co., D. R. P. 159129 of 1901; Wacker, Ber. 1902, 35, 2593; Friedländer and Schick, Zeitsch. Farb. Text. Ind. 1904, 3, 218; see also M. L. B., Eng. Pat. 8905 of 1903; U.S. Pat. 748375; D. R. P. 149780; Bayer & Co., D. R. P. 148767, 153517 of 1903; M. L. B., D. R. P. 174131 of 1905).

p-Toluidine also condenses with diazo-compounds (Mehner, J. pr. Chem. 1902, (2) 65, 401); with phenylurethane (Dixon, Chem. Soc. Trans. 1901, 79, 102); with methylene iodide (Senior and Goodwin, *ibid.* 1902, 81, 280); with acetylene tetrabromide (Sabanéoff and Rakovsky, J. Russ. Phys. Chem. Soc. 1902, 34, 408); with phenyl isocyanate (Walther and Stenz, Bull. Soc. chim. 1901, (3) 26, 395); with epichlorhydrin (Cohn and Friedländer, Ber. 1904, 37, 3034); and with trinitrotoluene, *p*-toluidine forms an additive compound, dark red crystals, m.p. 68° (Jackson and Clarke, Chem. Soc. Proc. 1906, 22, 84). *p*-Toluidine reacts with phenylazoisimide at 140° to form a substance, $C_{12}H_{11}N_3$, colourless needles, m.p. 116°, converted into a brown viscous mass on benzylation, from which benzo-*p*-toluidide is obtained by treatment with alcoholic hydrochloric acid (Wolff and Kolasius, Ann. 1912, 394, 59).

As in the case of *o*-toluidine, the *p*-isomeride when diazotised in sulphuric acid solution, then saturated with sulphur dioxide, treated with copper, filtered, washed with ammonia and the filtered filtrate treated with ferric chloride, the ferric toluene sulphinat, $Fe(C_6H_4(CH_3)SO_3)_3$, is formed (Thomas, Chem. Soc. Trans. 1909, 95, 13).

p-Toluidine condenses with aromatic aldehydes in the presence of its hydrochloride forming acridines (Ullmann, Ber. 1903, 35, 107). The other condensation products of *p*-toluidine with aldehydes, see Eibner and Amann (Ann. 1903, 329, 211); Friedländer (Ber. 1892, 25, 149); Eibner and Parucker (*ibid.* 1900, 33, 62); Hantzsch and Schwab (*ibid.* 1901, 34, 2, 841); Cohn and Friedländer (*ibid.* 1902, 35, 1265); Cohn and Blau (Monatsh. 1904, 25, 5), &c. On hydrogenation in presence of fused nickel, *p*-toluidine yields *p*-methyl-phenylamine, together with the corresponding secondary and tertiary bases (Sabatier and Senderens, Bull. Soc. chim. 1904, (3) 31, 709). When treated with ethyl alcohol in presence of

zinc chloride it yields aminomethylethylbenzene (Willgerodt and Brandt, J. pr. Chem. 1904, (2) 69, 433). With dichloroacetic acid it yields *p*-tolylamino-*p*-methyl-oxindole (Keller, Ann. 1904, 332, 247).

On exhaustive chlorination in acetic acid with moist chlorine *p*-toluidine yields heptachloromethylcyclohexanone. When *p*-toluidine is chlorinated in 97 p.c. sulphuric acid it is converted mainly into 3-chloro- and partly into 2-chloro-derivatives. The same products, together with 3:5-dichloro-*p*-toluidine, are obtained if 40 p.c. sulphuric acid is used. 3-Chloro-, 3:5-dichloro-, and higher chlorinated products are obtained by chlorinating aceto-*p*-toluidide (Hafner, Ber. 1889, 22, 2535; Wroblewsky, Ann. 1873, 168, 196; Lellmann and Klotz, *ibid.* 1885, 231, 308; Zincke, Ber. 1895, 28, 3121). Chlorinated products are obtained also when *p*-toluidine is electrolysed in an excess of hydrochloric acid (Elbs and Brunschweiler, J. pr. Chem. 1895, (2) 52, 559).

Formyl-derivative; together with the oxalyl-derivative by heating *p*-toluidine oxalate (Hübner, Ann. 1881, 209, 372); by boiling *p*-toluidine with formic acid (Tobias, Ber. 1892, 15, 2446). Very long needles, m.p. 52° (T.) or 53° (Bamberger and Wulz, *ibid.* 1891, 24, 2080). $NaC_6H_4NO + H_2O$ (T.); AgC_6H_4NO , needles (Cornstock and Clapp, Amer. Chem. J. 1891, 13, 527); $Hg(C_6H_4ON)_2$, needles (Wheeler and MacFarland, *ibid.* 1896, 18, 545); $HgClC_6H_4ON$, needles, (W. and M.); $(C_6H_4ON)_2HBrCuBr_2$, colourless prisms (Cornstock, *ibid.* 1898, 20, 79). For crystalline and liquid modifications of formyl-*p*-toluidide, see Orloff (J. Russ. Phys. Chem. Soc. 1905, 37, 439).

Acetyl-derivative; when *p*-toluidine is boiled for $\frac{1}{2}$ hour with an excess of acetic anhydride a mixture of 32 p.c. of the monoacetyl-derivative and 60 p.c. of the diacetyl-derivative is formed (Sudborough, Chem. Soc. Trans. 1901, 79, 537).

Dimorphous, crystallising in monoclinic forms (Pantebianco, Gazz. chim. ital. 1879, 9, 362; Riche and Berard, Ann. 1864, 129, 77), m.p. 147° (Hübner and Wallach, Ann. 1870, 154, 303; Kelbe, Chem. Soc. Abstr. 1883, 44, 915), 148°-149° (S.), or 153° (Feitler, Zeitsch. physikal. Chem. 1889, 4, 76), b.p. 307° (Beilstein and Kuhlberg, Ann. 1870, 156, 74). On oxidation with potassium permanganate it yields acetyl-*p*-aminobenzoic acid, and on treatment with phosphorus pentachloride the iminochloride $CH_3CCl=N(C_6H_4 \cdot CH_3)$ is formed (Wallach, Ann. 1882, 214, 203). The *nitrosoamine* is obtained by the action of nitrous acid on an acetic acid solution of aceto-*p*-toluidide (O. Fischer, Ber. 1877, 10, 959), or by treating a strongly alkaline solution of toluene-*p*-diazonium chloride at -5° with acetic anhydride (Pechmann and Frobenius, Ber. 1894, 27, 653). It forms needles, m.p. 80° (decomp.), and regenerates aceto-*p*-toluidide on reduction.

Aceto-*p*-toluidide forms compounds with sodium methoxide and ethoxide (Cohen and Archdeacon, Chem. Soc. Trans. 1896, 69, 93), and yields an *N*-chloro-derivative, four-sided prisms, m.p. 81°-82°, and an *N*-bromo-derivative, yellow four-sided prisms, m.p. 94°-95° (Chettaway and Orton, Chem. Soc. Trans. 1909, 77, 791).

For the halogen derivatives of aceto-*p*-

toluidide containing the halogen in the acetyl group, see Tommasi (Bull. Soc. chim. 1873, (2) 19, 400); Eckenroth and Donner (Ber. 1890, 23, 3287); Bischoff and Walden (Ann. 1894, 279, 65); Grothe (Archiv. der Pharmacie. 238, 589); Cech (Ber. 1877, 10, 879); Rugheimer and Hoffmann (*ibid.* 1885, 18, 2980); Judson (*ibid.* 1870, 3, 784); Cloëz (Ann. Chim. 1886, (6) 9, 216); Abenius (J. pr. Chem. 1889, (2) 40, 433); Meyer (Ber. 1875, 8, 1154); Keller (Ann. 1904, 332, 247).

Diacetyl-derivative: colourless crystals, m.p. 48° (Sudborough, Chem. Soc. Trans. 1901, 79, 537; cf. Clayton, Ber. 1898, 28, 1665), b.p. 153.5°–154.5°/11 mm., 177.5°–178.5°/30 mm., 211.5°–212°/100 mm. (Kay, Ber. 1893, 26, 2852). B'HCl, m.p. 120° (Dehn, J. Amer. Chem. Soc. 1912, 34, 1399).

Benzoyl-derivative: from *p*-toluidine and benzoyl chloride (Jaillard, Zeit. f. Chem. 1865, (2) 1, 440; Kelbe, Ber. 1875, 8, 875; Hübner, Ann. 1881, 208, 310; Wallach, Ann. 1882, 214, 217; Gudeman, Ber. 1888, 21, 2553; Müller, Ber. 1889, 22, 2404). Needles, m.p. 158°, b.p. 232°. *p*-Nitro-derivative, yellow needles, m.p. 197° (Gattermann, Ber. 1892, 25, 1082).

Phthalyl-derivative: m.p. 204° (Fröhlich, Ber. 1884, 17, 2679).

2-Chloro-p-toluidine: by reducing 2-chloro-4-nitrotoluene or 2-chloro-4-nitrobenzyl bromide with tin and hydrochloric acid (Witt, Ber. 1892, 25, 86; Lellmann, Ber. 1884, 17, 535); together with other products by reducing 2-chloro-4-nitrotoluene with sodium disulphide (Blanksma, Chem. Weekblad, 1909, 6, 899), or with iron powder in the presence of a small quantity of sulphuric acid (Wibaut, Rec. trav. chim. 1913, 32, 244), or almost quantitatively with iron filings and hydrochloric acid (Davies, Chem. Soc. Trans. 1921, 119, 868); by boiling acetyl-*p*-toluidine-2-diazopiperidine with concentrated hydrochloric acid (Wallach, Ann. 1886, 235, 253). Colourless crystalline solid, m.p. 26° (D.) or 23.1° (W.), b.p. 237°–238.5°, or 242°–244°/760 mm. (D.), or 245° (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151). B'HCl, very large needles; B₂H₂SO₄, small leaflets; B₂H₂PtCl₆.

Acetyl-derivative: m.p. (+1H₂O) 86° (W. and G.), 104°–105° (anhydrous) (Blanksma, l.c.; Kunkell and Lillig, J. pr. Chem. 1912, (2) 86, 517; Wibaut, l.c.); *benzoyl-derivative*: needles, m.p. 122° (Wibaut).

3-Chloro-p-toluidine: in poor yield by successive chlorination and hydrolysis of aceto-*p*-toluidide (Wroblewski, Ann. 1873, 168, 196; Lellmann and Klotz, Ann. 1885, 231, 309; Lellmann, Ber. 1894, 24, 4111); as the chief product by passing a rapid stream of chlorine through a boiling solution of aceto-*p*-toluidide in its own weight of acetic acid, followed by hydrolysis, a dichloro-derivative being simultaneously formed (Erdmann, Ber. 1891, 24, 2768); by chlorination of *p*-toluidine hydrochloride in 15 times its weight of 40 p.c. hydrochloric acid (Hafner, Ber. 1889, 22, 2536); together with 3:5-dichloro-*p*-toluidine and higher chlorinated products by the action of sulphuryl chloride on a suspension of aceto-*p*-toluidide in carbon disulphide, followed by hydrolysis (Wynne, Chem. Soc. Trans. 1892, 61, 1953); together with other products by the action of hydrochloric acid on *p*-nitrosotoluene

(Bamberger, Büsdorf and Szolayski, Ber. 1899, 32, 218); by treating aceto-*p*-toluidide in acetic acid with aqueous sodium chlorate followed by hydrolysis (Reverdin and Crépieux, Ber. 1900, 33, 2500); by reduction of 3-chloro-4-nitrotoluene (Reverdin and Crépieux, Ber. 1900, 33, 2505); in a yield of 50 p.c. by chlorination of aceto-*p*-toluidide by means of bleaching powder, followed by hydrolysis with alcohol and sulphuric acid (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 792). Oil, which solidifies at 0°, m.p. 7°, b.p. 218°–219°/732 mm. (L. and K.; Lellmann, Ber. 1891, 24, 4111), or 223°–224° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1337); D₂₀ 1.151 (W.). B'HCl; B'HNO₃; B₂H₂SO₄; B₂C₂H₂O₄.

Acetyl-derivative: Anorthic crystals (Poy Chem. Soc. Trans. 1892, 61, 1057), m.p. 118° (L. 115° (L. and K.), 111°–112° (E.), 113°–113.4° (Wynne; C. and D.); *N-chloro-derivative*: short prisms, m.p. 48° (C. and O.); *benzoyl-derivative*: m.p. 137°–139° (C. and D.).

2:3-Dichloro-p-toluidine: by reducing 2:3 dichloro-4-nitrotoluene with tin and hydrochloric acid (Cohen and Dakin). It is volatile with steam and melts at 40°–42°.

Acetyl-derivative: needles, m.p. 128°–129° (C. and D.).

2:5-Dichloro-p-toluidine: by reducing 2:5-dichloro-4-nitrotoluene (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 789; cf. Cohen and Dakin, *ibid.* 1901, 79, 1130; 1902, 81, 1347). It melts at 91°–92°.

2:6-Dichloro-p-toluidine: by reduction of 2:6-dichloro-4-nitrotoluene with iron filings and dilute hydrochloric acid (Davies, *ibid.* 1922, 121, 813). Colourless needles, m.p. 56°–57°. B'HCl, long colourless needles.

Acetyl-derivative: colourless slender needles, m.p. 220° (D.).

3:5-Dichloro-p-toluidine (see 3-chloro-*p*-toluidine); by successive chlorination and hydrolysis of aceto-*p*-toluidide and of 3-chloroaceto-*p*-toluidide (Lellmann and Klotz, Ann. 1885, 231, 322; cf. Cohen and Dakin); by other methods (Bamberger, Büsdorf and Szolayski; Wynne; Chattaway and Orton; Cohen and Dakin). Needles, scarcely volatile with steam, m.p. 60°. Sublimes.

Acetyl-derivative: crystals which sublime in long needles, m.p. 201° (L. and K.) or 199° (C. and D.). It is hydrolysed by heating with concentrated hydrochloric acid at 120°. *N-chloro-derivative*: slender four-sided prisms, m.p. 72° (C. and O.).

2:3:5-Trichloro-p-toluidine; *acetyl-derivative*, formed by the action of sodium chlorate on a solution of 3:5-dichloroaceto-*p*-toluidide in presence of acetic acid and hydrochloric acid (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1337); by the action of a mixture of hydrochloric and nitric acids on aceto-*p*-toluidide (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20). Colourless needles, m.p. 179°.

2-Bromo-p-toluidine: by reduction of 2-bromo-4-nitrotoluene (Neville and Winther, Ber. 1881, 14, 418; Chem. Soc. Trans. 1881, 39, 86); by boiling acetyl-*p*-toluidine-2-diazopiperidine with concentrated hydrobromic acid (Wallach, Ann. 1886, 235, 255); together with 3-bromo-*p*-toluidine by keeping a mixture of *p*-toluidine sulphate and bromine in the presence of sul-

phuric acid for 10 days (Hafner, Ber. 1889, 22, 2903); together with 2-bromo-4-aminobenzaldehyde by reduction of 2-bromo-4-nitrotoluene with sodium disulphide in presence of alcohol (Blanksma, Chem. Weekblad, 1909, 6, 899). It melts at 25°-26° (N. and W.), and boils at 254°-257° (H.). B'HCl, needles; B'HBr (W.).

Acetyl-derivative; m.p. 113° (B.). On boiling with potassium permanganate solution it yields 2-bromo-4-acetylamino benzoic acid.

3-Bromo-*p*-toluidine; by successive bromination and hydrolysis of aceto-*p*-toluidide (Wroblewski, Ann. 1873, 168, 153; Neville and Winther); together with other products by the action of hydrobromic acid on *p*-nitrosotoluene (Bamberger, Büsdorf and Szolayski, Ber. 1899, 32, 219); by bromination of *p*-toluidine hydrochloride (Klages and Liecke, J. pr. Chem. 1900 (2) 61, 326). Large plates, m.p. 26° (Claus and Steinberg, Ber. 1883, 16, 914), b.p. 240° D¹⁰⁰ 1.510 (W.), 1.498 (Hand, Ann. 1886, 234, 156). B'HCl, softens at 210° and melts at 221° (decomp.). B'HNO₃, plates, m.p. 182° B₂H₂SO₄ + 2H₂O. The bromotoluidine obtained by Pechmann (Ann. 1874, 173, 210) by distilling brominated *p*-aminotoluene *m*-sulphonic acid with potassium hydroxide is probably identical with the above.

Acetyl-derivative; needles, m.p. 117.5° (W.). *N*-bromo-*derivative*; yellow four-sided plate, m.p. 87°. On heating at 110° it yields 3:1 dibromoaceto-*p*-toluidide (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 795).

Diacetyl-derivative; thick prisms, m.p. 75°-75.5° (Ulffers and Janson, Ber. 1894, 27, 98).

Benzoyl-derivative, m.p. 140° (Ulffers and Janson, Ber. 1891, 24, 4170).

2:5-Dibromo-*p*-toluidine; by reduction of the corresponding nitro-derivative (Wroblewski, Ann. 1873, 168, 185; Neville and Winther, Ber. 1880, 13, 962; Chem. Soc. Trans. 1880, 37, 441). Prisms, m.p. 83° (W.), leaflets, m.p. 84° (N. and W.).

2:6-Dibromo-*p*-toluidine; by reduction of the corresponding nitro-derivative (Neville and Winther). It melts at 88°-89°.

3:5-Dibromo-*p*-toluidine; by the action of hydrobromic acid on *p*-nitrosotoluene (Bamberger, Büsdorf and Szolayski); from *p*-toluidine and bromine (Wroblewski, Ann. 1873, 168, 18; Neville and Winther; Klages and Liecke, J. pr. Chem. 1900, (2) 61, 326); together with 3-bromo-*p*-toluidine 5-sulphonic acid by the action of bromine on *p*-toluidine 3-sulphonic acid (N. and W.); cf. Pechmann, Ann. 1874, 173, 216). Long acroclinic needles, m.p. 73° (Jäger, Z. Kristall. 903, 38, 89), or 73.5°-74.5° (Bamberger, Ber. 1899, 32, 221). Does not combine with acid.

Acetyl-derivative; long needles, m.p. 113° (Claus and Herababy, Ann. 1891, 265, 3777) or rhombs, 199°-200° (Ulffers and Janson, Ber. 1894, 27, 98; cf. Kunckell, *ibid.* 1908, 41, 411); *benzoyl-derivative*; thick tables and prisms, m.p. 101°-101.5° (U. and J.).

3:4-Dibromo-*p*-toluidine; by reducing the corresponding nitro-compound (N. and Wroblewski). M.p. 98° (N. and W.), or 105° (V.).

2:3:5-Tribromo-*p*-toluidine; by brominating 2-bromo-*p*-toluidine hydrochloride (Neville and Winther, Ber. 1881, 14, 4181) or 2-bromo-

2:3:6-Tribromo-*p*-toluidine; by reducing the corresponding nitro-derivative with iron and acetic acid (N. and W.). Needles, m.p. 118°-119° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 514).

Pechmann (Ann. 1874, 173, 217) obtained a *tribromotoluidine*, long needles, m.p. 113°, by the action of bromine on *p*-aminotoluene *m*-sulphonic acid.

Tetrabromo-*p*-toluidine; by brominating 2:6-dibromo-*p*-toluidine hydrochloride (N. and W.); together with dibromonitrotoluene by heating *p*-nitrotoluene with bromine and a little iron bromide at 90° (Scheufelen, Ann. 1885, 231, 179). Slender needles, m.p. 226°-227°.

3-Chloro-5-bromo-*p*-toluidine; by brominating 3-chloro-*p*-toluidine in glacial acetic acid and boiling until most of the hydrogen bromide is removed (Orton and Reed, Chem. Soc. Trans. 1907, 91, 1570); from aceto-*p*-toluidide by successive bromination and chlorination with hydrochloric acid and sodium chlorate in glacial acetic acid, followed by hydrolysis (Cohen and Murray, *ibid.* 1915, 107, 847). Colourless needles, m.p. 65° (O. and R.) or 63.5° (C. and M.).

Acetyl-derivative; prisms, m.p. 189° (O. and R.), or 199° (C. and M.); *diacetyl-derivative*; m.p. 82° (C. and M.).

2-Iodo-*p*-toluidine; by reducing 2-iodo-4-nitrotoluene with ferrous sulphate in ammoniacal solution (Willgerodt and Gartner, Ber. 1908, 41, 2813); or together with 2-iodo-4-aminobenzaldehyde by reducing with sodium disulphide (Blanksma, Chem. Weekblad, 1909, 6, 899). Large white needles, m.p. 37°-38°. B'HCl, long dark needles; B₂H₂SO₄, leaflets; B'HNO₃, rhombs; B'C₂H₂O₄, small rhombs.

Acetyl-derivative; white needles, m.p. 130°, *iodochloride*, yellow needles, decomposing at 110° (W. and G.).

3-Iodo-*p*-toluidine; by the interaction of iodine and *p*-toluidine (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441). Colourless needles, m.p. 40°. B'HCl, m.p. 188° (decomp.) B'C₂H₂O₄, m.p. 119°-120° (decomp.).

Acetyl-derivative; long colourless needles, m.p. 133°; *benzoyl-derivative*; colourless needles, m.p. 161° (W. and L.). The acetyl-derivative when boiled with concentrated hydrochloric acid yields 3:5-di-iodo-*p*-toluidine.

2:5-Di-iodo-*p*-toluidine; by reducing 2:1-di-iodo-4-nitrotoluene with ferrous sulphate in ammonia. Buff-coloured prisms, m.p. 109° (Wheeler, &c., Amer. Chem. J. 1910, 44, 493).

3:5-Di-iodo-*p*-toluidine; by the action of iodine chloride on *p*-toluidine hydrochloride (Michael and Norton, Ber. 1878, 11, 115); by boiling 3-iodoaceto-*p*-toluidide with concentrated hydrochloric acid (Wheeler and Liddle) or by the action of 2 mols. of iodine on *p*-toluidine in presence of water and calcium carbonate (Wheeler and Liddle). Long slender needles, m.p. 124.5° (M. and N.).

Acetyl-derivative; stout colourless prisms, m.p. 226° (W. and L.).

2-Nitro-*p*-toluidine; together with 4-nitro-*p*-toluidine by partial reduction of 2:4-dinitrotoluene with alcoholic ammonium sulphate (Graeff, Ann. 1885, 229, 343; Anschütz and Heuseler, Ber. 1886, 19, 2161; Beilstein and Kuhlberg, Ann. 1876, 155, 14); together with little 3-nitro-*p*-toluidine by treating a solution

of *p*-toluidine in sulphuric acid with nitric acid, but when a large amount of sulphuric acid is used only the 2-nitro-isomeride is obtained (Hübner, Ber. 1877, 10, 1716; Nölting and Collin, *ibid.* 1884, 17, 263; Foth, Ann. 1885, 230, 299). Yellow glistening broad needles, m.p. 81.5° (Haibach, J. pr. Chem. 1902, (2) 65, 246). $BHCl$, m.p. 220° (decomp.); $BHNO_3$, m.p. 186°; $B_2H_4SO_4 + 2H_2O$, stellate needles; $4C_6H_4N_2O_3 + AgNO_3$, greenish-yellow crystals, m.p. 131°–132° (Mixer, Amer. Chem. J. 1880, 1, 241).

Formyl-derivative; white voluminous needle (Geigy & Co., U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

Acetyl-derivative; needles, m.p. 160° (Cunerth, Ann. 1874, 172, 229) or 144.5° (Wallach, *ibid.* 1886, 234, 354).

Benzoyl-derivative; pale yellow prisms, m.p. 172° (Bell, Chem. News, 1874, 30, 202).

3-Nitro-*p*-toluidine; by successive nitration and hydrolysis of benzoyl-*p*-toluidine, aceto-*p*-toluidide, or toluene *p*-sulphonyl-*p*-toluidide (Beilstein and Kuhlberg, Ann. 1870, 155, 23; Lorenz, *ibid.* 1874, 172, 77; Hübner, *ibid.* 1881, 208, 313; Lellmann, *ibid.* 1883, 221, 7; Cosack, Ber. 1880, 13, 1088; Ehrlich, *ibid.* 1882, 15, 2009; Gattermann, *ibid.* 1885, 18, 1483; Nölting and Collin, *ibid.* 1884, 17, 263; Reverdin and Crépieux, *ibid.* 1902, 35, 1439; Bull. Soc. chim. 1902, (3) 27, 743; Noyes, Amer. Chem. J. 1888, 10, 475); by heating 3-nitro-*p*-cresol with 35 p.c. ammonia for 16 hours at 170°–180° (Barr, Ber. 1888, 21, 1543); by the transformation of *p*-toluene nitroamine (Bamberger and Hoff, Ber. 1897, 30, 1258; Ann. 1900, 311, 93); or together with other products by the action of nitric anhydride on *p*-toluidine (B. and H.). Red monoclinic prisms (Panbianco, Gazz. chim. ital. 1879, 9, 358; Jäger, Z. Kristall, 1903, 38, 89), m.p. 114° (B. and K.; R. and C.), 116°–117° (Schraube and Romig, Ber. 1893, 26, 579), or 117°–118° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1401). Volatile with steam. $BHCl$, yellow prisms immediately decomposed by water; $BHNO_3$, six-sided yellow tables or slender needles (Hübner); $BHBr$, large laminae (Haibach, J. pr. Chem. 1902, (2) 65, 249).

Acetyl-derivative; slender yellow needles from water or concentrated alcoholic solution, long colourless needles from dilute alcoholic solution, m.p. 94°–95° (Gattermann). For the relation and properties of the two forms of 3-nitro-aceto-*p*-toluidide, see Schaum, Ann. 1898, 300, 224; Ber. 1898, 31, 129; Schenck, Zeitsch. physikal. Chem. 1900, 33, 450; Auwers, *ibid.* 1897, 23, 460.

Diacetyl-derivative; citron-yellow prisms, m.p. 78° (Ulffers and Janson, Ber. 1894, 27, 101).

Benzoyl-derivative; yellow needles, m.p. 146°–148° (M. and M.) or 143° (Hübner).

The electrolytic reduction of 3-nitro-*p*-toluidine yields a mixture of *p*-diamino-*o*-azoxytoluene and *p*-diamino-*o*-azotoluene (Elbs and Schwarz, J. pr. Chem. 1901, (2) 63, 562).

2:3-Dinitro-*p*-toluidine; by hydrolysis of the acetyl-derivative which is obtained as the sole product by nitrating 2-nitroaceto-*p*-toluidide with nitric acid alone; or together with 2:5-dinitroaceto-*p*-toluidide when the nitration is effected in presence of sulphuric acid by means

of potassium nitrate (Scott and Robinson, Chem. Soc. Trans. 1922, 121, 844). Orange-yellow needles, m.p. 124°. Weak base.

Acetyl-derivative; colourless silky needles, m.p. 174.5°.

2:5-Dinitro-*p*-toluidine (see above). Deep orange-red needles, m.p. 189°. Feeble base.

Acetyl-derivative; aggregates of colourless slender needles, m.p. 132.5° (S. and R.).

2:6-Dinitro-*p*-toluidine; by reduction of 2:4:6-trinitrotoluene with ammonium sulphide (Tiemann, Ber. 1870, 3, 218; Beilstein, *ibid.* 1880, 13, 243; Städel, Ann. 1884, 225, 384; Holleman and Boeseken, Rec. trav. chim. 1897, 16, 425); by reduction of 2:6-dinitro-*p*-tolylhydroxylamine with copper powder and hydrochloric acid; or together with 4:6-dinitro-*o*-toluidine by reducing 2:4:6-trinitrotoluene in hydrochloric acid solution in presence of cupric chloride at a copper cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 27; Cohen and McCandlish, *ibid.* 1905, 87, 1265). Yellow hair-like needles, m.p. 166.5°–168° (T. and B.), 171° (H. and B.), 168°–169° (C. and D.); Anschutz and Zimmermann, Ber. 1915, 48, 152). It exists in four distinct crystalline phases (Artini, Atti R. Accad. Lincei, 1917 [v.] 26, i. 392).

Acetyl-derivative; slender white needles, m.p. 223° (Körner and Contardi, *ibid.* 1916, [v.] 25, ii. 339).

3:5-Dinitro-*p*-toluidine; by successive nitration and hydrolysis of the acetyl- or benzoyl-derivative of *p*-toluidine (Beilstein and Kuhlberg, Ann. 1871, 158, 341; Jackson and Ittner, Amer. Chem. J. 1897, 19, 6; Hübner, Ann. 1881, 208, 278; 1884, 222, 73; Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 527); from 3:5-dinitro-*p*-cresol alkyl ether and alcoholic ammonia in the cold (Städel, Ann. 1883, 217, 185); by transformation of 3-nitro-*p*-toluene nitroamine (Bamberger and Voss, Ber. 1897, 30, 1257; Bamberger and Hoff, Ann. 1900, 311, 112). Yellow needles, m.p. 166° (B. and K.), 168° Hübner; B. and V.; Niementowski, Ber. 1886, 19, 717).

Acetyl-derivative; long yellow needles, m.p. 90.5° (B. and K.), or 105° (Friederici, Ber. 1878, 1, 1975).

Diacetyl-derivative; thick citron-yellow tables, m.p. 129.5° (Ulffers and Janson, Ber. 1894, 27, 101).

Benzoyl-derivative; needles, m.p. 186° (Hübner).

(β)-Dinitro-*p*-toluidine; by treating 2:3:4-trinitrotoluene with alcoholic ammonia at 100° (Hepp, Ann. 1882, 215, 371). Short golden-yellow needles, m.p. 94°.

3-Chloro-2-nitro-*p*-toluidine; by heating 2-nitrotolyl-*p*-hydroxylamine with hydrochloric acid (Brand and Zoller, Ber. 1907, 40, 3324). Pale yellow needles, m.p. 63° (B. and Z.) or 67°–68° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052).

Acetyl-derivative; m.p. 123°–124° (B. and Z.).

5-Chloro-2-nitro-*p*-toluidine; by treating dry 3-chloro-*p*-toluidine nitrate with 5 parts of sulphuric acid at –12° to –15° (Claus and Davidson, Ann. 1891, 265, 344; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1233); as a by-product of the action of hydrochloric acid

on 2-nitrotolyl-*p*-hydroxylamine (Brand and Zoller). Orange-red plates, m.p. 129.5° (Claus and Davidsen), 131° (B. and Z.).

Acetyl-derivative, m.p. 143° (Cl. and D.).

2-Chloro-5-nitro-*p*-toluidine; by successive nitration and hydrolysis of 2-chloroaceto-*p*-toluidide (Claus and Böcher, Ann. 1891, 265, 354; Davies, Chem. Soc. Trans. 1921, 119, 868); by adding 2-chloro-*p*-toluidine nitrate to well-cooled sulphuric acid (Cohen and Dakin, l.c.); together with 6-chloro-4-nitro-*m*-toluidine by the action of alcoholic ammonia on 2-chloro-4:5-dinitrotoluene; or from *o*-toluidine by nitration, replacement of the amino-group by chlorine, reduction, acetylation, nitration and hydrolysis (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1538, 1545). Golden-yellow plates, m.p. 165°.

Acetyl-derivative; pale yellow crystals, m.p. 112° (Blanksma, Rec. trav. chim. 1910, 29, 410), 113° (C. and B.).

3-Chloro-5-nitro-*p*-toluidine; by nitration of 3-chloroaceto-*p*-toluidide (Claus and Davidsen) in presence of glacial acetic acid at 20°, followed by hydrolysis with hydrochloric acid (Cohen and Dakin). Orange-red needles, m.p. 72°-73°, slowly volatile with steam (C. and D.) or orange-red plates, m.p. 70.5° (Cl. and D.).

Acetyl-derivative; m.p. 196° (Cl. and D.).

2:6-Dichloro-3-nitro-*p*-toluidine; by the gradual addition of 2:6-dichloroaceto-*p*-toluidide to nitric acid (D 1.49) cooled in ice-water, followed by hydrolysis with alcoholic sodium hydroxide (Davies, Chem. Soc. Trans. 1922, 121, 813). Minute orange needles, m.p. 130°-131°. B'HCl, clusters of colourless needles, immediately hydrolysed by cold water.

Acetyl-derivative; colourless needles, m.p. 180° (D.).

2-Chloro-3:5-dinitro-*p*-toluidine; by the gradual addition of 2-chloroaceto-*p*-toluidide to well-cooled nitric acid (D 1.5), keeping for 6 hours, followed by hydrolysis with cold sulphuric acid (Davies, *ibid.* 1921, 119, 808). Thin golden-yellow needles, m.p. 137°.

Acetyl-derivative; colourless leaflets, m.p. (D.).

2-Bromo-5-nitro-*p*-toluidine; by nitration and hydrolysis of 2-bromoaceto-*p*-toluidide (Blanksma, Chem. Weekblad, 1912, 9, 968). Orange-red needles, m.p. 165°.

Acetyl-derivative; pale yellow needles, m.p. (B.).

3-Bromo-5-nitro-*p*-toluidine; by nitration and hydrolysis of 3-bromoaceto-*p*-toluidide (Problewsky, Ann. 1878, 192, 202); by bromination and nitration (or *vice versa*) of aceto-*p*-toluidide, followed by hydrolysis (Neville and x, Ber. 1890, 13, 968; Chem. Soc. Trans. 37, 429). Orange-red needles, m.p. 64° (Cohen and Dutt, Chem. Soc. Trans. 1914, 510).

Acetyl-derivative; m.p. 210° (C. and D.); large greenish-yellow tables, 79° (Ulffers and Janson, Ber. 1894, 27, 50).

3-Bromo-6-nitro-*p*-toluidine; by dissolving 1 of dry 3-bromo-*p*-toluidine nitrate in 2 of sulphuric acid at -10° and keeping 2-3 days (Claus and Herbay, Ann. 1891, 265, 354). Yellow needles, m.p. 121° (C. and D.). Morgan and Clayton, Chem.

Soc. Trans. 1905, 87, 948), or 118°-119° (Cohen and Dutt, *ibid.* 1914, 105, 515).

3:5-Dibromo-2-nitro-*p*-toluidine; by bromination of 2-nitro-*p*-toluidine (Blanksma, Chem. Weekblad, 1909, 6, 717). Yellow crystals, m.p. 82°.

Acetyl-derivative; by nitrating 3:5-dibromoaceto-*p*-toluidide with fuming nitric acid (Kunckell, Ber. 1908, 41, 4111); by acetylating 3:5-dibromo-2-nitro-*p*-toluidine with acetic anhydride and a drop of sulphuric acid (B.). M.p. 238°.

3-Bromo-2:6-dinitro-*p*-toluidine; together with a little 3:5-dibromo-2:6-dinitro-*p*-toluidine by the action of bromine on 2:6-dinitro-*p*-toluidine in presence of sodium acetate and acetic acid (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339). Pale yellow prisms or short needles, m.p. 174°.

Acetyl-derivative; almost colourless plates, m.p. 151° (K. and C.).

3:5-Dibromo-2:6-dinitro-*p*-toluidine; by further bromination of the 3-bromo-derivative (K. and C.). Pale yellow prisms, m.p. 177°.

Acetyl-derivative; m.p. 265°-267°, by nitrating 3:5-dibromoaceto-*p*-toluidide with fuming nitric acid in presence of sulphuric acid (Kunckell, Ber. 1908, 41, 4111).

5-Iodo-3-nitro-*p*-toluidine; by warming 3-nitro-*p*-toluidine with iodine chloride in glacial acetic acid (Wheeler and Scholes, Amer. Chem. J. 1910, 44, 126). Golden needles, m.p. 98°.

Acetyl-derivative; by acetylating the above (W. and S.) or by nitration of 5-iodoaceto-*p*-toluidide (Wheeler and Liddle, *ibid.* 1909, 42, 441). Prisms, m.p. 202°-203°.

Methyl-*p*-toluidine; by methylation with dimethyl sulphate (Ullmann, Ann. 1903, 327, 104); together with dimethyl-*p*-toluidine by the action of methyl chloride on boiling *p*-toluidine. The product is extracted with ether and the unchanged *p*-toluidine precipitated by sulphuric acid. The remainder of the product is acetylated, fractionally distilled, and the acetyl-derivative hydrolysed with dilute hydrochloric acid or sodium hydroxide (Thomsen, Ber. 1877, 10, 1582); by the reduction of nitrosomethyl-*p*-toluidine with tin and hydrochloric acid (Nöling, Ber. 1878, 11, 2279); from *p*-toluidine and diazomethane (von Pechmann, *ibid.* 1895, 28, 858). Liquid, b.p. 208° (T.). B'HCl, m.p. 119.5° (Bamberger and Wulz, *ibid.* 1891, 24, 2081); B'H, PtCl.

Acetyl-derivative; large plates, m.p. 83°, b.p. 283°. It yields trinitromethyl-*p*-toluidine on boiling with nitric acid.

Nitrosoamine; large prisms, m.p. 54° (T.), or 52°-53° (B. and W.).

2-Nitromethyl-*p*-toluidine; by nitration of methyl-*p*-toluidine in presence of sulphuric acid below 0° (Pinnow, Ber. 1895, 28, 3040); by methylation of 2-nitro-*p*-toluidine (Jaeger, Bull. Soc. chim. 1899, (3) 21, 19). Yellow crystals, m.p. 45° (J.), or slender red needles or thick prisms, m.p. 57° (P.).

Acetyl-derivative; slender yellow needles, m.p. 128°-128.5° (P.).

Nitrosoamine; slender yellow needles or thick prisms, m.p. 58° (P.).

3-Nitromethyl-*p*-toluidine; from 3-nitro-*p*-toluidine, methyl iodide, and methyl alcohol; by the action

of nitric acid on *p*-tolylmethyl nitroamine in presence of acetic acid (Pinnow, Ber. 1897, 30, 835); by oxidation of 3-nitrodimethyl-*p*-toluidine with chromic acid in acetic acid (Pinnow, *l.c.* 3121; J. pr. Chem. 1900, (2) 62, 514). Red prisms, m.p. 84°–85° (G.).

Acetyl-derivative; small plates, m.p. 64°; *picrate*, yellow crystalline precipitate, m.p. 210°–212° (decomp.) (Niementowski, Ber. 1887, 20, 1876).

(γ) 2:3-Dinitromethyl-*p*-toluidine; see below (Pinnow). Long orange-yellow plates, with a bluish shimmer, m.p. 158°–159.5°. On treatment with nitric acid (D 1.52) it yields trinitrotolyl-*p*-methyl nitroamine; with alcoholic ammonium sulphide, γ -nitroaminomethyl-*p*-toluidine; with tin and hydrochloric acid 2:3-diaminomethyl-*p*-toluidine (Pinnow, J. pr. Chem. 1900, (2) 62, 507).

Acetyl-derivative; bright yellow needles, m.p. 90°–5°; *benzoyl-derivative*; m.p. 110°–5°.

Nitroamine; yellow needles, m.p. 128°–128.5° (Pinnow, Ber. 1897, 30, 840).

(β) 2:5-Dinitromethyl-*p*-toluidine; the nitration of dimethyl-*p*-toluidine in concentrated sulphuric acid and further treatment of the product with nitric acid in the presence of sodium nitrite yields dinitrotolylmethyl nitroamine. The latter on boiling with phenol and sulphuric acid in the presence of amyl alcohol yields a mixture of 2:5- and 2:3-dinitromethyl-*p*-toluidine (Pinnow, Ber. 1895, 28, 3040; 1897, 30, 836, 840; J. pr. Chem. 1900, (2) 62, 507). Also formed by the oxidation of dinitrodimethyl-*p*-toluidine (m.p. 103.5°–104°) with chromic acid and acetic acid (van Romburgh, Rec. trav. chim. 1889, 8, 248). Bright red prisms with a greenish reflex, m.p. 184.5°–185.5°. On reduction with alcoholic ammonium sulphide 2-amino-5-nitromethyl-*p*-toluidine is formed; with tin and hydrochloric acid at low temperatures it yields 2:5-diaminomethyl-*p*-toluidine, and at higher temperatures methyl-diaminocresol (Pinnow, J. pr. Chem. 1900, (2) 62, 507).

Acetyl-derivative; bright yellow needles, m.p. 151° (P.).

Nitroamine; m.p. 123°–124° (P.).

(α) 3:5-Dinitrotolyl-*p*-toluidine; by nitration of methyl-*p*-toluidine (Thomsen, Ber. 1877, 10, 1582; Gattermann, Ber. 1885, 18, 1487); by boiling 3:5-dinitrotolyl-*p*-methyl nitroamine with a little phenol (Van Romburgh, Ber. 1896, 29, 1015); by the transformation of the *N*-methyl ester of 3-nitro-*p*-toluene nitroamine with acids (Bamberger and Voss, Ber. 1897, 30, 1258); by the prolonged action of nitrous acid on methyl-*p*-toluidine (Störmer and Hoffmann, Ber. 1898, 31, 2535); by the transformation of an alcoholic solution of 3:5-dinitro-4-nitromethylamino-toluene in presence of sunlight (Reverdin, Bull. Soc. chim. 1913, [4] 13, 485; J. pr. Chem. 1913, (2) 88, 90). Light red needles, m.p. 129° (G.).

Nitroamine; yellow needles, m.p. 125° (Gattermann), or 128°–128.5° (Van Romburgh; Pinnow, Ber. 1897, 30, 840).

3:5-Dinitrotolyl-*p*-methylnitroamine; by the action of nitric acid (D 1.48) on dimethyl-*p*-toluidine (Van Romburgh, Rec. trav. chim. 1884, 3, 404; Gattermann, Ber. 1885, 18, 1488; cf. Pinnow, Ber. 1897, 30, 842); by boiling methyl-aceto-*p*-toluidide for 1–2 hours with 10 p.c.

nitric acid (Norton and Livermore, Ber. 1887, 20, 2269); by the action of fuming nitric acid on 3:5-dinitrodimethyl-*p*-toluidine (Pinnow and Mateovich, Ber. 1898, 31, 2518); by the gradual addition of 50 c.c. nitric acid (D 1.48) to a solution of 5 c.c. of dimethyl-*p*-toluidine in 5 c.c. of glacial acetic acid (Van Romburgh, Ber. 1896, 29, 1015); by the action of nitrous acid on a solution of 3-nitrodimethyl-*p*-toluidine in 40 p.c. nitric acid (Pinnow, Ber. 1895, 28, 3044); by dissolving methyl-*p*-tolyl-nitrosoamine in a mixture of acetic acid and nitric acid (D 1.4) with cooling (Pinnow). Yellow serrated needles, m.p. 126° (P.), or 138° (Van R.).

2:3:5-Trinitromethyl-*p*-toluidine; by boiling a mixture of 2:3:5-trinitro-*p*-tolylmethyl-nitroamine, phenol, sulphuric acid, and amyl alcohol (Pinnow, Ber. 1897, 30, 838); by nitration of mono- or dinitromethyl-*p*-toluidine (Gattermann, Ber. 1885, 18, 1488). Orange-red needles, m.p. 129.5°–130° (P.), or yellow needles or large prisms, m.p. 137°–138° (G.).

Nitroamine; yellow plates, m.p. 108°–109° (P.). The *nitroamine* is obtained by heating 2-nitro-*p*-tolylmethyl-nitrosoamine with nitric acid (D. 1.52) at 100°. It melts at 156.5°–157° (P.).

*Dimethyl-*p*-toluidine*; together with isomerides and homologues by heating the trimethylammonium iodide, $C_6H_5N(CH_3)_3I$, at 220°–230° (Hofmann, Ber. 1872, 5, 707); from *p*-toluidine, methyl iodide or methyl chloride (Thomsen, Ber. 1877, 10, 1586; Clarke, Amer. Chem. J. 1905, 33, 496); by heating its trimethylammonium iodide with water and lead oxide and distilling the product (Hübner, Tölle and Athenstädt, Ann. 1884, 224, 337); together with dimethyleneditoluidine by the electrolytic reduction of *p*-nitrotoluene in presence of alcohol, hydrochloric acid and 40 p.c. formaldehyde (Löb, Zeit. Elektrochem. 1898, 4, 428). Liquid, b.p. 209.5°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 623, 646), or 211.2° (Perkin, Chem. Soc. Trans. 1896, 69, 1245), D_4^{20} 0.92870 (K.), L_4^{20} 0.9502, D_{15}^{15} 0.9424, D_{25}^{25} 0.9364 (P.); magnetic rotatory power at 15.4° 22.84 (P.). Refractive power, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218).

*Dimethyl-*p*-toluidine oxide*; by the action of hydrogen peroxide on dimethyl-*p*-toluidine at 60°–70° (Bamberger and Tschirner, Ber. 1899, 32, 353). *Picrate*; sulphur-yellow needles or prisms, m.p. 106°–107°.

2-Nitrodimethyl-*p*-toluidine; by nitration of dimethyl-*p*-toluidine (M. L. B., D. R. P. 69188 of 1891; cf. Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 947); by methylation of 2-nitro-*p*-toluidine (Haibach, J. pr. Chem. 1902, (2) 66, 246). Orange-red prisms, m.p. 35° (H.), or 37° (M. and C.).

3-Nitrodimethyl-*p*-toluidine; by the action of a concentrated aqueous solution of sodium nitrite on a solution of dimethyl-*p*-toluidine in hydrochloric acid (D 1.06) (Pinnow, Ber. 1895, 28, 3041; 1897, 30, 3119). Six-sided columns, m.p. 24.5°–25°. On reduction with tin and hydrochloric acid a mixture of dimethyltoluenediamine, dimethylbenzimidazole and a compound containing chlorine is obtained.

3-Bromo-6-nitrodimethyl-*p*-toluidine; by heating the hydrobromide of 3-bromo-6-nitro-*p*-

toluidine with methyl alcohol for 8 hours at 140° – 180° . The resultant mixture is treated with acetic anhydride to remove any unaltered base or secondary amines (Morgan and Clayton, *l.c.*). Yellow needles, m.p. 38° .

3:5-Dinitrodimethyl-*p*-toluidine; by the action of 30 p.c. nitric acid on a solution of dimethyl-*p*-toluidine dissolved in dilute sulphuric acid (Pinnow and Mateovich, *Ber.* 1898, 31, 2518). Bright red needles or four-sided prisms, m.p. 95° . With fuming nitric acid it yields 3:5-dinitro-tolyl-*p*-methyl nitroamine, m.p. 138° – 139° .

2:5-Dinitrodimethyl-*p*-toluidine; together with other products by the action of sodium nitrite on 2-nitrodimethyl-*p*-toluidine dissolved in hydrochloric acid (Pinnow, *Ber.* 1895, 28, 3041); together with 2-nitrodimethyl-*p*-toluidine by nitrating dimethyl-*p*-toluidine and pouring the product into water so that the temperature rises to 30° – 40° (M. and C.). Glistening red plates, m.p. 103.5° – 104° (P.), dark red needles, or scarlet scales, m.p. 103° (M. and C.).

Ethyl-*p*-toluidine; from *p*-toluidine by heating with hydriodic acid or hydrobromic acid and ethyl alcohol (N. and L.); from *p*-toluidine and ethyl iodide by heating for 2 days at 100° (Morley and Abel, *Ann.* 1854, 93, 313). Liquid, b.p. 217° , $D_{20}^{25} = 0.9391$. $B^{\circ}_x H_x SO_4$; $B^{\circ}_x C_x H_x O_4$; $B^{\circ}_x H_x PtCl_x$, pale yellow crystals.

Acetyl-derivative; liquid, b.p. 258° (Norton and Livermore, *Ber.* 1887, 20, 2271).

2-Nitroethyl-*p*-toluidine; by nitrating a solution of *p*-ethyltoluidine in 20 parts of sulphuric acid (Nölting and Stricker, *Ber.* 1886, 19, 549); by ethylation of 2-nitro-*p*-toluidine (Jaubert, *Bull. Soc. chim.* 1899, (3) 21, 20). Long flat red prisms, m.p. 47° – 48° (N. and S.), or yellow needles, m.p. 50° (J.).

3-Nitroethyl-*p*-toluidine; by ethylating 3-nitro-*p*-toluidine (Gattermann, *Ber.* 1885, 18, 1483); by successive nitration and hydrolysis of ethylaceto-*p*-toluidine in presence of sulphuric acid (Nölting and Abt, *Ber.* 1887, 20, 3000). Large bright red crystals, m.p. 58° – 59° .

3:5-Dinitroethyl-*p*-toluidine; by nitration of 3-nitroethyl-*p*-toluidine at about 30° (Gattermann, *l.c.*, 1485). Long orange-yellow needles, m.p. 126° – 126.5° .

Nitrosamine; large yellow rhombic crystals, m.p. 77° – 78° (G.).

3:5-Dinitrotolyl-*p*-ethyl nitroamine; by adding diethyl-*p*-toluidine to nitric acid ($D_{1.48}^{1.5}$) and boiling the solution until it becomes yellow (Van Romburgh, *Rec. trav. chim.* 1884, 3, 409; Gattermann); by boiling ethylaceto-*p*-toluidine with 10 p.c. nitric acid (Norton and Livermore, *Ber.* 1887, 20, 2271). Long straw-yellow needles, m.p. 116° . On boiling with 4 p.c. sodium hydroxide it yields dinitro-*p*-cresol, m.p. 83° .

Diethyl-*p*-toluidine; by heating potassium *p*-toluidine *m*-sulphonate with ethyl bromide and absolute alcohol at 150° (Schmidt, *J. pr. Chem.* 1893, (2) 48, 46); from ethyl-*p*-toluidine and ethyl iodide (Morley and Abel, *l.c.*); in 95 p.c. yield by heating *p*-toluidine hydrobromide or hydriodide with 5 p.c. excess of ethyl alcohol for 8 hours at 150° (Reinhardt and Stadel, *Ber.* 1883, 16, 29). Liquid, b.p. 227° – 228° , $D_{20}^{25} = 0.9242$. $B^{\circ}_x HCl$, m.p. 157° (Schmidt); $B^{\circ}_x H_x PtCl_x$, rhombohedra (Söfiling, *Beiblätter zu den Annalen der Physik und Chemie*, 8, 190);

$B^{\circ}_x HBr$, monoclinic crystals; $B^{\circ}_x HNO_3$, monoclinic crystals; $B^{\circ}_x HI$, crystals; $B^{\circ}_x HClH_2Cl_2 + \frac{1}{2}H_2O$, triclinic crystals. The salts are described by Söfiling (*Jahresbericht*, 1884, 463).

Phenyl-*p*-toluidine; by distilling tritolyl-rosaniline acetate (Hofmann, *Ann.* 1864, 132, 291); together with diphenylamine and ditolylamine by heating *p*-toluidine and aniline hydrochloride at 210° – 240° (Girard, de Laire and Chapoteaut, *Ann.* 1866, 140, 347; *Bull. Soc. chim.* 1867, (2) 7, 360); by heating phenol with *p*-toluidine and zinc chloride, or *p*-cresol with aniline and zinc chloride at 260° – 300° , or with antimony trichloride (Buch, *Ber.* 1884, 17, 2634); by heating *p*-toluidine with bromobenzene and soda lime at 360° – 380° , or *p*-bromotoluene, aniline, and soda lime in a similar manner (Merz and Paschkowesky, *J. pr. Chem.* 1893, (2) 48, 455; see also Merz and Weith, *Ber.* 1881, 14, 2345). Crystals, m.p. 87° , b.p. 334.5° (H.), or 317° – 318° /727.5 mm. (Graebe, *Ann.* 1887, 238, 363). Dissolves in nitric acid with a blue colour. $B^{\circ}_x HCl$, leaflets.

Acetyl-derivative; m.p. 51° (Bonna).

Nitrosamine; slender yellow needles, m.p. 82° (Bonna, *Ann.* 1887, 239, 56), or 45° (Reichold, *Ann.* 1889, 255, 163).

***p*-Nitroso-derivative**; blue prisms or tables from alcohol, or green leaflets from benzene, m.p. 163° (Reichold).

For condensation with nitrochlorobenzenes, see Schöpf (Ber. 1890, 23, 1843); Jacobson and Lischke (*Ann.* 1898, 303, 377); Engelhardt and Latschinow (*Zeit. f. Chem.* 1870, (2) 6, 233); Willgerodt (*Ber.* 1876, 9, 980); Hepp (*Ann.* 1882, 215, 369); Jackson and Ittner (*Amer. Chem. J.* 1897, 19, 10, 199, 205; *Ber.* 1895, 28, 3063); Laubenheimer (*Ber.* 1878, 11, 1157); Ritzenstein (*J. pr. Chem.* 1903, 68, 251); Kahrman and Kragler (*Ber.* 1901, 34, 1102).

Di-*p*-tolylamine; by heating *p*-cresol with ammonium-zinc chloride and ammonium chloride at 330° – 340° (Merz and Müller, *Ber.* 1887, 20, 546); by heating a mixture of *p*-bromotoluene, *p*-toluidine, and soda lime at 390° (Merz and Paschkowesky, *J. pr. Chem.* 1893, (2) 48, 463). It melts at 79° , and boils at 328.5° /727.5 mm. or 330.5° /760 mm. (Graebe, *Ann.* 1887, 238, 363).

Nitrosamine; m.p. 100° – 101° (Lehne, *Ber.* 1880, 13, 1544), or 103° (Cosack, *ibid.* 1093). For its nitro-derivatives, see Leilmann (*Ber.* 1882, 15, 831); Jaubert (*ibid.* 1895, 28, 1649); and Lehne (*l.c.*).

Anhydro-formaldehyde-*p*-toluidine; from formaldehyde and *p*-toluidine (Wellington and Tollens, *Ber.* 1885, 18, 3302). It exists in two forms: (a) readily soluble form which crystallises in long needles from ether, m.p. 127° – 128° (Eibner, *Ann.* 1898, 302, 352) or 123° (Eberhardt and Welter, *Ber.* 1894, 27, 1804); (b) sparingly soluble form, m.p. 225° – 227° (E.), 207° – 209° (E. and W.). The lower melting substance is converted on sublimation into the higher melting modification. Both forms have the same molecular weight (Bischoff, *Ber.* 1898, 31, 3253).

For condensation with benzaldehyde and potassium cyanide, see von Miller, Föchl and Sieber (*Ber.* 1898, 31, 2711).

Methylene-di-*p*-tolylid-imide; by heating a mixture of *p*-toluidine, alcoholic potassium hydroxide, and formaldehyde (Eberhardt and

Walter, Ber. 1894, 27, 1808); by the action of formaldehyde on an alcoholic solution of *p*-toluidine (Eibner, Ann. 1898, 302, 350).

Rhombic tables, m.p. 86° (E. and W.) or 89° (E.). On heating with *p*-toluidine or on long boiling with alcohol it yields anhydroformaldehyde-*p*-toluidine, whilst on heating with *p*-toluidine hydrochloride it yields diaminoditolylmethane, silky needles, m.p. 92° . It is also stated that two compounds possessing the constitution $(\text{CH}_3\text{C}_6\text{H}_4\text{NH})_2\text{CH}_2$, are formed by heating 1 mol. of methylene chloride with 4 mols. of *p*-toluidine for 34 hours at 100° . One is a syrup, b.p. above 350° with decomposition and forms the salts, $\text{B}'\text{HCl}$, $\text{B}'_2\text{H}_2\text{PtCl}_6$, and $\text{B}'\text{HAuCl}_4$, all of which are amorphous. The other is an amorphous solid, m.p. about 156° , b.p. above 350° , with decomposition. All the salts of the latter with the exception of the acid oxalate are amorphous and unstable (Grünhagen, Ann. 1890, 256, 286). The same author states that di-methylene-di-*p*-toluidine is sometimes formed during the above reaction.

Tolyl-p-hydroxylamine; by reducing *p*-nitrotoluene with zinc dust in the presence of aqueous alcohol and calcium chloride (Lumière and Seyewitz, Bull. Soc. chim. 1894, (3) 11, 1040; Bamberger, Ber. 1895, 28, 245, 1221); by oxidising *p*-toluidine with a persulphate in presence of ether and in contact with ice (Bamberger and Tschirner, Ber. 1899, 32, 1677; see also Wöhl, Eng. Pat. 11216 of 1894; Fr. Pat. 239173; D. R. P. 84138 of 1893; Kalle & Co., D. R. P. 89978 of 1895). Leaflets, m.p. 92° – 93° (L. and S.), 93.5° – 94° (B.). At 115° it decomposes into *p*-azoxytoluene, and when warmed with dilute sulphuric acid it yields *p*-azoxytoluene, *p*-cresol, amino-cresol, *p*-hydrotoluquinone, and a little *p*-toluidine. Oxidation with chromic acid yields *p*-nitrosotoluene. On treatment with thionyl-aniline in benzene solution it yields *p*-toluidine phenylsulphonate, white plates, m.p. 236° , and (probably) *o*-toluene-azo-*p*-toluene, m.p. 68° – 72° (Michaelis and Petou, Ber. 1898, 31, 988).

Nitroso-p-tolylhydroxylamine; from *p*-nitrotoluene and hydroxylamine in presence of sodium ethylate (Angeli and Angelico, Atti R. Accad. Lincei, 1899, (v.) 8, ii. 28); from *p*-nitrosotoluene and the sodium salt of nitrohydroxylaminic acid (Angeli and Angelico, *ibid.* 1901, (v.) 10, i. 167). Leaflets, m.p. 59° – 59.5° .

2-Nitrotolyl-p-hydroxylamine; by electrolytic reduction of 2:4-dinitrotoluene in nearly neutral solution (Brand and Zöller, Ber. 1907, 40, 3324). Compact yellow crystals, m.p. 90° (B. and Z.) or 106° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052).

2:6-Dinitrotolyl-*p*-hydroxylamine; together with 4:6-dinitro-*o*-toluidine by reduction of 2:4:6-trinitrotoluene in cold alcoholic ammoniacal solution with hydrogen sulphide (Anschütz and Zimmermann, Ber. 1915, 48, 152; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 27; Cohen and McCandlish, *ibid.* 1905, 87, 1205); together with 4:6-dinitrotolyl-*o*-hydroxylamine by reducing 2:4:6-trinitrotoluene in almost neutral solution at a silver cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; Ber. 1916, 49, 673). It melts at 135° – 136° , and is converted by boiling concentrated

hydrochloric acid into 2:6-dinitro-*p*-toluidine and 2:6-dinitro-4-azoxytoluene.

o-Toluidine 3-sulphonic acid; by reduction of 2-nitrotoluene 3-sulphonic acid (von Pechmann, Ann. 1874, 173, 215); from tolyl-*o*-hydroxylamine and sulphurous anhydride (Brotschneider, J. pr. Chem. 1897, (2) 55, 291). Microscopic needles. The aqueous solution forms an intensive reddish-yellow colour when warmed with ferric chloride.

o-Toluidine 4-sulphonic acid; by reducing the corresponding nitro-acid (Bek, Zeit. f. Chem. 1869, (2) 5, 211; Beilstein and Kuhlberg, Ann. 1870, 155, 21) or *o*-nitrotoluene *p*-sulphonyl chloride with tin and hydrochloric acid (Reverdin and Crépieux, Ber. 1901, 34, 2993); sulphonation of *o*-toluidine sulphate with 30 p.c. or 50 p.c. fuming sulphuric acid (Claus and Immel, Ann. 1891, 265, 71; cf. Weckwarth, *ibid.* 1874, 172, 193; Hayduck, *ibid.* 1874, 172, 204; 1874, 174, 343; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 745). Long needles or four-sided prisms. The aqueous solution forms a dark violet coloration with ferric chloride (Herzfeld, Ber. 1884, 17, 904). With bromine it yields a dibromo-derivative. $\text{NaA}' + \text{H}_2\text{O}$, small lustrous scales (W. and B.); $+3\text{H}_2\text{O}$ (C. and I.); $+4\text{H}_2\text{O}$ (B.); $\text{KA}' + \text{H}_2\text{O}$ (W. and B.); $\text{CaA}'_2 + 6\text{H}_2\text{O}$, small prisms (W. and B.); $\text{BaA}'_2 + 2\text{H}_2\text{O}$, tables (W. and B.); PbA' , anhydrous (H.).

Amide; by reduction of 2-nitrotoluene 4-sulphonamide with ammonium sulphide (Paysan, Ann. 1883, 221, 210; cf. Reverdin and Crépieux, *l.c.*). Large four-sided columns, m.p. 175° . $\text{B}'\text{HCl}$, long silky needles, m.p. 240° .

o-Toluidine 5-sulphonic acid; by heating *o*-toluidine with fuming sulphuric acid at 160° – 180° (Gerver, Ann. 1873, 169, 374), or *o*-toluidine ethylsulphate at 200° (Pagel, Ann. 1875, 176, 292); by reducing 2-nitrotoluene 5-sulphonic acid with ammonium sulphide (Foth, Ann. 1864, 230, 306); by heating *o*-toluidine hydrogen sulphate at 220° – 230° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 628; Wynne, *ibid.* 1892, 61, 1037; cf. Claus and Immel, Ann. 1891, 265, 67); by heating di-*o*-tolylurea at 150° with concentrated sulphuric acid (Cazeneuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 23). Large monoclinic prismatic crystals $+ \text{H}_2\text{O}$ (Zepharovich, Ber. 1888, 21, 1803; cf. Hasse, Ann. 1885, 230, 287) or needles $+ \text{H}_2\text{O}$ (Wynne). $\text{NaA}' + 4\text{H}_2\text{O}$, tables (N. and W.; Wynne); $\text{KA}' + \text{H}_2\text{O}$, tables and prisms (N. and W.); $\text{BaA}'_2 + 7\text{H}_2\text{O}$ (N. and W.; Foth); PbA' , long flat prisms; AgA' , anhydrous prisms.

The aqueous solution when treated with a little lead peroxide is coloured rose-red, then green and finally, on adding more lead peroxide, blackish-violet. On bromination it yields monobromo-*o*-toluidine 5-sulphonic acid and 3:5-dibromo-*o*-toluidine. On nitration the chief product is 3:5-dinitro-2-nitroaminotoluene, yellow explosive crystals, m.p. 92° (Zincke and Malkomeius, Ann. 1905, 339, 202).

Acetyl-derivative, needles (Jungmann, Ber. 1900, 33, 1366).

o-Toluidine 3:5-disulphonic acid; by sulphonating 2-toluidine 5-sulphonic acid at 150° – 170° for $\frac{1}{2}$ hour (Neville and Winther, Chem. Soc. Trans. 1882, 41, 421; Ber. 1882, 15, 2993;

Hasse, Ann. 1885, 230, 243; cf. Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 731). Slender needles $+1\frac{1}{2}\text{H}_2\text{O}$. Decomposed at 240° , forming 2-toluidine 5-sulphonic acid.

Salts (see Hasse). $\text{Na}_2\text{A}''+6\text{H}_2\text{O}$, tables; $\text{K}_2\text{A}''$ (anhydrous) (W. and B.); $\text{K}_2\text{A}''+2\text{H}_2\text{O}$, monoclinic plates (H.); $\text{CaA}''+5\text{H}_2\text{O}$, tables; $\text{BaH}_2\text{A}''+3\frac{1}{2}\text{H}_2\text{O}$, microscopic needles or prisms; $\text{BaA}''+3\text{H}_2\text{O}$, triclinic crystals; $\text{PbA}''+6\frac{1}{2}\text{H}_2\text{O}$, quadratic prisms; $\text{PbA}''+2\text{H}_2\text{O}$, columns.

Chloride, pale yellow prismatic crystals, m.p. 95° (W. and B.), 132° (H.).

o-Toluidine 4:5-disulphonic acid; by sulphonating *o*-toluidine 4-sulphonic acid, finally at 160° (Wynne and Bruce, *loc. cit.*). Needles, $\text{K}_2\text{A}''+2\text{H}_2\text{O}$, thin scales; $\text{K}_2\text{A}''$, short slender anhydrous needles; $\text{BaA}''+1\frac{1}{2}\text{H}_2\text{O}$, small thin scales (W. and B.).

3-Bromo-o-toluidine 5-sulphonic acid; by brominating *o*-toluidine 5-sulphonic acid (Neville and Winther, Ber. 1880, 13, 1942; Chem. Soc. Trans. 1880, 37, 429, 625; Claus and Immel, Ann. 1891, 265, 68; Wynne, Chem. Soc. Trans. 1892, 6, 1037). Lustrous needles or prisms $+ \text{H}_2\text{O}$. On heating with water or hydrochloric acid at 160° a mixture of bromo-*o*-toluidine, m.p. 56° , dibromo-*o*-toluidine, m.p. 46° , and a liquid bromotoluidine is obtained.

KA' , anhydrous thin scales (W.); $\text{NaA}' + 18\text{H}_2\text{O}$, small rectangular prisms, which rapidly lose $17\frac{1}{2}\text{H}_2\text{O}$ on exposure to air; $\text{BaA}' + 3\text{H}_2\text{O}$, long lustrous needles (C. and I.; W.).

Pagel (Ann. 1875, 176, 200) by heating *o*-toluidine with sulphuric acid obtained *o*-toluidine sulphonic acid, the amino-group of which was replaced by bromine, and the bromosulphonic acid nitrated and reduced. The product formed microscopic prisms; $\text{BaA}' + \text{H}_2\text{O}$, thick needles; whilst Gerver (Ann. 1873, 169, 380) by treating an aqueous solution of *o*-toluidine 5-sulphonic acid with bromine obtained a dibromo-*o*-toluidine 5-sulphonic acid together with a tribromo-*o*-toluidine, m.p. 112° . The former compound yielded $\text{BaA}' + 4\text{H}_2\text{O}$, long needles; $\text{PbA}' + 3\text{H}_2\text{O}$, needles or prisms. The validity of the latter author's work is questioned by Neville and Winther.

3:5-Dibromo-o-toluidine 4-sulphonic acid; by brominating *o*-toluidine 4-sulphonic acid (Hayduck, Ann. 1874, 172, 211). Long slender needles $+ \text{H}_2\text{O}$ (see also Kornatzki, Ann. 1883, 221, 191); $\text{BaA}' + 9\text{H}_2\text{O}$, aggregates of small needles (H.).

4-Iodo-o-toluidine 5-sulphonic acid; by heating diazotised 2-nitro-*p*-toluidine 5-sulphonic acid with concentrated hydriodic acid (Foth, Ann. 1885, 230, 308). Slender silky needles $+ \text{H}_2\text{O}$; BaA' , rhombic plates.

3-Nitro-o-toluidine 5-sulphonic acid; by nitrating acetyl-*o*-toluidine 5-sulphonic acid (Nietaki and Pollini, Ber. 1890, 23, 138); by heating aceto-*o*-toluidide with 3 parts of 20 p.c. fuming sulphuric acid at 100° and nitrating the cold product with mixed acids (Gnehm and Blumer, Ann. 1899, 304, 105). Small yellow crystals. On heating with dilute sulphuric acid it yields 3-nitro-*o*-toluidine.

6-Nitro-o-toluidine 4-sulphonic acid; by passing hydrogen sulphide into an ammoniacal solution of 2:3-dinitrotoluene 4-sulphonic acid (Marckwald, Ann. 1893, 274, 353). Slender

needles. KA' , leaflets; CaA' , needles; $\text{BaA}' + 2\frac{1}{2}\text{H}_2\text{O}$, needles; $\text{AgA}' + \frac{1}{2}\text{H}_2\text{O}$, needles.

Methyl-o-toluidine 4-sulphonic acid; by treating methyl-*o*-toluidine with 30 p.c. fuming sulphuric acid with cooling and then heating to 50° (Gnehm and Blumer, Ann. 1899, 304, 109). Leaflets or tables. NaA' , leaflets; $\text{BaA}' + 2\text{H}_2\text{O}$, small irregular crystals.

Acetyl-derivative; by acetylation of the amino-acid or sulphonation of methylacetato-*o*-toluidide. BaA' , flat prisms (G. and B.).

Methyl-o-toluidine (?)sulphonic acid; by sulphonation of methyl-*o*-toluidine with monohydrate at 180° - 210° (G. and B.). Needles. BaA' , readily soluble in water.

Dimethyl-o-toluidine (?)sulphonic acid; by heating dimethyl-*o*-toluidine with 4 parts of sulphuric acid at 180° - 210° (Michler and Sampaio, Ber. 1881, 14, 2168). Large glistening prisms which become opaque on exposure to air. CaA' , nodules; BaA' , leaflets; ZnA' , needles.

m-Toluidine 2-sulphonic acid; together with *m*-toluidine 2:4-disulphonic acid by heating *m*-toluidine with fuming sulphuric acid at 160° - 175° (Lorenz, Ann. 1874, 172, 185). The products are separated by crystallisation from water in which the disulphonic acid is more soluble.

Rhombic tables or leaflets, charring above 275° without melting. $\text{BaA}' + 9\text{H}_2\text{O}$, thin tables or long prisms; $\text{PbA}' + 3\frac{1}{2}\text{H}_2\text{O}$, nodules.

m-Toluidine 4-sulphonic acid; 2-bromotoluene 4-sulphonic acid is nitrated, reduced and then treated with sodium amalgam to remove the bromine (Hayduck, Ann. 1874, 174, 350). Microscopic needles. BaA' , amorphous; PbA' , voluminous flocks.

6-Chloro-m-toluidine 4-sulphonic acid; by reducing sodium 2-chloro-5-nitrotoluene *p*-sulphonate with iron filings and dilute acetic acid. Thin small colourless anhydrous plates which turn red on exposure to air and light (Davies, Chem. Soc. Trans. 1921, 119, 865).

m-Toluidine 2:4-disulphonic acid; by heating *m*-toluidine with fuming sulphuric acid (Lorenz, Ann. 1874, 172, 185). One sulphonic group is removed readily with formation of *m*-toluidine sulphonic acid. $\text{BaA}'' + 12\frac{1}{2}(\text{?})\text{H}_2\text{O}$, needles; $\text{PbA}'' + 2\text{H}_2\text{O}$, crusts.

Aceto-p-toluidide 2-sulphonic acid, small colourless needles, m.p. about 160° (decomp.), is obtained by the action of aqueous sodium sulphite on aceto-*p*-toluidide 2-sulphonylchloride (Johnson and Smiles, Chem. Soc. Trans. 1923, 123, 2384).

p-Toluidine 2-sulphonic acid; together with *p*-toluidine 3-sulphonic acid and *p*-toluidine disulphonic acid by heating *p*-toluidine with fuming sulphuric acid (Sell, Ann. 1903, 126, 155; Malyschew, Zeit. f. Chem. 1869, (3) 5, 212); by reducing 4-nitrotoluene 2-sulphonic acid (Bollstein and Kuhlberg, Ann. 1874, 172, 220; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 743; cf. Brackett and Hayes, Amer. Chem. J. 1887, 9, 400); from *p*-nitrotoluene (Jannsen, Ann. 1874, 172, 233); by heating di-*p*-toluides with concentrated sulphuric acid at about 150° (Caseneuve and Moreau, Bull. Soc. chim. 1906 (3) 19, 22). Monoclinic crystals $+ \text{H}_2\text{O}$ (Zapfrovich, Ber. 1893, 21, 2189) or rhombic (Himelke, Ann. Acad. Sci. Fennicae, 1911

[A] 10, 1). The cold aqueous solution is coloured yellowish-red on treatment with lead peroxide, and with ferric chloride a bordeaux-red colour is produced on warming (Janowsky and Reimann, Ber. 1888, 21, 1217). It reduces ammoniacal silver solution forming a mirror. On diazotisation and boiling with absolute alcohol toluene *o*-sulphonic acid is formed (Ascher, Ann. 1872, 161, 8; Jenssen) and *p*-ethoxytoluene *o*-sulphonic acid (Remsen and Palmer, Amer. Chem. J. 1886, 8, 245). KA' , leaflets or prisms; BaA' , $+H_2O$, leaflets; PbA' , crystalline powder.

Acetyl-derivative; by sulphonating aceto-*p*-toluidide; *acetylsulphonylchloride*, m.p. 124°; *acetylsulphonanilide*, m.p. 220°–221° (Zincke and Rollhauser), or 230° (Johnson and Smiles, Chem. Soc. Trans. 1923, 123, 2384). The acetyl-sulphonyl chloride when reduced with zinc dust yields 4-acetyl-amino-*o*-tolylmercaptan, m.p. 95°, which, on hydrolysis, yields 4-amino-*o*-tolylmercaptan, m.p. 47° (Hess, Ber. 1881, 14, 488, gives 42°) (Zincke and Rollhauser, Ber. 1912, 45, 1495; see also Johnson and Smiles, l.c.).

Amide; by reducing 4-nitrotoluene 2-sulphonamide with hydrogen sulphide in warm ammoniacal solution (Heffter, Ann. 1883, 221, 208). Silky needles or pearly plates, m.p. 164°. By the action of nitrous acid on a mixture of the amide and concentrated hydrochloric acid, *p*-chlorotoluene *o*-sulphonamide is formed, and with nitrous acid and alcohol toluene *o*-sulphonamide is obtained.

p-Toluidine 3-sulphonic acid; by baking *p*-toluidine sulphate or hydrogen sulphate (Neville and Winther, Ber. 1880, 13, 1947; Chem. Soc. Trans. 1880, 37, 631; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 739); together with *p*-toluidine 2-sulphonic acid and a disulphonic acid by heating *p*-toluidine with twice its weight of fuming sulphuric acid at 180°. In the latter case, the chief product is *p*-toluidine 3-sulphonic acid, but on further heating a greater proportion of the other products is obtained (von Pechmann, Ann. 1874, 173, 195); by treating tolyl-*p*-hydroxylamine in cold 60 p.c. alcoholic solution with sulphur dioxide (Bretschneider, J. pr. Chem. 1897, (2) 55, 292); by heating di-*p*-tolylurea with concentrated sulphuric acid at 150° (Cazeneuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 22).

The 2- and 3-acids may be separated by means of alcohol, in which only the latter is soluble (Buff, Ber. 1870, 3, 796; cf. von Pechmann), or by means of the lead salts, that of the 3-acid being the less soluble; or by means of aqueous potassium hydroxide (Schneider, Amer. Chem. J. 1886, 8, 274). Yellow needles $+ \frac{1}{2}H_2O$ or H_2O (P.). Its aqueous solution gives a wine-red colour with a little lead peroxide (Janowsky, Ber. 1888, 21, 1804). On bromination it yields 5-bromo-*p*-toluidine 3-sulphonic acid and 2:5-dibromo-*p*-toluidine (N. and W.). The sulphonic group is hydrolysed by water at 180°. $KA' + \frac{1}{2}H_2O$ (Malyschew, Zeit. f. chem. 1869, 212; Schneider); $BaA' + 3H_2O$, six-sided plates (P.); $PbA' + 2H_2O$, long needles (P.); AgA' , shining crystals.

Acetyl-derivative; by sulphonating aceto-*p*-toluidide (Junghahn, Ber. 1900, 33, 1366). Leaflets.

p-Toluidine 2:5-disulphonic acid; by heat-

ing *p*-toluidine 2-sulphonyl chloride with chlorosulphonic acid at 150° or with fuming sulphonic acid at 180° (Richter, Ann. 1885, 230, 331; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 743). Long silky needles $+ 2\frac{1}{2}H_2O$, hydrolysed at 200° with formation of *p*-toluidine 2-sulphonic acid.

$K_2A'' + 2H_2O$, long needles; BaH_2A'' , $+ \frac{1}{2}H_2O$, nodules, $+ \frac{1}{2}H_2O$, silky needles; BaA' , $+ H_2O$, tables; $PbA'' + \frac{1}{2}H_2O$.

p-Toluidine 3:5-disulphonic acid; by heating *p*-toluidine with fuming sulphuric acid at 200° (von Pechmann, Ann. 1874, 173, 217); by heating *p*-toluidine 3-sulphonic acid with chlorosulphonic acid for 2 hours at 120° and then for 2 hours at 140°–160°, or by heating with fuming sulphuric acid for $1\frac{1}{2}$ hours at 160° (Richter, Ann. 1885, 230, 315). The product obtained by the latter author was originally regarded as *p*-toluidine 2:3-disulphonic acid, but was shown by Wynne and Bruce (Chem. Soc. Trans. 1898, 73, 739) to be the 3:5-disulphonic acid. Microscopic needles $+ 2H_2O$, converted by heating at 200°, or with water at 140°, into *p*-toluidine 3-sulphonic acid. Salts (Richter). $K_2A'' + 2H_2O$, long acicular prisms; $BaH_2A'' + 3H_2O$, nodules; $BaA'' + 3H_2O$, leaflets or tables; $PbA'' + 2H_2O$, slender needles; PbA' , silky needles.

Bromo-p-toluidine 2-sulphonic acid; by adding bromine to a boiling solution of *p*-toluidine 2-sulphonic acid (Jenssen, Ann. 1874, 172, 234). Slender needles. $KA' + H_2O$, prisms; BaA' , $+ 7H_2O$, prisms or needles.

5(?) *Bromo-p*-toluidine 3-sulphonic acid; together with 3:5-dibromo-*p*-toluidine by treating *p*-toluidine 3-sulphonic acid with bromine (von Pechmann, Ann. 1874, 173, 210; Neville and Winther, Chem. Soc. Trans. 1880, 37, 631). Yellowish nodules consisting of grouped needles $+ \frac{3}{2}H_2O$, or fine sulphur-yellow needles $+ \frac{3}{2}H_2O$. KA' , thick prisms; $BaA' + 2H_2O$, small rhombic tables; PbA' , glistening needles; AgA' , long colourless needles (P.).

2-Nitro-*p*-toluidine 5-sulphonic acid; from 2-nitro-*p*-toluidine and fuming sulphuric acid at 135°–150° or chlorosulphonic acid at 160° (Foth, Ann. 1885, 230, 300). Yellow needles, which carbonise without melting. $KA' + H_2O$, small orange-red prisms; $BaA' + 4H_2O$, small yellowish-red prisms $+ H_2O$, red nodules; $PbA' + 3\frac{1}{2}(?)H_2O$, small red needles; ammonium salt, golden-yellow needles; silver salt, white prisms, blackened by light.

Ethyl-p-toluidine 2-sulphonic acid; by sulphonating ethyl-*p*-toluidine (Schmidt, J. pr. Chem. 1893, (2) 48, 62). Yellow prisms $+ H_2O$. $KA' + H_2O$, yellow tables.

Diethyl-p-toluidine 2-sulphonic acid; by sulphonation of diethyl-*p*-toluidine at 180°–200° (Schmidt); by ethylation of potassium-*p*-toluidine 2-sulphonate with ethyl bromide and absolute alcohol at 150° (Schmidt). Prisms $+ H_2O$. $KA' + 2H_2O$, triclinic tables; $CaA' + 3H_2O$; $BaA' + 4H_2O$, triclinic tables.

Diethyl-p-toluidine 3-sulphonic acid; by ethylating potassium *p*-toluidine 3-sulphonate in a similar manner (Schmidt). Monoclinic prisms $+ H_2O$, m.p. 243°. $KA' + \frac{1}{2}H_2O$, tables, m.p. 297°.

Some toluidine sulphonic acids of unknown orientation are described by Pagel (Ann. 1875,

176, 305); Haydock (*ibid.* 1875, 177, 57) Schäfer (*ibid.* 1874, 174, 360).

2:3-Toluylenediamine; by reducing 3-nitro-*o*-toluidine with tin and hydrochloric acid (Lellmann, Ann. 1885, 228, 243) or with hydroiodic acid (Gabriel and Thieme, Ber. 1919, 52, 1079). Crystals, m.p. 61°–62°, b.p. 255° (L.) or m.p. 63°–64° (G. and T.).

6-Chloro-2:3-toluylenediamine; by reducing 6-chloro-2:3-dinitrotoluene with stannous chloride and hydrochloric acid (Cohn, Monatsch. 1901, 22, 477); by reducing 6-chloro-3-nitro-*o*-toluidine with zinc dust and ammonium chloride in dilute alcohol (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 788). Colourless needles, m.p. 46°–47°.

Hydrochloride, nacreous leaflets, decomposing at 263° (M. and D.).

Acetyl-derivative; m.p. 201°–203° (M. and D.).

4:6-Dichloro-2:3-toluylenediamine; by reducing 2:4-dichloro-5:6-dinitrotoluene (See lig. Ann. 1887, 237, 164). Leaflets, m.p. 110°. On boiling with acetic anhydride for 25 hours it yields an *anhydro-base*, m.p. 170°.

4:5:6-Trichloro-2:3-toluylenediamine; by reducing the corresponding dinitro-compound with stannous chloride in hot 5 p.c. alcoholic solution (Seelig, Ber. 1885, 18, 82; Prenntzell Ann. 1897, 298, 182). M.p. 195°–207°.

Anhydro-base; by boiling with acetic anhydride for 40–50 hours. Glistening brown needles, m.p. about 300° (S.).

5-Bromo-2:3-toluylenediamine; by successive bromination, nitration, hydrolysis, and reduction of aceto-*o*-toluidide (Hübner and Schupphaus, Ber. 1884, 17, 776). Small needles m.p. 59°. B'HCl, needles; B'H₂SO₄, plates.

5-Nitro-2:3-toluylenediamine; by reducing 3:5-dinitro-*o*-toluidine with sodium sulphide. Orange-red felted needles.

Diacetyl-derivative; obtained by warming the base with acetic anhydride. Pale yellow needles, m.p. 234°. When the free base is boiled with glacial acetic acid and formic acid it is converted into 5-nitro-2:7-dimethylbenzimidazole, glistening needles, m.p. 186° and 5-nitro-7-methylbenzimidazole, white needles m.p. 199°–200°.

6-Chloro-2-methyl-2:3-toluylenediamine; by reducing 6-chloro-3-nitromethyl-*o*-toluidine with zinc dust and ammonium chloride in aqueous alcoholic solution. Oil. B'HCl, colourless needles. **Diazoimine**, flesh-coloured prismatic needles, m.p. 238°–239° (Morgan and Jones Chem. Soc. Trans. 1921, 119, 191).

2:3-Toluylenediamine 5-sulphonic acid; by reducing 3-nitro-*o*-toluidine 5-sulphonic acid with stannous chloride and hydrochloric acid (Nietzki and Pollini, Ber. 1890, 23, 139). Needles.

2:4-Toluylenediamine, m-toluylenediamine by reducing 2:4-dinitrotoluene (Hofmann Jahresbericht, 1861, 513) or 4-nitro-*o*-toluidine with tin and hydrochloric acid (Nötting and Collin, Ber. 1894, 17, 268); by treating 2:4-dinitrobenzyl chloride with tin and hydrochloric acid (Krasusky, J. Russ. Phys. Chem. Soc. 1895, 27, 237). Long needles, or rhombic prisms, m.p. 99°, b.p. 290°. Its aqueous solution darkens in the air. When treated with sodium peroxide solution at a moderate temperature 4-nitro-*o*-toluidine is obtained, whilst when the mixture is boiled 2:4-dinitrotoluene is

formed (O. Fischer and Trost, Ber. 1893, 26, 3084).

Salts, see Hofmann; Hell and Schoop, Ber. 1879, 12, 723. B'HCl (Bernthsen and Trompeter, Ber. 1878, 11, 1759); B'2HCl, B'H₂PtCl₄; B'2HBr; B'H₂SO₄ + 2H₂O, long monoclinic prisms (Strauss, Ann. 1868, 148, 157; cf. Beilstein and Kuhlberg, Ann. 1871, 158, 251). Reactions with sulphur, see Kalle and Co., D. R. P. 86096 of 1894; Clayton Aniline Co., Eng. Pat. 4792 of 1900; D. R. P. 120504 of 1900; Cassella & Co., Eng. Pat. 11771 of 1902; U.S. Pat. 714542; Fr. Pat. 321122; D. R. P. 139430 of 1902.

With formaldehyde in neutral aqueous or alcoholic solution it yields *anhydroformaldehyde-m-toluylenediamine*, powder, m.p. 150°–180°, whilst in acid solution 3:3'-dimethyl-4:6:4':6'-tetraaminodiphenylmethane, m.p. 203°–204°, is formed (Ullmann and Naef, Ber. 1900, 33, 913; D. R. P. 130943 of 1898).

2-Acetyl-derivative; by reducing 4-nitro-aceto-*o*-toluidide, needles, m.p. 140° (Wallach Ann. 1886, 234, 360).

4-Acetyl-derivative; by prolonged boiling of 2:4-toluylenediamine with acetic acid (Tiemann, Ber. 1870, 3, 221; Schiff and Ostrogoich, Ann. 1896, 293, 371), or by heating 1 part of the diamine with $\frac{1}{2}$ part of acetamide initially at 110° and finally at 160°–170° (S and O.). Long yellow prisms or needles m.p. 161.5° (S. and O.) or 159°–160° (T.).

Diacetyl-derivative (Koch, Ann. 1870, 153, 132; Tiemann, Ber. 1870, 3, 8; Ladenburg *ibid.* 1875, 8, 1211). Long needles, m.p. 221° (T.) or 224° (L.). By boiling with 1 mol. *o*-potassium hydroxide 4-acetamino-2-aminotoluene is obtained (K.).

Formyl-derivative; transparent pyramids m.p. 113°–114°; **diformyl-derivative**; bunches of white needles, m.p. 176°–177° (Geigy & Co. U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

4-Benzoyl-derivative; by reducing *o*-nitro-4-benzoylaminotoluene with tin and hydrochloric acid (Bell, Ber. 1874, 7, 1506). Prisms m.p. 142°.

Dibenzoyl-derivative; tables, m.p. 224° (Ruhemann, Ber. 1881, 14, 2656).

Benzylidene-derivative; yellow tables, m.p. 90°–91° (Meyer and Gross, Ber. 1898, 31, 2358); **dibenzylidene-derivative**; yellowish crystalline mass, m.p. 122°–128° (Schiff 1866, 146, 98).

5-Chloro-2:4-toluylenediamine; by 5-chloro-2:4-dinitrotoluene with tin and hydrochloric acid (Reverdin and Crépiaux, Ber. 1903, 33, 2507); by successive chlorination and hydrolysis of diacetyl-2:4-toluylenediamine (Morgan, Chem. Soc. Trans. 1900, 77, 1209). Leaflets or rectangular plates, m.p. 120°–121° (M.) or 123° (R. and C.).

Acetyl-derivative; m.p. 170° (R. and C.) **diacetyl-derivative**, small acicular prisms, m.p. above 260° (R. and C.; Morgan, Chem. Soc. Trans. 1902, 81, 95).

Formyl-derivative; colourless silky needles m.p. 166° (Morgan).

Dibenzoyl-derivative; colourless acicular leaflets, m.p. 205° (M.).

6-Chloro-2:4-toluylenediamine; by reducing 2:4-chloro-4:6-dinitrotoluene with stannous

chloride and hydrochloric acid in presence of alcohol, or with zinc dust, ammonium chloride and alcohol (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 788).

5:6-Dichloro-2:4-toluylenediamine; by reduction of 2:3-dichloro-4:6-dinitrotoluene (Seelig, Ann. 1887, 237, 164). Slender needles, m.p. 137°.

5-Bromo-2:4-toluylenediamine; by reducing either 5-bromo-2:4-dinitrotoluene (Grete, Ann. 1875, 177, 231) or 5-bromo-4-nitro-*o*-toluidine (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 950); by brominating dibenzoyl-2:4-toluylenediamine (Ruhemann, Ber. 1881, 14, 2659; Morgan and Clayton) or diacetyl-2:4-toluylenediamine (Tiemann, Ber. 1870, 3, 220) and hydrolysing the product. Lustrous needles, m.p. 104°-107° (decomp.) (M. and C.), rhombic tables 107° (G.), leaflets 104° (R).

Monoacetyl-derivative, leaflets, m.p. below 100° (Koch, Ann. 1870, 153, 134).

Acetyl-derivative, m.p. 254° (M. and C.).

Dibenzoyl-derivative, m.p. 214° (R).

Dibromo-4-acetyl-2:4-toluylenediamine; by brominating 4-acetyl-2:4-toluylene-diamine (Tiemann, l.c.). Long needles, m.p. 208° with blackening.

3:5:6-Tribromo-2:4-toluylenediamine; by reducing the corresponding dinitro-compound or 3:5:6-tribromo-4-nitro-*o*-toluidine with iron and acetic acid (Blanksma, Chem. Weekblad, 1914, 11, 185). Colourless crystals, m.p. 180°.

Nitroso-2:4-toluylenediamine; m.p. 195° (Täuber and Walder, D. R. P. 123375 of 1900).

6(?) Nitro-2:4-toluylenediamine; by successive nitration and hydrolysis of diacetyl or dibenzoyl-2:4-toluylenediamine (Tiemann, Ber. 1870, 3, 219; Ladenburg, *ibid.* 1875, 8, 1211; Ruhemann, *ibid.* 1881, 14, 2656). Reddish-yellow needles, with a violet sheen, m.p. 154°. Weak base, whose salts are decomposed by water.

Diacetyl-derivative; needles, m.p. 253° (decomp.) (L.). **Dibenzoyl-derivative**; citron-yellow needles, m.p. 245° (R.).

6-Nitro-2:4-toluylenediamine(?); by reducing 2:4:6-trinitrotoluene with alcoholic ammonium sulphide (Tiemann, l.c.). Small red prisms, m.p. 132°; **hydrochloride**, yellow needles.

3:5-Dinitro-2:4-toluylenediamine; together with a mononitro-derivative by nitration of diacetyl-2:4-toluylenediamine in presence of urea nitrate, followed by hydrolysis with dilute sulphuric acid (Nietzki and Rösel, Ber. 1890, 23, 3216); from 2:4-dibromo-3:5-dinitrotoluene and alcoholic ammonia at 150° (Blanksma, Chem. Weekblad, 1912, 9, 968); by heating 3:4:5-trinitro-2-methoxytoluene with ammonia in a sealed tube (Blanksma, Rec. trav. chim. 1910, 29, 410). Dark brown crystals, m.p. 254°.

Acetyl-derivative; does not melt below 300° (B.).

2-Methylamino-4-aminotoluene; by reducing 4-nitro-methyl-*o*-toluidine with tin or zinc dust (Gnehm and Blamer, Ann. 1899, 304, 106). Colourless oil, b.p. 273°.

2-Amino-4-methylaminotoluene; colourless viscid oil, b.p. 276°-276.5° (corr.), coloured brown by exposure to air; **sulphate**, white needles. For its use in the preparation of azines and indulines, see Bayer & Co., Eng. Pat. 16915 of

1892; Fr. Pat. 225086; D. R. P. 92014 of 1892; B. A. S. F., D. R. P. 77228 of 1892.

Nitrosoamine; yellow needles, m.p. 83°; **picrate**, needles, m.p. 103°-105° (Pinnow and Oesterreich, Ber. 1898, 31, 2928).

Nitroamine; by heating 2-nitromethyl-*p*-tolylnitroamine with alcoholic ammonium sulphide at 100°. Dull red prisms, m.p. 83.5° (P. and O.).

5-Nitro-2-amino-4-methylaminotoluene; from 2:5-dinitromethyl-*p*-toluidine and alcoholic ammonium sulphide (Pinnow, J. pr. Chem. 1900, (2) 62, 508). Brown leaflets with a bronze lustre, m.p. 168°.

Acetyl-derivative; yellowish-brown needles, m.p. 205.5°-207° (P.).

3:5-Dinitro-2-amino-4-methylaminotoluene; by heating 2:3:5-trinitromethyl-*p*-toluidine with alcoholic ammonia at 100° (Sommer, J. pr. Chem. 1903, (2) 67, 535); from 3:5-dinitro-2-amino-*p*-tolylnitroamine by heating with twice its weight of phenol for 2 hours at 140°-160° (S.); from the ethyl-ether of 3:5-dinitro-4-methylamino-*o*-cresol by heating with concentrated absolute alcoholic ammonia at 100° (Sommer, l.c. 559). Orange needles with a yellow reflex, m.p. 206°-208°.

Nitrosoamine; by the action of ammonia on the nitrosoamine of 2:3:5-trinitromethyl-*p*-toluidine. Brownish-yellow prisms, m.p. 164° (Sommer, l.c. 562).

2-Dimethylamino-4-aminotoluene; by reducing 4-nitrodimethyl-*o*-toluidine with stannous chloride and hydrochloric acid (Ullmann and Mühlhauser, Ber. 1902, 35, 332; Möhlau, Klimmer and Kahl, Zeit. f. Farb. u. Textilchem., 1902, 1, 313). Yellowish oil, coloured red by air, b.p. 248° (M., K. and K.) or 257°-259°/730 mm. with slight decomposition (U. and M.).

Dihydrochloride; columns, m.p. 208°; **sulphate**; m.p. 209° (M., K. and K.).

Acetyl-derivative; needles, m.p. 103° (M., K. and K.).

2-Amino-4-dimethylaminotoluene; by reducing 2-nitrodimethyl-*p*-toluidine (M. L. B., D. R. P. 69188 of 1891) with tin and hydrochloric acid (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 948).

Acetyl-derivative; white needles, m.p. 135° (M. and C.).

For the use of this base in the preparation of azines, see M. L. B., D. R. PP. 69188 of 1891; 85231, 85232 of 1892; 87500 of 1895; of safranines, Leonhardt & Co., D. R. P. 86608 of 1892; and of other dyes, Act. Ges. f. Anilfabr., Eng. Pat. 12899 of 1900; Fr. Pat. 301793; D. R. P. 118392 of 1900.

5-Bromo-2-amino-4-monoethylaminotoluene; by brominating 2-acetyl-amino-4-dimethylaminotoluene in glacial acetic acid, followed by hydrolysis (Morgan and Clayton, l.c.); by reducing 3-bromo-6-nitrodimethyl-*p*-toluidine with tin and hydrochloric acid (M. and C.). Pearley leaflets, m.p. 40°.

Acetyl-derivative; crystals, m.p. 163°; **benzoyl-derivative**; m.p. 177°-178°; **2-benzene-sulphonyl-derivative**; m.p. 178°-179° (M. and C.).

3:5-Dinitro-2:4-monomethylaminotoluene; by the action of methylamine on a concentrated boiling alcoholic solution of 2:3:5-trinitro-methyl-*p*-toluidine (Sommer, J. pr. Chem. 1903, (2) 67, 547). It exists in two modifications:

(a) red plates, m.p. 168° – 170° ; (b) yellow needles, m.p. 110° , converted into the red modification at 140° . Both modifications yield with aqueous potassium hydroxide according to the concentration 3:5-dinitro-2:4-dihydroxytoluene and 3:5-dinitro-2-methylamino-*p*-cresol (S.).

4-Nitrosoamine; from the nitrosoamine 2:3:5-trinitromethyl-*p*-toluidine and methylamine. Small yellow needles, m.p. 186° – 187° .

2:4-Dinitrosoamine; from either of the above compounds in acetic acid solution with sodium nitrite. Very stable white leaflets glistening cubes, m.p. 132° (S.).

3:5-Dinitro-2-dimethylamino-4-methylaminotoluene; from 2:3:5-trinitromethyl-*p*-toluidine and dimethylamine in alcoholic solution (Sommer, l.c. 565). Yellow needles, m.p. 115° .

3:5-Dinitro-2:4-di(methylnitroamino)toluene; colourless crystals, m.p. 169° (Blankens Rec. trav. chim. 1910, 29, 410).

Tetramethyl-2:4-toluylenediamine; together with the methylammonium bromide; by heating 2:4-toluylenediamine hydrobromide with methyl alcohol in a sealed tube at 180° (Morga Chem. Soc. Trans. 1902, 81, 653). Yellowish brown oil, b.p. 148° – 150° /24–26 mm., 255° – 256° /757 mm.; D_{20}^{25} 0.9661. $B'H_2PtCl$ yellow prisms; picrate, yellow prisms, m. 162° – 163° .

2-Ethylamino-4-aminotoluene; by reducing 4-nitroethyl-*o*-toluidine with zinc dust and hydrochloric acid (MacCallum, Chem. Soc. Trans. 1895, 67, 247). Liquid, b.p. 274° – 275° .

2-Amino-4-ethylaminotoluene; by reducing the corresponding nitro-compound (Nölting and Stricker, Ber. 1886, 19, 549). Liquid, b.p. 280° – 283° (N. and S.) or 289° – 291° (Jaubert, Bull. So. chim. 1899, (3) 21, 20).

2-Diethylamino-4-aminotoluene; by reducing 4-nitrodiethyl-*o*-toluidine with stannous chloride and hydrochloric acid (Ullmann and Mühlhause Ber. 1902, 35, 335; Möhlau, Klinmer and Kah l.c.). Yellowish oil, b.p. 259° (M., K. and K.), 265° – 266° /730 mm. (U. and M.). Volatile with steam $B'2HCl+H_2O$, m.p. 213° – 215° (decomp.) (M. K. and K.).

2-Amino-4-phenylaminotoluene; by heating 1 part of 2:4-toluylenediamine with $1\frac{1}{2}$ parts of aniline hydrochloride and 3 parts of aniline at 240° – 250° for 10 hours (Bayer & Co., Eng. Pat. 8610 of 1894; Fr. Pat. 240571; D. R. P. 809 of 1894). Prisms, m.p. 76° – 77° . Used for the preparation of azines (Bayer & Co., Eng. Pat. 8610 of 1894; Fr. Pat. 240621; D. R. PP. 819 and 84504 of 1894).

3:5-Dinitro-2-phenylamino-4-methylaminotoluene; from 2:3:5-trinitromethyl-*p*-toluidine and aniline (Sommer, J. pr. Chem. 1903, (2) 6, 137). Thick prisms, m.p. 197° .

4-Nitrosoamine; orange needles, m.p. 122° .

3:5-Dinitrosoamine; sulphur-yellow needles decomposing at 100° (S.).

2:4-Dinitrophenyl-2:4-toluylenediamine; by boiling a mixture of 2:4-toluylenediamine, chloro-2:4-dinitrobenzene and alcohol (Leyman, Ber. 1882, 15, 1237). Red tables, m.p. 184° .

Acetyl-derivative; m.p. 163° – 164° (L.).

3-Ethylamino-4-phenylaminotoluene; by heating 3-amino-4-phenylaminotoluene with ethyl bromide at 150° – 175° for 10 hours (Bayer & Co., Eng. Pat. 8176 of 1893; Fr. Pat. 240571).

D. R. P. 87667 of 1895). Crystals, m.p. 59° – 60° . Used for the preparation of azines (Bayer & Co., Eng. Pat. 9794 of 1895; Fr. Pat. 240621; D. R. P. 87975 of 1895).

2:4-Toluylenediamine 5-sulphonic acid; by warming 2-nitro-*p*-toluidine 5-sulphonic acid with stannous chloride and hydrochloric acid (Foth, Ann. 1885, 230, 309). Small glistening pyramids or rhombohedra. $KA'+H_2O$, glistening prisms; $BaA'+5\frac{1}{2}H_2O$, glistening leaflets or tables; $B'HCl+H_2O$, large rhombic prisms, decomposed by boiling water; $B'HBBr+H_2O$.

This sulphonic acid is possibly identical with that prepared by Wiesinger (Ber. 1874, 7, 464) by sulphonating 2:4-toluylenediamine, although the water content of some of its salts differs from those enumerated above.

2:4-Toluylenediamine 6-sulphonic acid; by reducing 2:4-dinitrotoluene 6-sulphonic acid. Prisms (Oehler, Fr. Pat. 199568; D. R. P. 51862 of 1889).

Anhydroformaldehyde-2:4-toluylenediamine; from 2:4-toluylenediamine and formaldehyde in neutral aqueous or alcoholic solution (Ullmann and Naef, Ber. 1900, 33, 913; D. R. P. 130643 of 1898). Slightly coloured powder, m.p. 150° – 180° . On heating in dilute acid solution it yields acridines (Ges. f. Chem. Ind. Basel, D. R. P. 130617 of 1902).

2:5-Toluylenediamine, *p*-toluylenediamine; by reducing 5-nitro-*o*-toluidine (Beilstein and Kuhlberg, Ann. 1871, 158, 352), *o*-aminoazotoluene (Nietzki, Ber. 1877, 10, 832) or *m*-aminoazotoluene (Nietzki, l.c. 1158) with tin and hydrochloric acid; by reducing 6-nitro-*m*-toluidine (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 306). Colourless prisms, m.p. 64° , b.p. 273° – 274° . By treating a solution of the base containing a little *o*-toluidine with oxidising agents such as potassium dichromate, manganese dioxide, and ferric chloride an intense green coloration is formed (N.).

Dihydrochloride; leaflets; sulphate, powder.

Diacyl-derivative; large prisms, m.p. 221° (Nietzki, Ber. 1877, 10, 1157; *ibid.* 1879, 1, 2237).

4-Chloro-2:5-toluylenediamine; by reducing 4-chloro-2:5-toluquinonedioxime with stannous chloride and hydrochloric acid in presence of alcohol.

Diacyl-derivative; silky snow-white needles (Kehrmann, Silva and Keleti, Ber. 1915, 4, 2028).

Chloro-2:5-toluylenediamine; by saturating an alcoholic, ethereal or glacial acetic solution of *N*-nitroso-*o*-tolylglycine with dry hydrogen chloride (Vörlander and Schröder, Ber. 1901, 34, 1651). White scales rendered violet by air, m.p. 146° . It reduces cold ammoniacal silver nitrate. Ferric chloride-chlorine water, &c., give a green coloration.

Dihydrochloride and sulphate are crystalline. Diacyl-derivative; fine white needles, m. above 300° (V. and S.).

3:4:6-Trichloro-2:5-toluylenediamine; by reducing a glacial acetic acid solution of 2:4-trichlorodinitrotoluene with stannous chloride and aqueous hydrochloric acid (Beilg, Ann. 1897, 237, 143; Ber. 1895, 18, 430). Shaded needles, m.p. 196° .

Tetra-acetyl-derivative; needles, m.p. 220° .

2-Amino-3-dimethylaminotoluene; by heating

ducing nitroso-dimethyl-*m*-toluidine with tin and hydrochloric acid (Wurster and Riedel, Ber. 1879, 12, 1801). Long needles, m.p. 28°.

Acetyl-derivative; m.p. 158° (W. and R.).

5-Amino-2-dimethylaminotoluene; by reducing 5-nitrodimethyl-*o*-toluidine with zinc dust and hydrochloric acid at 0° (Bernthsen, Ber. 1892, 25, 3134). Oil, which solidifies in a freezing mixture and melts at 47°, b.p. 253°–254°. $B \cdot H_2SO_4$, small needles. Ferric chloride yields a bluish-red colour and potassium dichromate a purple-red colour.

Tetramethyl-2:5-toluylenediamine; by heating 5-dimethylamino-*o*-toluidine with methyl alcohol and hydrochloric acid at 180° (Wurster and Riedel, l.c. 1802). Oil, b.p. 260°. Ferric chloride yields an intensive blue colour which disappears on adding hydrochloric acid.

5-Amino-2-ethylaminotoluene; by reducing 5-nitroso-ethyl-*o*-toluidine (Kock, Ann. 1888, 243, 307) with stannous chloride and hydrochloric acid (Weinberg, Ber. 1892, 25, 1611). Viscid liquid, b.p. (in atmosphere of hydrogen) 264° (K.), 272° (W.).

Dihydrochloride, m.p. 124° (decomp.); *sulphate*, large crystals.

5-Amino-2-diethylaminotoluene; by reducing 5-nitrodiethyl-*o*-toluidine (Bernthsen, Ber. 1892, 25, 3138, 3367); by hydrolysis of its acetyl-derivative (Weinberg). M.p. 24° (Weinberg, Ber. 1893, 26, 308), b.p. 266°–267°.

Hydrochloride; glistening leaflets; *sulphate*, $+2H_2O$, prisms.

2-Ethylamino-5-benzoylamintoluene; small needles, m.p. 174° (O. Fischer, Ann. 1895, 286, 166).

4-Nitro-2:5-toluylenediamine; by nitration of diacetyl-2:5-toluylenediamine in glacial acetic acid with a mixture of nitric acid (D 1.47) and glacial acetic acid, followed by hydrolysis (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1398). Needles, varying in different crystallisations from bright red to dark green with a bronze reflex, m.p. 173°.

Diacetyl-derivative; short pale yellow prisms, m.p. 158° (M. and M.).

2:6-Toluylenediamine; by reducing 6-nitro-*o*-toluidine with tin and hydrochloric acid (Cunerth, Ann. 1874, 172, 227; Ullmann, Ber. 1884, 17, 1959). Prisms, m.p. 103.5°–105°. With ferric chloride it yields a deep blue colour, and with *p*-nitrosodimethylaniline first a green and then a dark blue solution.

Hydrochloride, crystals; *sulphate*, $+1\frac{1}{2}H_2O$, small slender needles.

Diacetyl-derivative; sublimes in white woolly flocks, m.p. 202°–203° (Green and Lawson, Chem. Soc. Trans. 1891, 59, 1017).

3:5-Dinitro-2:6-toluylenediamine; by the action of alcoholic ammonia on 2:6-dibromo-3:5-dinitrotoluene at 150° (Blanksma, Chem. Weekblad, 1912, 9, 968).

Acetyl-derivative; colourless crystals, decomposing above 300° (B.).

3:5-Dinitro-2:6-dimethyltoluylenediamine; by the action of methylamine on 2:6-dibromo-3:5-dinitrotoluene (Blanksma). Orange-red crystals, m.p. 216°.

2:6-Toluylenediamine sulphonic acid; by boiling the corresponding thiosulphonic acid with concentrated hydrochloric acid (Peri, Ber. 1885, 18, 69). Silky needles. $BA_2 + 2H_2O$, microscopic needles.

2:6-Toluylenediamine 4-sulphonic acid; by reducing 2:6-dinitrotoluene 4-sulphonic acid or 6-nitro-2-aminotoluene 4-sulphonic acid with tin and hydrochloric acid (Schwanert, Ann. 1877, 186, 380; Marckwald, Ann. 1893, 274, 351). Rhombic pillars, not melting at 280° (S.). $BaA_2 + 4H_2O$, amorphous; $B \cdot HCl + 2H_2O$, small rhombic pillars; $B \cdot HBr + 2H_2O$; $B \cdot HNO_3 + H_2O$, rhombic needles; $B_2 \cdot H_2SO_4 + H_2O$, rhombic plates (S.).

3:4-Toluylenediamine; reduction of 3-nitro-*p*-toluidine or 3-nitro-*p*-aminobenzyl alcohol with tin and hydrochloric acid (Beilstein and Kuhlberg, Ann. 1871, 158, 351; Meyer and Rohmer, Ber. 1900, 33, 254). Scales, m.p. 88.5°, b.p. 265° (B. and K.). Its aqueous solution darkens in the air. $B \cdot 2HCl$, needles (Hübner, Ann. 1881, 209, 364); *sulphate*, $+1\frac{1}{2}H_2O$, scales.

3-Acetyl-derivative; by reducing 4-nitro-aceto-*m*-toluidide with iron and acetic acid. Nodular aggregates, melting indefinitely at 96°. The corresponding *anhydro-base* melts at 145°–150° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1400); *4-acetyl-derivative*; by reduction of 3-nitroaceto-*p*-toluidide, leaflets, m.p. 130°–131° (Bössneck, Ber. 1886, 19, 1757); *picrate*, leaflets (Bankiewicz, Ber. 1889, 22, 1399); *diacetyl-derivative*; long slender needles, m.p. 210° (Bistrzycki and Ulfers, Ber. 1890, 23, 1878). The diacetyl-derivative yields a *nitro-compound*, long needles, m.p. 239°, and a *dinitro-compound*, fine silky needles, m.p. 251°–252° (Bistrzycki and Ulfers, l.c. 1991).

3-Benzoyl-derivative; by reducing 4-nitro-benzoyl-*m*-toluidine with iron and acetic acid. Colourless felted needles or prismatic crystals, m.p. 158° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1403); *4-benzoyl-derivative*; crystals, m.p. 193°–194°, together with phenyl-tolimidazole by reducing 3-nitrobenzyl-*p*-toluidine with tin and hydrochloric acid (Hübner, Ann. 1881, 208, 314) or together with the dibenzoyl-derivative by direct benzoylation (Bistrzycki and Cybulski, Ber. 1891, 24, 633); *dibenzoyl-derivative*; by the further treatment of the 4-benzoyl-derivative with benzoyl chloride (Hübner; Bistrzycki and Cybulski) or from *m*-methylbenzimidazole with benzoyl chloride and sodium hydroxide (Bamberger and Berlé, Ann. 1893, 273, 349). It forms glistening needles, m.p. 263°–264° (Hinsberg and Udransky, Ann. 1889, 254, 255), and yields a *nitro-derivative*, prisms or needles, m.p. 246° (Bistrzycki and Ulfers, Ber. 1892, 25, 1994).

2-Chloro-3:4-toluylenediamine; by reducing 2-chloro-4-nitro-*m*-toluidine with zinc dust, dilute alcohol and ammonium chloride (Morgan and Glover, Chem. Soc. Trans. 1921, 119, 1706). Pale brown needles, m.p. 55°–56°.

6-Chloro-3:4-toluylenediamine; obtained quantitatively as the hydrochloride by reducing 6-chloro-4-nitro-*m*-toluidine with zinc dust, ammonium chloride and dilute alcohol, or with alcoholic stannous chloride (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 790; Morgan and Challenor, *ibid.* 1921, 119, 1539). Pale brownish-yellow leaflets, m.p. 143°.

5-Bromo-3:4-toluylenediamine; by reducing 5-bromo-3-nitro-*p*-toluidine with stannous chloride and hydrochloric acid (Bistrzycki, Ber. 1890, 23, 1045). Long flat needles, m.p. 81°–82°.

4-Acetyl-derivative; by reducing 5-bromo-3-nitroaceto-*p*-toluidide at a low temperature with stannous chloride and hydrochloric acid. It forms crystals, m.p. 167°-168° (Hartmann, Ber. 1890 23, 1049); diacetyl-derivative; by direct acetylation, glistening needles, m.p. 222°-223°; dibenzoyl-derivative, needles, m.p. 244°.

4-Methylamino-3-aminotoluene; by reducing 3-nitro-4-methylaminotoluene or its nitrosamine with tin and hydrochloric acid (Gattermann, Ber. 1885, 18, 1487; O. Fischer, Ber. 1893, 26, 194); by reducing methyl-*p*-toluidine azobenzene 4-sulphonic acid with stannous chloride and hydrochloric acid (Bamberger and Wulz, Ber. 1891, 24, 2082). Quadratic tables, m.p. 46°-44°, b.p. 260°/752 mm. (Pinnow, Ber. 1887, 20, 3121). B²HCl, small glistening prisms, decomposing at 180°-185° (B. and W. or 175°-180° (F.)); B²C₂H₅SO₄, deliquescent needles (F.); B²C₂H₅O₄, glistening needles, m.p. 124° (F.); picrate, small yellow crystals, m.p. 164° (F.). Symm-diacetyl-derivative; hexagonal plates, m.p. 183°-184° (Pinnow, J. pr. Chem. 1900, (2) 62, 514).

6-Chloro-4-amino-3-methylaminotoluene; by reducing 6-chloro-4-nitromethyl-*m*-toluidine with zinc dust, alcohol and ammonium chloride (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1542). Sublimes in arborescent needles, m.p. 60°.

5-Nitro-4-methylamino-3-aminotoluene; by reducing 3:5-dinitromethyl-*p*-toluidine with hydrogen sulphide in presence of alcohol and ammonia (Pinnow, J. pr. Chem. 1901, (2) 63, 180). Bluish-red plates or short prisms with green sheen, m.p. 131°-132°.

3-Amino-4-dimethylaminotoluene; together with a compound whose picrate melts at 254°-5° by the gradual addition of tin to a solution of 3-nitro-4-dimethylaminotoluene in hydrochloric acid (Pinnow, Ber. 1895, 28, 3042; J. pr. Chem. 1901, (2) 63, 354). Oil, b.p. 234°. Coloured ferric chloride. B²HCl, crystals, m.p. 192°; B²H₂HgCl₂, crystals, m.p. 205°-206°; picrate, yellow-brown prisms, m.p. 150°-151°; acetyl-derivative; plates, m.p. 111°-112° (P.).

5-Nitro-3-acetylamino-4-dimethylaminotoluene; by reducing 3:5-dinitrodimethyl-*p*-toluidine with ammonium sulphide, followed by treatment with acetic anhydride (Pinnow and Matovich, Ber. 1898, 31, 2514). Yellow needles or prisms, m.p. 97°.

6-Nitro-3-acetylamino-4-dimethylaminotoluene; by nitrating 3-acetylamino-4-dimethylaminotoluene with mixed acids below 0° (Pinnow, Ber. 1901, 34, 1181). Bright yellow rhombic tables, m.p. 142°-143°.

Tetramethyl-3:4-toluylenediamine; from 3:4-toluylenediamine and methyl iodide (Niemeiswaki, Ber. 1887, 20, 1888; cf. O. Fischer and Rignard, *ibid.* 1902, 35, 1263). Liquid, b.p. 245°-225°/717 mm. (N.), 259°-260°/740 mm. (F. and R.). Ferric chloride gives a red color. Red crystalline plates. B²HCl, needles (F. and R.).

5-Amino-3-aminotoluene; by reducing methyl-*p*-toluidine with tin and hydrochloric acid (Gattermann, Ber. 1885, 18, 148; O. Fischer, *ibid.* 1893, 26, 199). Large tables, m.p. 54°-55°. Unstable. B²HCl, m.p. 176° (F.); B²C₂H₅O₄, needles, m.p. 151° (F.).

Symm. diacetyl-derivative; obtained together with 2:5-dimethyl-1-ethylbenzimidazole by the action of acetic anhydride on the base (O. Fischer and Rignard, Ber. 1901, 34, 4206). Crystals, m.p. 177°.

3-Ethylamino-4-aminotoluene; by reducing 4-nitro-ethyl-*m*-toluidine with tin and hydrochloric acid (O. Fischer and Rignard). Needles, m.p. 59°, coloured violet in presence of air and moisture. With ferric chloride it yields a deep red oxidation product.

Symm. diethyl-3:4-toluylenediamine; from the diethyl-derivative of dibenzeneulphone-3:4-toluylenediamine and concentrated hydrochloric acid at 160° (Hinsberg, Ann. 1891, 265, 191; cf. O. Fischer and Rignard, Ber. 1902, 35, 1265). Liquid, b.p. 285° (H.). B²HCl, needles. With ferric chloride in presence of hydrochloric acid it forms a reddish-brown colour; a colourless precipitate is formed on the addition of potassium ferrocyanide to the aqueous solution (H.).

6-Chloro-3-phenylamino-4-aminotoluene; by reducing 6-chloro-4-nitrophenyl-*m*-toluidine with zinc dust and ammonium chloride (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 191). Pink needles, m.p. 109°-5°.

Diazoimine; silky pink needles, m.p. 119°-120° (M. and J.).

3 (or 2)-Nitro-2 (or 3)-amino-4-methylaminotoluene; in small yield by reducing 2:3(γ)-dinitromethyl-*p*-toluidine with ammonium sulphide (Pinnow, J. pr. Chem. 1900, (2) 62, 516). Nearly black prisms, m.p. 127°-128°.

3:5-Toluylenediamine; by reducing 3:5-dinitrotoluene (Städell, Ann. 1883, 217, 200) or 2:4-dibromo-3:5-dinitrotoluene (Davis, Chem. Soc. Trans. 1902, 81, 873). Liquid, b.p. 263°-285° (S.); syrupy liquid (D.). B²HCl, white needles, m.p. 255°-260° (decomp.).

Diacetyl-derivative; pike-shaped hemimorphic prisms, m.p. 235°-236°, which become strongly electrical when dry (D.).

2-Chloro-3:5-toluylenediamine; by reducing 2-chloro-3:5-dinitrotoluene with stannous chloride and hydrochloric acid (Nietzki and Rehe, Ber. 1892, 25, 3006). Long needles, m.p. 73° (N. and R.) or 74° (Morgan, Chem. Soc. Trans. 1902, 81, 97).

2:4-Dinitro-3:5-toluylenediamine; by heating an alcoholic solution of 2:4-dinitro-3:5-dibromotoluene with ammonia in a sealed tube at 150° (Blankama, Rec. trav. chim. 1904, 23, 125). Yellow crystals, m.p. 199°.

Trinitro-3:5-toluylenediamine; by the action of alcoholic ammonia on 3:5-dibromo-trinitrotoluene at 100° (Palmer, Ber. 1898, 31, 3501). Small yellow prisms, m.p. 222°.

2:4-Dinitro-3:5-dimethylaminotoluene; from 2:4-dinitro-3:5-dibromotoluene and dimethylamine (Blankama). Bright red crystals, m.p. 140°. On nitration it yields 2:4:6-trinitrodimethylnitroaminotoluene; colourless crystals, m.p. 199°-200° (decomp.) (B.).

2:4-Dinitro-3:5-diphenylaminotoluene; similarly to the preceding dimethyl-compound using aniline (B.). Red crystals, m.p. 163°.

2:4:6-Trinitro-3:5-dimethylaminotoluene; red crystals, m.p. 156°. On treatment with nitric acid (1:52) it yields 2:4:6-trinitrodimethylnitroaminotoluene.

2:4:6-Trinitro-3:5-diphenylaminotoluene; red crystals, m.p. 156°.

4-Chloro-3:5-toluylenediamine 1-sulphonic acid; by reducing 3:5-dinitro-4-chlorobenzyl-sulphonic acid with iron and acetic acid (B. A. S. F., D. R. P. 134988 of 1901). White needles. An aqueous solution on treatment with ferric chloride gives a red colour which gradually changes through violet to blue.

6-Aminodiacyl-3:4-toluylenediamine; by nitration and reduction of diacyl-3:4-toluylenediamine (Maron and Salzberg, Ber. 1911, 44, 2999). M.p. 238°.

Triacyl-derivative; m.p. 273°–274° (M. and S.).

5-Aminodiacyl-2:4-toluylenediamine; by nitration and reduction of diacyl-2:4-toluylenediamine (Maron and Salzberg, l.c.; Kym and Ringer, *ibid.* 1915, 48, 1671). M.p. 252°–253°.

Triacyl-derivative (M. and S.; K. and R.)

2-Acetyl-amino-3:5-toluylenediamine; from 3:5-dinitroaceto-*o*-toluidide and reducing agents, such as iron and acetic acid or mineral acids (Bayer & Co., U.S. Pat. 742845 of 1903; D. R. P. 183843 of 1902). Yellow needles, m.p. 210°–211°.

Triaminotoluene; by reducing trinitrotoluene with iron and dilute hydrochloric acid at 60°–80°. It serves as an intermediate product, as a dye for cotton, silk and wool, and as a photographic developer (Bielouss, Eng. Pats. 137529, 166934 of 1920).

ALDEHYDE DERIVATIVES.

Tolualdehydes are obtained from *o*-, *m*-, and *p*-xylene by passing the vapour mixed with air over a metallic oxide, other than vanadium oxide, of the fifth or sixth periodic group at 300° to a dull red heat, the period of contact being about 0.3 second (The Barrett Co., Eng. Pat. 189107).

***o*-Tolualdehyde, *o*-toluic aldehyde**; by boiling *o*-chloro-*o*-xylene with lead nitrate solution (Lauth and Grimaux, Bull. Soc. chim. 1867, (2) 7, 233; Rayman, *ibid.* 1877, (2) 27, 498); by oxidation of *o*-xylene with chromyl chloride (Bornemann, Ber. 1884, 17, 1467), or with manganese dioxide and sulphuric acid (Fournier, Compt. rend. 1901, 133, 635), or of *o*-tolylcarbinol with potassium dichromate and sulphuric acid (Fournier, *ibid.* 1903, 137, 716). Liquid, b.p. 90°/20 mm., or 197°/atm. (F.). **Anti-oxime**, m.p. 48°–49°, obtained in the usual manner (Dollfus, Ber. 1892, 25, 1922) or together with *p*-tolualdoxime and the nitrile by treating toluene with mercury fulminate and aluminium chloride containing small quantities of the hydrated chloride and aluminium hydroxide. The oximes are primarily obtained in the syn-form, but on separating from the nitrile, alkalis are used and the anti-forms are produced (Scholl and Kačer, Ber. 1903, 36, 322); **semicarbazone**, small white needles, m.p. 196° (Law and Perkin, Trans. Faraday. Soc. 1904, 1) or 200° (Fournier); **phenylbenzylhydrazone**, m.p. 57° (Fournier); **diphenylhydrazone**, white needles, m.p. 103°–104° (Maurenbrecher, Ber. 1906, 39, 3583; Rorive and Tollens, *ibid.* 1907, 40, 3107); **5-dimethylamino-derivative**, from dimethyl-*m*-toluidine and formaldehyde, leaflets, m.p. 67° (Geigy & Co., D. R. P. 105103 of 1898).

***p*-Chloro-*o*-tolualdehyde**; by chlorinating 4-keto-1-methyl-1-dichloromethylidihydrobenzene

with phosphorus pentachloride and heating the crude product with water at 160°–180° (Auwers and Keil, Ber. 1905, 38, 1693). Oil, b.p. 228°, solidifying to colourless crystals; D_{17}^{20} 1.277.

Semicarbazone; colourless needles, m.p. 224° (A. and K.).

***m*-Tolualdehyde**; by boiling *o*-chloro-*m*-xylene with lead nitrate solution (Gundelach, Bull. Soc. chim. 1876, (2) 26, 44; Müller, Ber. 1887, 20, 1213; cf. Lauth and Grimaux, l.c.); by treating *m*-xylene with chromyl chloride (Étard, Ber. 1881, 14, 848; Ann. Chim. 1881, (5) 22, 218; Bornemann, Ber. 1884, 17, 1464); together with 3:3'-dimethyldibenzyl by oxidising *m*-xylene with potassium persulphate (Moritz and Wolfenstein, Ber. 1899, 32, 2533); by oxidising *m*-xylyl alcohol with potassium dichromate and dilute sulphuric acid (Sommer, Ber. 1900, 33, 1078). Liquid, with an almond odour, b.p. 199°; D_0^{20} 1.037; D_{20}^{20} 1.024. It forms an **anilide**, b.p. 313°–314°; **semicarbazone**, needles, m.p. 216° (Sommer); **phenylhydrazone**, prisms, m.p. 91° (B.) or 88° (Rudolph, Ann. 1888, 248, 100); **diphenylhydrazone**, light yellow plates, m.p. 74°–75° (Maurenbrecher; Rorive and Tollens). For condensation products with ammonia and ethyl cyanoacetate, see Guareschi (Atti R. Accad. Sci. Torino, 1901–02, 37, 593).

2-Nitro-*m*-tolualdehyde; together with the 4-nitro-isomeride by nitrating *m*-tolualdehyde (Mayer, Ber. 1914, 47, 406; cf. Gilliard, Monnet and Cartier, Eng. Pat. 25634 of 1898; U.S. Pats. 662074, 662075; D. R. P. 113604 of 1898). The isomerides are separated by fractionation *in vacuo*. The product obtained by Bornemann (Ber. 1884, 17, 1473) and M. L. B. (Eng. Pat. 3216 of 1882; U.S. Pats. 276889, 276890; Fr. Pat. 149935; D. R. P. 21683 of 1882) is a mixture of the isomerides. Crystals, m.p. 64° (G., M. and C.; M.) or 61° (Reissert and Scherk, Ber. 1898, 31, 392); b.p. 135°–145°/2 mm. With acetone it yields the greenish-blue dimethylindigotin. **Ammonia-derivative**, m.p. 93°; **anilide**, m.p. 79°; **oxime**, m.p. 134°–135°; **phenylhydrazone**, m.p. 131°–132°; **hydrobenzamide**, m.p. 93°.

4-Nitro-*m*-tolualdehyde (see above). Yellow needles, m.p. 44°. With acetone it yields the reddish-blue dimethyl-indigotin. **Ammonia-derivative**; m.p. 140°; **anilide**, m.p. 51°–5°; **oxime**, m.p. 104°–105°; **phenylhydrazone**, m.p. 141°–142°; **hydrobenzamide**, m.p. 140° (G., M. and C.).

Dinitro-*m*-tolualdehyde; long silky needles, m.p. 110°–112° (Bornemann).

2-Iodo-*m*-tolualdehyde; m.p. 55°–56° (Mayer, Ber. 1914, 47, 406).

4-Iodo-*m*-tolualdehyde; m.p. 83°–84° (M.).

6-Amino-*m*-tolualdehyde; by heating 4-nitro-*m*-xylene with a solution of sulphur in sodium hydroxide (Geigy & Co., D. R. P. 87255 of 1895; see also Böhringer, D. R. P. 108026 of 1898). Sinters above 90° and melts at 99°–101° (B.) or 92° (G.).

4-Chloro-derivative; yellow crystals, m.p. 153° (Geigy & Co., D. R. P. 105103 of 1898).

6-Methylamino-*m*-tolualdehyde; colourless leaflets or needles, m.p. 114° (Geigy & Co., Fr. Pat. 280514; D. R. P. 103578 of 1898); **4-chloro-derivative**, yellowish needles, m.p. 157° (Geigy & Co., D. R. P. 105103 of 1898); the

p-dimethylaminoanilide, yellowish-green prisms, melts at 162°, and the phenylhydrazone at 124° (Ullmann and Frey, Ber. 1904, 37, 863).

6-Ethylamino-*m*-tolualdehyde, needles or pale yellow prisms, m.p. 70°; 4-chloro-derivative, yellowish needles, m.p. 78°–79° (Geigy & Co.); oxime, m.p. 82°; phenylhydrazone, m.p. 95° (U. and F.; G.).

m-Tolualdehyde *o*-sulphonic acid; by sulphonation of *m*-tolualdehyde at low temperatures. With aromatic amines it yields dyes fast to alkalis (Fr. Pat. 311739 of 1901).

p-Tolualdehyde; by heating a mixture of calcium *p*-toluate and calcium formate (Cannizzaro, Ann. 1862, 124, 254); by oxidising *p*-xylene with chromyl chloride (Bornemann, Ber. 1884, 17, 1467); by the action of hydrocyanic acid and hydrochloric acid on toluene in presence of aluminium chloride (Bayer & Co., Eng. Pat. 19204 of 1897; Fr. Pat. 270334; D. R. P. 99568 of 1897); by passing a mixture of carbon monoxide and hydrogen chloride through toluene in presence of aluminium chloride and cuprous chloride (Gattermann and Kock, Ber. 1897, 30, 1623; Bayer & Co., Eng. Pat. 13709 of 1897; Fr. Pat. 268168; D. R. P. 98706 of 1897; cf. Reformatzki, J. Russ. Phys. Chem. Soc. 1901, 33, 157); by the action of boiling dilute sulphuric acid on *p*-methylbenzylazoisimide (Curtius and Darapsky, Ber. 1902, 35, 3229); together with a little *p*-toluic acid by electrolytic oxidation of a warm solution of *p*-xylene with an excess of current at a lead peroxide anode (Fichter and Grisard, Helv. Chim. Acta. 1921, 4, 928); by heating *p*-tolylglyoxylic acid with aniline and hydrolysing the product (Bouveault, Bull. Soc. chim. 1897, (3) 17, 367); by the action of nickel carbonyl on toluene in presence of aluminium chloride (Dewar and Jones, Chem. Soc. Trans. 1904, 85, 212) and by other methods (Fournier, Compt. rend. 1903, 136, 557; Bodroux, Compt. rend. 1904, 138, 92; Bull. Soc. chim. 1904, (3) 31, 586). Oil with a peppery odour, b.p. 204° (G.); D_{20}^{25} 1.072; n_D^{25} 1.5484 (Hanzlik and Bianchi, Ber. 1899, 32, 1286).

p-Tolualdehyde ammonia; m.p. 43°–44° (Francis, Ber. 1909, 42, 2216); hydro-*p*-toluamide, white needles, m.p. 92° (Gattermann, Ann. 1906, 347, 347); bisulphite-compound, scales; semicarbazone, m.p. 215° (Fournier); diacetate, colourless glistening leaflets, m.p. 69°, forming a leuco-malachite Green with dimethyl-aniline and zinc chloride (Claussner, Ber. 1905, 38, 2860); phenylhydrazone, yellow compound, m.p. 113°, coloured red by exposure to light (Law and Perkin, Trans. Faraday Soc. 1904, 1); phenylbenzylhydrazone, m.p. 140° (Fournier, Compt. rend. 1903, 137, 716); diphenylhydrazone, white needles, m.p. 83°–84° (Maurenbrocher, l.c.; Rorive and Tollens, l.c.); anti-oxime, m.p. 79°–80°; syn-oxime, m.p. 108°–110° (Hantzsch, Zeitsch. physikal. Chem. 1904, 13, 523); dioxime peroxide, white shining plates, decomposing with a slight explosion at 121° (Ponzo, Atti R. Accad. Lincei, 1906, [v.] 15, ii. 42, 118; Techugaeff and Spiro, Ber. 1908, 41, 2219); nitroso-derivative, silvery needles, m.p. 128° (Gattermann, l.c.).

p-Tolualdehyde when exposed to light in presence of iodine for 3 years yields *p*-

toluic acid, a trimeric tolualdehyde, thin colourless prismatic crystals, m.p. 215°, and *p*-tolyl *p*-toluate, pale yellow oil, b.p. 213°–217°/15 mm. (Muscarelli and Russi, Atti R. Accad. Lincei, 1910, [v.] 19, ii. 239). With ethyl iodide and magnesium it yields *p*-tolylethylcarbinol, a dimeride of *p*-tolualdehyde, m.p. 130°, and *p*-xylyl alcohol (Oddo, Gazz. chim. ital. 1911, 41, i. 273).

2-Nitro-*p*-tolualdehyde; by nitration of *p*-tolualdehyde with mixed acids below 0° (Hanzlik and Bianchi, Ber. 1899, 32, 1288). Needles, m.p. 43°–44° (H. and B.) or 48°–49° (Gattermann, Ann. 1906, 347, 347). Diacetate, monoclinic tables, m.p. 98°–98.5° (Hanzlik and Bianchi, l.c., 2286); phenylhydrazone, orange crystals, m.p. 112°; *p*-nitrophenylhydrazone, reddish-brown crystalline powder, m.p. 223°–224° (H. and B.).

3-Nitro-*p*-tolualdoxime; needles, m.p. 128° (M. L. B., Fr. Pat. 290643 of 1899; D. R. P. 107095 of 1898).

CARBOXYLIC ACID DERIVATIVES.

o-Toluic acid; by boiling *o*-xylene with dilute nitric acid (1 vol. D 1.4 to 2 vols. water) (Fittig and Bieber, Ann. 1870, 156, 242); by the action of sodium amalgam on a mixture of ethylchloroformate and *o*-iodotoluene, followed by hydrolysis of the ester formed (Kekulé, Ber. 1874, 7, 1007); in a yield of 97 p.c. by boiling phthalide (phthalic aldehyde) with hydriodic acid (b.p. 127°) and yellow phosphorus in an atmosphere of carbon dioxide (Hessert, Ber. 1878, 11, 238; Racine, Ann. 1887, 239, 72); from toluene *o*-sulphonic acid by heating with potassium cyanide and hydrolysing the product (Fittig and Ramsay, Ann. 1873, 168, 246; Zeit. f. Chem. 1871, (2) 7, 584); by boiling the nitrile (Weith, Ber. 1874, 7, 722); from *o*-toluidine via the nitrile (Cahn, Ann. 1887, 240, 280); by heating naphthalene 1 : 3-disulphonic acid, 1 : 3-dihydroxynaphthalene, α -naphthol or α -naphthylamine 3-sulphonic acid, β -naphthol- or β -naphthylamine 4-sulphonic acid with sodium hydroxide at 150°–300° (Kalle & Co., Eng. Pat. 16559 of 1894; Fr. Pat. 241109; D. R. P. 79028 of 1893; Friedländer and Rüdte, Ber. 1896, 29, 1611). Crystals, readily volatile with steam, m.p. 103.5°–104° (Kellaa, Zeitsch. physikal. Chem. 1897, 24, 221); b.p. 258.5°–259°/751 mm. (Serkow, J. Russ. Phys. Chem. Soc. 1893, 25, 633); D_{20}^{25} 1.0621; molecular refractive power 62 (Eykman, Rec. trav. chim. 1893, 12, 178). Oxidised to phthalic acid with permanganate or dilute nitric acid, whilst it is charred by chromic acid mixture. Bromine vapour above 100° yields phthalide, whilst in the cold bromine forms bromo-*o*-toluic acid, m.p. 167°. It condenses with tertiary aromatic amines to form dyestuffs of the Malachite Green series (Bayer & Co., D. R. P. 101426 of 1897). $\text{NaA} + 2\text{H}_2\text{O}$, glistening leaflets, m.p. 227°–228° (R.); $\text{CaA} + 2\text{H}_2\text{O}$, small needles (F. and B.); $\text{BaA} + 2\text{H}_2\text{O}$, small needles (F. and B.).

Hydroxylamine salt, m.p. 105° (Oesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 3424).

Methyl-ester, b.p. 207°–208° (Kellaa, Zeitsch. physikal. Chem. 1897, 24, 245) or 213°; D_{20}^{25}

1-073 (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

Ethyl-ester; b.p. 219.5°/713 mm. (Ador and Rilliet, Ber. 1879, 12, 2301) or 227°; D_4^{25} 1-0479, D_{15}^{15} 1-039, D_{25}^{25} 1-0321; magnetic rotatory power 15-064 at 15.2° (Perkin, Chem. Soc. Trans. 1896, 69, 1238).

Benzyl-ester; oil, b.p. 315°, D_{17}^{17} 1-12 (Hodgkinson, Chem. Soc. Proc. 1891, 7, 167).

Chloride; b.p. 211°/733 mm. (A. and R.), 110°-111°/29 mm. (Klages and Lickroth, Ber. 1899, 32, 1861), 102°/7 mm. (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1311; cf. Frankland and Aston, *ibid.* 1899, 75, 494).

Anhydride; m.p. 36°-38° (Racine, Ann. 1887, 239, 74) or 39° (K. & L.), b.p. above 325° (R.) or 220°-221°/11 mm. (K. and L.).

Peroxide; irregular prisms, m.p. 60° (Vanino and Thiele, Ber. 1896, 29, 1727).

Amide; needles, m.p. 138° (Weith, Ber. 1873, 6, 420), 142.8° (Remsen and Reid, Amer. Chem. J. 1899, 21, 290). *Sodium-derivative* (Wheeler, *ibid.* 1900, 23, 466).

Methylamide; colourless needles, m.p. 75°; *dimethylamide*, b.p. 147°, D_{25}^{25} 1-033 (van S.).

Nitrile; by heating potassium toluene *o*-sulphonate or tri-*o*-tolyl phosphate with potassium cyanide (Heim, Ber. 1883, 16, 1776); by heating tolyl isothiocyanate with copper powder (Weith, Ber. 1873, 6, 419); by the action of heat on tolyl isocyanide (Weith, Ber. 1874, 7, 722); by heating *o*-iodotoluene with silver cyanide at 350° (Merz and Weith, Ber. 1877, 10, 751); by boiling the formyl-derivative of *o*-toluidine with zinc dust (Gasirowski and Merz, Ber. 1884, 17, 74; 1885, 18, 1004); from *o*-toluidine by Sandmeyer's reaction (Cahn, Ber. 1886, 19, 756); by the action of mercury fulminate on toluene in presence of aluminium chloride (Scholl, Ber. 1903, 36, 10). Liquid, b.p. 203°-204° (W.), or 205.2°; D_4^{25} 1-0061, D_{15}^{15} 0-9975, D_{25}^{25} 0-9912; magnetic rotatory power 12-98 at 15.7° (Perkin, Chem. Soc. Trans. 1896, 69, 1244). On boiling with alcoholic potassium hydroxide it yields the amine and with concentrated hydrochloric acid at 200° it yields *o*-toluic acid. In a well-cooled solution *o*-toluonitrile is converted at a lead peroxide anode into *o*-cyanobenzoic acid. If the cooling is not efficient the nitrile is hydrolysed to *o*-toluic acid which is oxidised to phthalic acid (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). Fuming sulphuric acid at 60°-70° forms *iminodi-o-toluidamide*, prisms, m.p. 103° (Krafft and Karstens, Ber. 1892, 25, 455). Concentrated hydriodic acid yields $C_7H_7CN_2HI$, lemon-yellow crystals, m.p. 135°-140° (decomp.) (Biltz, Ber. 1892, 25, 2540). $(CH_3)_2C_6H_4(CN)(Cu_2Cl_2)$, white crystals (Rabaut, Bull. Soc. chim. 1898, (3) 19, 787).

Isocyanide; liquid, b.p. 75°/10 mm., 101°/55 mm., 183°-184°/753 mm. (with slight decomp.); D_{24}^{24} 0-968. At 240° it is converted into the nitrile (Nef, Ann. 1892, 270, 309).

3-Chloro-o-toluic acid; by careful addition of sodium nitrite in excess to a hot solution of the amide (Kenner and Witham, Chem. Soc. Trans. 1921, 149, 1458). Long slender needles, m.p. 102°.

Nitrile; from 2-cyano-*m*-toluidine by the

Sandmeyer reaction. Long slender prisms, m.p. 82°-83°, b.p. 143°/38 mm.

Amide; by heating a solution of the nitrile with diluted sulphuric acid at 100°-110° for 1½ hours. Scales, m.p. 167° (K. and W.).

4-Chloro-o-toluic acid; together with 5-chloro-*o*-toluic acid by boiling the corresponding chloroxylylene with nitric acid (D 1-2) (Krüger, Ber. 1885, 18, 1757); together with the 5-acid by passing chlorine through a solution of *o*-toluic acid in glacial acetic acid (Claus and Bayer, Ann. 1893, 274, 308). M.p. 137° (C. and B.), and not 166° as given by Krüger. Its salts are more sparingly soluble than those of the 5-chloro-isomeride. $CaA_2 + 2H_2O$, prisms.

5-Chloro-o-toluic acid; see 4-chloro-*o*-toluic acid. The nitrile is obtained from 5-chloro-*o*-toluidine by the Sandmeyer reaction (Claus and Stapelberg, Ann. 1893, 274, 287). Small needles m.p. 170° (C. and B.), not 130° as given by Krüger. $KA + H_2O$, needles; $CaA_2 + 3H_2O$, needles; $BaA_2 + 4H_2O$, needles.

Ethyl-ester; oil, b.p. 258° (C. and S.).

Nitrile; long needles, m.p. 67° (C. and S.).

Amide; m.p. 183° (C. and S.).

6-Chloro-o-toluic acid; by boiling 3-chloro-*o*-xylene with dilute nitric acid (Krüger, Ber. 1885, 18, 1758). Needles, m.p. 154° (Kr.) or 156° (Claus and Bayer). Oxidation with potassium permanganate yields 3-chlorophthalic acid. $CaA_2 + 2H_2O$, long prisms.

3:5-Dichloro-o-toluic acid; from the nitrile which is prepared from 3:5-dichloro-*o*-toluidine by the Sandmeyer reaction (Claus and Stapelberg, Ann. 1893, 274, 292). Glistening needles, m.p. 181°.

Nitrile; needles, m.p. 92° (C. and S.).

A *dichlorotoluic acid* was obtained by Holleman (Ann. 1867, 144, 269) by oxidising crude dichloroxylylene (m.p. 22°) with chromic acid mixture. $CaA_2 + 9H_2O$.

ω-Dichloro-o-toluic acid; needles, m.p. 155°. Its chloride is obtained by chlorinating *o*-toluoyl chloride. The *amide* melts at 117°.

ω-Trichloro-o-toluic acid; obtained by the action of formic acid at 50° on its chloride, which is formed by chlorinating *o*-toluoyl chloride, crystallises from benzene in needles, m.p. 141°-144° (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2213).

4-Bromo-o-toluic acid; by keeping *o*-toluic acid in contact with excess of bromine for 24 hours (Jacobsen and Wieras, Ber. 1883, 16, 1956; Racine, Ann. 1887, 239, 74); from 2-nitro-*p*-toluidine by replacing the amino- by bromine and the nitro-group by carb (von Meyer and Geiringer, Ber. 1895, 28, 11). Long needles, volatile with steam, m.p. 167° $CaA_2 + H_2O$; $BaA_2 + 5H_2O$.

Methyl-ester; leaflets, m.p. 44°-46° (R.).

A *bromo-o-toluic acid*, slender needles, m.p. 118°, whose *nitrile* melts at 42°, has been obtained by oxidising bromo-ethylxylylene with dilute nitric acid at 200° (Claus and Plescock, Ber. 1886, 19, 3083; Claus and Kunath, J. pr. Chem. 1889, (2) 39, 489). This acid is not identical with that of Jacobsen (Ber. 1884, 17, 2375), obtained by oxidising bromo-*o*-xylene with dilute nitric acid. Jacobsen's product forms stellate groups of silky needles, m.p. 174°-176°, yielding $BaA_2 + 2H_2O$, small hard prisms, and is probably identical with the following acid.

5-Bromo-o-toluic acid; by saponification of the nitrile (Nourrisson, Ber. 1887, 20, 1016). Sublimes in needles, m.p. 187° (N.) or 175° (Konowaloff, J. Russ. Phys. Chem. Soc. 1904, 36, 537). $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (C. and K.).

Amide; pearly plates subliming in needles, m.p. 181°–182°.

Nitrile; long needles, volatile with steam, m.p. 70° (N.).

3:5-Dibromo-o-toluic acid; by hydrolysis of the amide with concentrated hydrochloric acid at 250° (Claus and Beck, Ann. 1892, 269, 215). Needles, m.p. 157°. $\text{BaA}'_2 + \text{H}_2\text{O}$, crystalline crusts.

Amide; glistening needles or columns, m.p. 198°.

Nitrile; from 3:5-dibromo-o-toluidine by Sandmeyer's reaction. Glistening needles, m.p. 86° (C. and B.).

4:5-Dibromo-o-toluic acid; by heating 5-bromo-o-toluic acid with 1 mol. of bromine in the presence of water at 120° for 3 hours (Claus and Beck, Ann. 1892, 269, 213). Glistening needles, m.p. 210°. $\text{BaA}'_2 + 6\text{H}_2\text{O}$, glistening needles.

When nitrated at 0°, o-toluic acid yields a mixture of 4-nitro-o-toluic acid, m.p. 178°–178.5°, and 6-nitro-o-toluic acid, m.p. 184°–184.5°, the latter being probably identical with Jacobsen and Wierss' β -nitro-acid, m.p. 145°. The methyl-ester, amide, methylamide, and dimethylamide of o-toluic acid yield the corresponding derivatives of the 4- and 6-nitro-acids when nitrated at 0°. When nitrated at ordinary temperatures, o-toluic acid and its 4- and 6-mononitro-derivatives yield 4:6-dinitro-o-toluic acid. The methyl-ester under similar conditions yields methyl-4:6-dinitro-o-toluate, m.p. 73°–73.5°. The amide and methylamide yield the 4:6-dinitro-acid, but the dimethylamide yields the 4-nitro-acid (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

3-Nitro-o-toluic acid; from 3-nitro-o-toluidine via the nitrile (Mayer, J. pr. Chem. 1915, (2) 92, 137) or the amide (Gabriel and Thieme, Ber. 1919, 52, 1079). The latter authors could not prepare it by hydrolysis of the nitrile. Colourless needles, or short rods, m.p. 151°–152° (G. and T.), or colourless silky needles, m.p. between 200°–210° (M.). It sublimes, and it is stated to undergo certain physical changes when exposed to air for a few days, e.g. it becomes less soluble in water, and melts at about 180°–185° (M.).

$\text{NaA}' + 3\frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}'_2 + 3\text{H}_2\text{O}$ (G. and T.).

Amide; by the action of sulphuric acid on the nitrile. Needles, m.p. 158° (G. and T.).

Nitrile; from the amine by the Sandmeyer reaction and treatment of the crude product with alcohol or nitric acid. Silvery leaflets, m.p. 109°–110° (G. and T.), or yellow silky needles on subliming, m.p. 89°–91° (M.).

Methyl-ester; by the action of methyl sulphate. M.p. 72°–75° (M.), or from the acid chloride (m.p. 41°) by the action of methyl alcohol, when needles and leaflets, m.p. 50°, are formed (G. and T.). **Ethyl-ester**, oil (G. and T.).

Anhydride; six-sided plates, m.p. 174° (G. and T.).

(a)-4-Nitro-o-toluic acid; together with the nitro-acid by warming o-toluic acid with alic acid (D 1.4) at 100° (Jacobsen and Wierss,

Ber. 1883, 16, 1957); together with the 5-nitro-acid by oxidising 4-nitro-o-xylene with dilute nitric acid (Jacobsen, Ber. 1884, 17, 162). Small needles, slowly volatile with steam, m.p. 179°. $\text{KA}' + \text{H}_2\text{O}$, long needles; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, slender needles.

Nitrile; by nitration of o-toluenitrile, needles, m.p. 105°, subliming at 100° (Landsberger, Ber. 1898, 31, 2880).

Amide; by warming the nitrile for $\frac{1}{2}$ hour with six times its weight of concentrated sulphuric acid, fine needles, m.p. 173° (L.); **methylamide**, slender needles, m.p. 160°; **dimethylamide**, m.p. 105°–106° (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

Methyl-ester; oblong prisms, m.p. 69°.

Chloride; colourless needles, m.p. 59°–60° (van S.).

(\gamma)-5-Nitro-o-toluic acid; together with the 4-acid by boiling a mixture of 25 grms. of 4-nitro-o-xylene, 250 c.c. of nitric acid (D 1.4) and 500 c.c. of water for 48 hours. The mixture is converted into the barium salts, which are separated mechanically (Jacobsen, Ber. 1884, 17, 162); from 5-nitro-o-toluidine via the nitrile (Mayer, l.c.; Gabriel and Thieme, l.c.). It melts at 152°–153° (G. and T.). $\text{BaA}'_2 + 5\text{H}_2\text{O}$, long transparent flat prisms (J.).

Nitrile; colourless leaflets, m.p. 100° (G. and T.), or long yellow felted needles, which sublime, m.p. 113°–115° (M.).

(\beta)-6-Nitro-o-toluic acid; see the 4-nitro-acid, and van Scherpenzeel, l.c. Long needles, m.p. 145° (J. and W.), or 184°–184.5° (van S.). Slowly volatile with steam. $\text{CaA}'_2 + 2\text{H}_2\text{O}$, crusts; $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (J. and W.).

Methyl-ester; pale yellow needles, m.p. 66° (van S.).

Amide; colourless needles, m.p. 163°; **methylamide**, m.p. 131°–132°; **dimethylamide**, m.p. 69.5°–70° (van S.).

Chloride; m.p. 68°–68.5° (van S.).

Nitrile, m.p. 69.5° (Nölting, Ber. 1904, 37, 1025).

3:4-Dinitro-o-toluic acid; together with 3:4-dinitrophthalic acid by oxidising 3:4-dinitro-o-xylene with dilute nitric acid in a sealed tube (Warner, Chem. Soc. Proc. 1913, 29, 61). Stout colourless needles, m.p. 182°.

Ethyl-ester; colourless rectangular plates, m.p. 63° (W.).

4:6-Dinitro-o-toluic acid; together with 3:5-dinitrophthalic acid by oxidising 3:5-dinitro-o-xylene in a similar manner (Warner); by keeping 4- or 6-nitro-o-toluic acid with a mixture of equal volumes of sulphuric acid and fuming nitric acid for 24 hours (Jacobsen and Wierss). Very long brittle needles, m.p. 206°. With dilute nitric acid at 170° it yields 3:5-dinitrophthalic acid. $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (Racine, Ann. 1887, 239, 77).

Methyl-ester; needles, m.p. 73°–74° (R.).

3:4:6 (or 3:5:6)-Trinitro-o-toluic acid; by oxidising 3:4:6-trinitro-o-xylene with chromic acid (Giua, Gazz. chim. ital. 1922, 52, i. 183). White needles, m.p. 201°–202°. It gives a reddish-brown coloration with alkalis.

\omega-Chloro-5-nitro-o-toluic acid; amide; by warming the nitrile for 2 hours with concentrated sulphuric acid (Gabriel and Landsberger, Ber. 1898, 31, 2734). White felted needles, melting at 228° when heated rapidly. When heated

for some time at 110° it yields 5-nitro-pseudo-phthalimidine, needles, m.p. 158°.

Nitrile; by nitration of *o*-cyanobenzyl chloride (G. and L.).

Yellow crystals, m.p. 94°. When heated with acetic and hydrochloric acids at 140°–150° it yields 5-nitrophthalide.

5-Chloro-3-nitro-o-toluic acid; from 5-chloro-3-nitro-*o*-toluidine via the nitrile (Claus and Stapelberg, Ann. 1893, 274, 297). Glistening needles, m.p. 189°.

Nitrile; golden-yellow glistening prisms, m.p. 140° (C. and S.).

5-Chloro-4-nitro-o-toluic acid; together with 5-chloro-6-nitro-*o*-toluic acid, by treating 5-chloro-*o*-toluic acid with nitric acid (D 1-52) at 110°–120° (C. and S.). On pouring into water, the 6-nitro-acid gradually separates. Large glistening prisms, m.p. 193°. $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, prisms; $\text{MgA}'_2 + 4\text{H}_2\text{O}$, four-sided pillars. The salts are more sparingly soluble in water than those of the 6-nitro-isomeride.

Nitrile; from 5-chloro-4-nitro-*p*-toluidine. Thick glistening pillars, m.p. 86° (C. and S.).

5-Chloro-6-nitro-o-toluic acid; see above. Glistening pillars, m.p. 186°. $\text{KA}' + \text{H}_2\text{O}$, crusts; $\text{MgA}'_2 + 5\text{H}_2\text{O}$, glistening needles (C. and S.).

3:5-Dichloro-6-nitro-o-toluic acid; by oxidising 3:5-dichloro-6-nitro-*o*-xylene with nitric acid (D 1-15) for 6 hours at 180°–190° (Crossley, Chem. Soc. Trans. 1904, 85, 281). Feathery needles, m.p. 187°–189°.

5-Chloro-4:6-dinitro-o-toluic acid; by prolonged boiling of 5-chloro-*o*-toluic acid, 5-chloro-4-nitro-*o*-toluic acid, or 5-chloro-6-nitro-*o*-toluic acid with mixed acids (C. and S.). Needles, m.p. 212°.

5-Bromo-3-nitro-o-toluic acid; from the amide by heating with concentrated hydrochloric acid at 230°–250° for 8–10 hours (Claus and Beck, Ann. 1892, 269, 212). Fine needles, m.p. 226°.

Amide; by boiling the nitrile with 50 p.c. sulphuric acid. Vitreous needles, m.p. 235°.

Nitrile; from 5-bromo-3-nitro-*o*-toluidine by Sandmeyer's reaction. Glistening yellow needles, m.p. 106°–107°.

5-Bromo-4-nitro-o-toluic acid; together with 5-bromo-6-nitro-*o*-toluic acid, by nitrating 5-bromo-*o*-toluic acid for 6–8 hours at 50°. The greater part of the 5-bromo-4-nitro-*o*-toluic acid separates on cooling (C. and B.). Needles, m.p. 200°, which sublime. $\text{NaA}' + 4\text{H}_2\text{O}$, large pearly plates; $\text{KA}' + \text{H}_2\text{O}$, silky needles; $\text{MgA}'_2 + 7\text{H}_2\text{O}$, vitreous needles; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, long needles.

5-Bromo-6-nitro-o-toluic acid; see above. The two acids may be separated by means of their magnesium salts. Small needles, m.p. 220°, which sublime. The magnesium salt is extremely soluble in water. $\text{BaA}'_2 + \text{H}_2\text{O}$, nodules.

3-Amino-o-toluic acid; obtained as the hydrochloride, together with 3-methyl-benzisoxazole-3-one and *m*-toluidine hydrochloride, by reducing 3-nitro-*o*-toluamide with tin and hydrochloric acid, or as the free acid by reducing 3-nitro-*o*-toluic acid with ferrous sulphate in ammoniacal solution (Gabriel and Thieme, Ber. 1919, 52, 1079). Needles, m.p. 125°–126°. According to Mayer (J. pr. Chem. 1915, (2) 92, 137), reduction of the acid with tin and hydro-

chloric acid yields initially the amino-acid, but this could not be isolated, as it was converted into *m*-toluidine during evaporation.

Nitrile; by reducing 3-nitro-*o*-toluonitrile with hydriodic acid and phosphorus. It melts at 127°–128° (G. and T.).

4-Amino-o-toluic acid; small prisms, m.p. 196° (Jacobsen and Wiersma, Ber. 1883, 16, 1959; Jacobsen, *ibid.* 1884, 17, 164).

Nitrile; by reducing 4-nitrotoluonitrile. It melts at 88°, its hydrochloride at about 220°, and its picrate at 177°–179° (Landsberger, Ber. 1898, 31, 2881).

5-Amino-o-toluic acid; by reducing 5-nitro-*o*-toluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1884, 17, 164); by heating *p*-nitrophthalide with hydriodic acid and phosphorus at 205° (Hönig, Ber. 1885, 18, 3449). Needles which sublime, m.p. 153° (H.) or 165° (decomp.) (J.).

Nitrile; by reducing 5-nitro-*o*-toluonitrile with stannous chloride and hydrochloric acid. Rhombic crystals, m.p. 90° (G. and T.).

6-Amino-o-toluic acid; small vitreous needles, m.p. 191° (Jacobsen; Jacobsen and Wiersma).

Nitrile; silky needles, m.p. 95-5° (Nöling, Ber. 1904, 37, 1025).

m-Toluic acid; by reducing bromo-*m*-toluic acid (Ahrens, Zeit. f. Chem. 1869, (2) 5, 106; Richter, Ber. 1872, 5, 424; Böttger and Ramsay, Ann. 1873, 168, 255); by oxidising *m*-xylene with dilute nitric acid (Tawildarow, Ber. 1873, 4, 410; Brückner, Ber. 1876, 9, 406; Reuter, Ber. 1884, 17, 2028); by hydrolysing the nitrile (Weith and Landolt, Ber. 1875, 8, 720) or the 6-sulphonamide (Jacobsen, Ber. 1881, 14, 2349); by boiling ω -chloroxylene with dilute nitric acid (Senff, Ann. 1883, 220, 247; cf. Ador and Rilliet, Ber. 1879, 12, 2300; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149). Very long needles, volatile with steam, m.p. 110-5° (Jacobsen; Bornemann, Ber. 1887, 20, 1382) or 108°–109° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 221), b.p. 283° (J.); $D_4^{11} 6$ 1-0543; molecular refractive power 62-01 (Eykmann, Rec. trav. chim. 1893, 12, 178). $\text{CaA}'_2 + 3\text{H}_2\text{O}$, flat needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, small plates; AgA' ; $(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{HK}$, long needles; $(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{H}\cdot\text{NH}_4$, tabular crystals (Farmer, Chem. Soc. Trans. 1903, 83, 1443).

Hydroxylamine salt; m.p. 83° (Oesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 2424).

Methyl-ester; b.p. 214°–215° (Kellas) or b.p. 220-5°–221°/758 mm., $D_4^{15} 1-066$ (van S.).

Ethyl-ester; b.p. 224-5°–226-5°/710 mm. (Ador and Rilliet).

Chloride; b.p. 218°/724 mm. (A. and R.), 120°/38 mm. (Klages and Lückroth, Ber. 1899, 32, 1560), 109°/8 mm. (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1311), 109°/15 mm. (Frankland and Aston, *ibid.* 1899, 75, 494), 219°–220°/773 mm. (van S.); m.p. –23° (van S.); $D_4^{20} 1-173$ (K. and L.).

Amide, m.p. 94° (Remsen and Reid, Amer. Chem. J. 1899, 21, 290; van S.); *methylamide*, m.p. 44-5°–45° (van S.); *dimethylamide*, oil, b.p. 148°, $D_4^{15} 1-043$ (van S.).

Nitrile; from *m*-toluidine by the Sandmeyer

reaction (Buchka and Schachtebeck, Ber. 1889, 22, 841). Liquid, b.p. 206°–210° (B. and S.) or 212°–214° (Biltz, Ber. 1892, 25, 2539). See also Weith and Landolt (l.c.).

Meraptan; b.p. 195.4°/760 mm., D_4^{20} 1.06251 (Bourgeois, Rec. trav. chim. 1899, 18, 426).

Anhydride; m.p. 71°, b.p. 230°/17 mm. (Denham, Chem. Soc. Trans. 1909, 95, 1240).

Pseudo-m-toluic acid; m.p. 47° (Perkin and Simonis, *ibid.* 1907, 91, 840).

4-Chloro-m-toluic acid; by oxidising 3-acetyl-*p*-chlorotoluene (Claus, J. pr. Chem. 1892, (2) 46, 27). Needles, m.p. 167°.

5-Chloro-m-toluic acid; together with a chloronitroxylene and other products by boiling dihydro-5-chloroxylene with 30 p.c. nitric acid for 20 hours (Klages and Knoevenagel, Ber. 1895, 28, 2045). Needles, m.p. 178°. With potassium permanganate it yields 5-chloroisophthalic acid and a little 5-hydroxyisophthalic acid.

6-Chloro-m-toluic acid; by replacing the nitro-group by chlorine in 6-nitro-*m*-toluic acid (Beilstein and Kreusler, Ann. 1867, 144, 182; Remsen and Kuhara, Amer. Chem. J. 1881, 3, 431); by oxidising 4-chloro-*m*-xylene with chromic acid mixture (Vollrath, Ann. 1867, 144, 266; Bull. Soc. chim. 1867, (2) 7, 342; Jacobsen, Ber. 1885, 18, 1761). M.p. 203° (V.), 204° (corr.) (R. and K.), 210° (corr.) (J.). $\text{CaA}'_2 + 3\text{H}_2\text{O}$, fine needles; $\text{BaA}'_2 + 3\text{H}_2\text{O}$ (V.).

Ethyl-ester; b.p. 260°–265° (V.).

ω -Chloro-m-toluic acid; by boiling the nitrile with concentrated hydrochloric acid (Reinglass, Ber. 1881, 24, 2418). Fine needles, m.p. 135°.

Amide; m.p. 124°.

Nitrile; by chlorination of *m*-toluonitrile at 150°. Plates or prisms, m.p. 67°, b.p. 258°–260° (R.).

4:6-Dichloro-m-toluic acid; by heating 1 part of 4:6-dichloro-*m*-xylene with 15 parts of dilute nitric acid (D 1:18) (Claus and Burstert, J. pr. Chem. 1890, (2) 41, 557; cf. Hollemann, Ann. 1867, 144, 269). Vitreous needles, m.p. 170°. $\text{BaA}'_2 + 2\text{H}_2\text{O}$, needles or pillars. Hollemann's product melted at 101° and yielded $\text{CaA}'_2 + 9\text{H}_2\text{O}$ and AgA' .

ω -Dichloro-m-toluic acid; m.p. 132°, is formed from its chloride, m.p. 49°.

ω -Trichloro-m-toluic acid: obtained from its chloride, which is formed by chlorinating *m*-toluoyl chloride (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2214). Sparkling laminae, m.p. 142°.

4-Bromo-m-toluic acid; together with the 3-bromo-isomeride by keeping a mixture of *m*-toluic acid and an excess of bromine (Jacobsen, Ber. 1884, 14, 2351); by heating 4-bromoisoxylene with dilute nitric acid at 130°–135° (Kelbe and Czarnomski, Ann. 1886, 235, 295); from 4-bromo-2-nitro-toluene by heating with alcohol and potassium cyanide at 220°, and hydrolysing the nitrile with alcoholic potassium hydroxide (Richter, Ber. 1872, 5, 425); by oxidising 3-acetyl-4-bromotoluene with permanganate (Claus, J. pr. Chem. 1892, (2) 46, 21). slender needles, m.p. 152°–153° (K. and C.). Alkaline fusion yields 4-hydroxy-*m*-toluic acid, and oxidation yields 4-bromoisophthalic acid.

CaA'_2 , long needles (J.); $\text{BaA}'_2 + 4\text{H}_2\text{O}$, needles (C.).

6-Bromo-m-toluic acid; by oxidising bromo-*m*-xylene with chromic acid mixture (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 32; Jacobsen, Ber. 1881, 14, 2352); together with the 4-acid by brominating *m*-toluic acid (Jacobsen); by oxidising 6-bromoisoxylene with dilute nitric acid (Kelbe, Ber. 1882, 15, 41); from 6-nitro-*m*-toluic acid (Remsen and Kuhara, l.c.). Crystalline powder, m.p. 209° (Jacobsen). Sodium amalgam yields *m*-toluic acid, and alkaline fusion yields 6-hydroxy-*m*-toluic acid. $\text{CaA}'_2 + 3\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, long needles; AgA' .

Ethyl-ester; solidifies at –5°, b.p. 270°–275° (F., A. and M.).

Bromo-m(?) -toluic acid; together with 6-bromo-*m*-toluic acid by oxidising crude bromoxylene (b.p. 200°–208°) with chromic acid mixture (Ahrens, Zeit. f. Chem. 1869, (2) 5, 106), m.p. 185°–190°. $\text{CaA}'_2 + 8\text{H}_2\text{O}$, small needles, more soluble in water than the salt of 6-bromo-*m*-toluic acid.

Dibromo(?) -toluic acid; by oxidising crude dibromoxylene with chromic acid mixture (F., A. and M.). Microscopic needles, m.p. 185°–186°. $\text{BaA}'_2 + 9\text{H}_2\text{O}$, long needles; AgA' .

ω -Bromo-m-toluic acid; by brominating *m*-toluic acid in bromoform (Zalkind and Semenow, J. Russ. Phys. Chem. Soc. 1914, 46, 512). White crystals, m.p. 151°–152°.

Ethyl-ester; b.p. 160°–161°/10 mm.

4:6-Dibromo-m-toluic acid; by oxidising 4:6-dibromo-*m*-xylene with nitric acid (Eckert and Seidel, J. pr. Chem. 1921, (2) 102, 338). White crystals, m.p. 174°.

Methyl-ester; m.p. 43°, b.p. 203°–206°/758 mm.

Amide; white needles, m.p. 188°.

2-Nitroso-m-toluic acid; grey prisms, m.p. 172°–173° (Freundler, Bull. Soc. chim. 1911, [4] 9, 657).

2-Nitro-m-toluic acid; together with 4-nitro-*m*-toluic acid (Jacobsen, Ber. 1881, 14, 2347; Findekle, *ibid.* 1905, 38, 3553; Jürgens, *ibid.* 1907, 40, 4409; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; Wheeler and Hoffman, Amer. Chem. J. 1910, 44, 113, 507) and the 6-nitro-acid (Müller, Ber. 1909, 42, 430) when *m*-toluic acid is nitrated. The 2-nitro-acid is formed also by boiling 2-nitro-*m*-xylene with nitric acid (D 1:4) (Nölting and Gachot, Ber. 1906, 39, 73). Monoclinic prisms, m.p. 219° (Jacobsen; Findekle; Müller; Jürgens), 217.5°–218° (Nölting and Gachot).

The 2- and 4-nitrotoluic acids may be separated by means of their barium salts. $\text{BaA}'_2 + 2\text{H}_2\text{O}$. This acid is identical with one of the three acids which Ahrens (Zeit. f. Chem. 1867, (2) 3, 525; 1869, (2) 5, 106) obtained by the action of nitric acid on a mixture of toluic acids.

Amide; m.p. 192° (Jürgens).

Nitrile; needles, m.p. 84° (Gabriel and Thieme, Ber. 1919, 52, 1079; Jürgens; cf. Reissert and Scherk, Ber. 1898, 31, 390).

Methyl-ester; m.p. 74° (Jürgens).

4-Nitro-m-toluic acid; see 2-nitro-*m*-toluic acid. It melts at 182° (Jacobsen) or 134° (F.; M.). The barium salt is sparingly soluble (Jacobsen).

Amide; stout flat needles, m.p. 176°–177° (F.).

Methyl-ester; stout needles, m.p. 78°–79° (M.).

A number of derivatives of both 2- and 4-nitro-*m*-toluic acids have been prepared by van Scherpenzeel (Rec. trav. chim. 1901, 20, 149), but are of doubtful orientation.

5-Nitro-m-toluic acid; by warming an acetic acid solution of 5-nitro-*m*-xylene with potassium permanganate on the water-bath (Thöl, Ber. 1885, 18, 359) or by heating with nitric acid (D 1·16) in a sealed tube for 50 hours at 100° (Müller, *ibid.* 1909, 42, 430). Long silky needles, m.p. 170° (M.) or 167° (T.). $\text{BaA}_2 + 4\text{H}_2\text{O}$, groups of microscopic needles (T.).

Nitrile; m.p. 104°–105° (G. and T.).

Amide; small needles, m.p. 164°–165° (G. and T.).

Methyl-ester; tables, m.p. 84°–85° (M.).

6-Nitro-m-toluic acid; by oxidising crude nitroxylenes (Beilstein and Kreusler, Ann. 1867, 144, 168; Kreusler, Zeit. f. Chem. 1866, (2) 2, 320) or nitroisocymene (Kelbe, Ann. 1883, 221, 161); together with the 2- and 4-nitro-acids by nitrating *m*-toluic acid (Müller, *l.c.*).

Crystalline powder, m.p. 211° (B. and K.), 214° (K.), or pointed needles, m.p. 215°–216° (M.). $\text{NH}_4\text{A}' + 2\text{H}_2\text{O}$; $\text{MgA}'_2 + 7\text{H}_2\text{O}$; $\text{CaA}'_2 + 2\text{H}_2\text{O}$ yellow prisms; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, fine needles.

Nitrile; m.p. 80° (B. and K.; G. and T.).

Amide; leaflets, m.p. 151° (B. and K.), or prisms, m.p. 190° (Wheeler and Hoffman, Amer. Chem. J. 1910, 44, 113, 507).

Methyl-ester; m.p. 81°–82° (M.) or 72° (Herre, Ber. 1895, 28, 597).

2:4-Dinitro-m-toluic acid; m.p. 173°.

Methyl-ester, m.p. 104°–105° (van Scherpenzeel).

Bromonitro-m-toluic acid; by warming bromo-*m*-toluic acid with fuming nitric acid (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 347). Crystals, m.p. 175°–176°. $\text{CaA}'_2 + 3\text{H}_2\text{O}$, nodules; $\text{BaA}'_2 + 3\text{H}_2\text{O}$, long needles.

2-Amino-m-toluic acid; by reduction of the corresponding nitro-compound (Jacobsen; Findekle, Jürgens, *l.c.*). It melts at 172°.

Acetyl-derivative; glistening needles, m.p. 193°–194° (Miller and Meyer, Ber. 1891, 24, 1909).

Nitrile; m.p. 38° (Gabriel and Thieme).

Amide; m.p. 149° (Gabriel and Thieme; Jürgens).

Methyl-ester; oil with an odour of orange peel (Jürgens).

Ethyl-ester; large transparent prisms, m.p. 71°–72°.

Diethyl-ester; long slender needles, m.p. 55°–57° (Wheeler and Hoffman).

4-Amino-m-toluic acid; by reduction of the corresponding nitro-compound (Jacobsen; Findekle, *l.c.*). It melts at 132° (Jacobsen), 175° (Findekle), or 172° (P.). $\text{B}'\text{HCl}$, long needles (Panaotović, J. pr. Chem. 1886, (2) 33, 62).

Nitrile; glistening needles and plates, m.p. 60°–61° (Ehrlich, Ber. 1901, 34, 3366).

Amide; monoclinic prisms, m.p. 178° (P.) or 179° (F.).

Anilide; pearly rhombic tables, m.p. 240° (P.).

Acetyl-derivative; fibrous needles, m.p. 193°–194° (von Miller and Ohler, Ber. 1891, 24, 1910).

Methyl-ester, m.p. 62° (P.).

5-Amino-m-toluic acid; in a yield of 50 p.c. by reducing the corresponding nitro-compound with ferrous sulphate and ammonia (Müller, Ber. 1909, 42, 423). Small needles with a pink tint, m.p. 183° (M.).

Nitrile; needles, m.p. 75° (Gabriel and Thieme, Ber. 1919, 52, 1079).

6-Amino-m-toluic acid; by reducing 6-nitro-*m*-toluic acid with tin and hydrochloric acid (Beilstein and Kreusler, Ann. 1867, 144, 177; Kreusler, Zeit. f. Chem. 1866, (2) 2, 320) or with ferrous sulphate and ammonia (Müller). Long needles, m.p. 168°–169°. $\text{B}'\text{HCl}$; $\text{B}'\text{HNO}_2$; $\text{B}'_2\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$, long prisms.

Nitrile; long colourless needles, m.p. 95° (Gabriel and Thieme).

Amide; crystals $+\text{H}_2\text{O}$, which when anhydrous melt at 115° (B. and K.).

Methyl-ester; prisms, m.p. 115° (Herre, Ber. 1895, 28, 598).

Ethyl-ester; colourless needles, m.p. 79° (H.).

ω-Amino-m-toluic acid; by heating *m*-cyanobenzylphthalimide with concentrated hydrochloric acid at 200° (Reinglass, Ber. 1891, 24, 2419). Scales, m.p. 215°–218°. *Platinichloride*, ochre-yellow crystalline precipitate; *aurochloride*; yellow prisms, m.p. 175°–177° (R.).

When *m*-toluic acid is sulphonated a mixture of the 5- and 6-monosulphonic acids is formed, which could not be separated. On alkaline fusion, 5-hydroxy-*m*-toluic acid and 6-hydroxy-*m*-toluic acid respectively are formed (Jacobsen, Ber. 1881, 14, 2355).

p-Toluic acid; by oxidising *p*-xylene (Beilstein and Yessel, Ann. 1866, 137, 302; Kekulé and Dittmar, Ann. 1871, 162, 339; Brückner, Ann. 1880, 205, 113), cymene (Noad, Ann. 1847, 63, 289; Phil. Mag. 1848 (3) 32, 19), or terpenes (Hirzel, Zeit. f. Chem. 1866, (2) 2, 205) with dilute acid; by heating *p*-bromotoluene with ethylchloroformate and sodium amalgam followed by hydrolysis of the product (Wurtz, Compt. rend. 1869, 68, 1293); from *p*-bromotoluene, carbon dioxide and sodium (Kekulé, Ann. 1866, 137, 184); by reducing bromo-*p*-toluic acid with sodium amalgam (Remsen and Morse, Amer. Chem. J. 1880, 1, 138); from the acid chloride, obtained by the action of phosgene on toluene in presence of aluminium chloride (Ador and Crafts, Ber. 1877, 10, 2176); from the amide, obtained by the action of aluminium chloride on a mixture of toluene, carbon disulphide and chloroformamide (Gattermann and Schmidt, Ann. 1888, 244, 51; Ber. 1887, 20, 858); by heating a mixture of toluene and acetic acid at 110° in presence of zinc chloride and phosphorus oxychloride, and treatment of the product with dilute sodium hydroxide (Frey and Horowitz, J. pr. Chem. 1891, (2) 43, 114); together with benzoic acid by fusing tolylbenzoic acid with potassium hydroxide (Friedel and Crafts, Bull. Soc. chim. 1881, (2) 35, 508); by passing gaseous cyanic acid and hydrogen chloride into toluene at 100° in presence of aluminium chloride (Gattermann and Rossolym, Ber. 1890, 23, 1195); by heating dinitro-*p*-tolylmethane at about 130° (Ponzo, Atti R. Acad. Lincei, 1906, [v.] 15, ii, 42, 118).

Needles, m.p. 176°–177° (B. and Y.), 177°–

178° (A. and C.), or 180° (Fischli, Ber. 1879, 12, 615), b.p. 264° (Cannizzaro, Ann. 1862, 124, 254) or 274°-275° (F.), volatile with steam. When oxidised with chromic acid it yields terephthalic acid which is formed also when *p*-toluic acid is oxidised in presence of acetone and sulphuric acid at a lead peroxide anode (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). When treated with potassium persulphate it yields dibenzyl-4:4'-dicarboxylic acid (Fischer and Wolfenstein, Ber. 1904, 37, 3215). $\text{NH}_4\text{A}'$, plates (Lossen, Ann. 1897, 298, 72); KA' (B. and Y.); $\text{MgA}'_2 + 3\text{H}_2\text{O}$ (B. and Y.); $\text{CaA}'_2 + 3\text{H}_2\text{O}$, needles (B. and Y.); $\text{BaA}'_2 (\text{N.}) + 2\text{H}_2\text{O}$, fine needles (Buchka and Irish, Ber. 1887, 20, 1764); $\text{CuA}'_2 (\text{N.})$; $\text{AgA}'_2 (\text{N.})$; KHA'_2 , large laminæ (Farmer, Chem. Soc. Trans. 1903, 83, 1443); $\text{NH}_4\text{HA}'_2$, long needles (Farmer).

Hydroxylamine salt; m.p. 128° (Vesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 2424).

Methyl-ester; m.p. 32°; b.p. 217° (Fischli), or m.p. 34°-35° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 245).

Ethyl-ester; liquid, b.p. 228° (N.) or 235.5° (Perkin, Chem. Soc. Trans. 1896, 69, 1238) (D_4^{20} 1.0393; D_{15}^{15} 1.0306; D_{25}^{25} 1.024 (P.); magnetic rotatory power at 15° 14.74 (P.).

Chloride; liquid, b.p. 107°/8 mm. (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1311), 102° (or 108°)/15 mm. (Frankland and Aston, *ibid.* 1899, 75, 494), 224°-226°/720 mm. (Ador and Rilliet, Ber. 1879, 12, 2298), 214°-216° (Cahours, Ann. 1858, 108, 316), D 1.175 (C.).

Amide; m.p. 160.8° (Remsen and Reid, Amer. Chem. J. 1899, 21, 290), fine needles or large tables, m.p. 151° (Fischli), 156° (Gattermann and Schmidt, Ann. 1888, 244, 51; Ber. 1887, 20, 120), 158°-159° (Holleman, Rec. trav. chim. 1887, 6, 78; cf. Spica, Ber. 1878, 9, 82; Vollrath, Zeit. f. Chem. 1866, (2) 2, 489); *methylamide*, m.p. 143° (G. and S.), 144°-145.5° (Wheeler, and Atwater, Amer. Chem. J. 1900, 23, 146; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149); *dimethylamide*, m.p. 41°, b.p. 156°/10 mm. (van S.); *ethylamide*, m.p. 90° (G. and S.).

The methyl-ester, amide, and methylamide when nitrated at 0° yield derivatives of the 2-nitro-acid (van S.).

Anhydride; plates, m.p. 95° (Frankland and Wharton, Chem. Soc. Trans. 1899, 75, 344).

Nitrile; by distilling potassium toluene *p*-sulphonate with potassium cyanide (Merz, Zeit. f. Chem. 1868, (2) 4, 33); by heating tri-*p*-tolyl phosphate with potassium cyanide (Heim, Ber. 1883, 16, 1775); by heating *p*-tolyl isocyanate with copper (Weith, Ber. 1873, 6, 421); from *p*-toluidine by the Sandmeyer reaction (Glock, Ber. 1888, 21, 2650; Herb, Ann. 1890, 258, 9); by the action of mercury fulminate on toluene in presence of aluminium chloride (Scholl, Ber. 1903, 36, 10).

Crystals, m.p. 38° (Pinner and Caro, Ber. 1894, 27, 3275), b.p. 217.8° (Spica and Paternò, Ber. 1875, 8, 441; cf. Vollrath, Zeit. f. Chem. 1866, (2) 2, 489), or m.p. 29.5°, b.p. 215° (Kröber, Ber. 1890, 23, 1030), or b.p. 217.8°, D_{20}^{20} 0.9805, D_{25}^{25} 0.9751; magnetic rotatory power at 31° 12.84 (Perkin, Chem. Soc. Trans. 1896, 69,

1244). When reduced with sodium and alcohol a small quantity of *p*-methylbenzylamine is formed, but the greater part is saponified (Bamberger and Lodter, Ber. 1887, 20, 1710), and on hydrogenation with hydrogen at 250° in presence of reduced nickel it yields *p*-methylbenzylamine and di-*p*-methylbenzylamine (Frebault, Compt. rend. 1905, 140, 1036; cf. Sabatier and Senderens, *l.c.* 482). On oxidation at a lead peroxide anode it readily yields *p*-cyanobenzoic acid (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). For its polymeride, see Glock (*l.c.*) and Piepes-Poratyński (Bull. Acad. Sci. Cracow, 1900. Cf. Chem. Soc. Absts. 1900, 78, 648).

Isocyanide; m.p. 21°, b.p. 99°/32 mm., D_{24}^{24} 0.96 (Nef, Ann. 1892, 270, 320; Smith, Amer. Chem. J. 1894, 16, 374).

Mercaptan; b.p. 195°/760 mm. (Bourgeois, Rec. trav. chim. 1899, 18, 426).

2-Chloro-p-toluic acid; by oxidising 2-chlorocymene with dilute nitric acid (Fleischer and Kekulé, Ber. 1873, 6, 1090; Gerichten, *ibid.* 1877, 10, 1249). Large plates, m.p. 194°-196° (199°-201° corr.) (Gerichten, *ibid.* 1878, 11, 366). $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, columns (Claus and Böcker, Ann. 1891, 265, 363); $\text{CaA}'_2 + 3\text{H}_2\text{O}$, nodules; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, needles (G.).

Nitrile; from 2-chloro-*p*-toluidine by the Sandmeyer reaction, small pillars or needles, m.p. 48°-48.5° (Claus and Davidsen, J. pr. Chem. 1889, (2) 39, 498).

Amide; glistening plates (C. and D.).

Ethyl-ester; b.p. 149°-150° (C. and D.).

3-Chloro-p-toluic acid; together with other acids by boiling 1 part of 3-chlorocymene with 15 parts of nitric acid (D 1.24-1.29) (Fleti and Crosa, Gazz. chim. ital. 1886, 16, 290). Needles, m.p. 155°-155.5°.

Salts, see Claus and Davidsen (*l.c.*). $\text{NaA}' + \text{H}_2\text{O}$ crusts; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, prisms; $\text{BaA}'_2 + 5\text{H}_2\text{O}$, prismatic needles; AgA' , silvery plates.

Nitrile; leaflets or flat needles, which sublime, m.p. 61°-62° (C. and D.).

Amide; glistening prismatic needles, m.p. 182° (C. and D.).

ω -Chloro-p-toluic acid; from the nitrile, obtained by passing chlorine into nearly-boiling *p*-toluonitrile, by hydrolysis with 25 parts of boiling hydrochloric acid for 1½ hours (Mellinghoff, Ber. 1889, 22, 3208); from *ω -chloro-p-toluoil chloride* by dissolving in 98 p.c. sulphuric acid and maintaining at 0°-5° until the evolution of hydrogen chloride ceases (B. A. S. F., D. R. P. 239311 of 1910). Silky microscopic needles or pillars, m.p. 199° (M.) or 190°-192° (B. A. S. F.).

Amide; thin plates, m.p. 173° (M.). *Nitrile*, rhombic prisms, m.p. 79.5°, b.p. 263° (Fock, Ber. 1889, 22, 3208).

Ethyl-ester; b.p. 260°-280° (Einhorn and Papastavros, Ann. 1900, 310, 205).

2:5-Dichloro-p-toluic acid; from 5-chloro-2-amino-*p*-toluic acid by the diazo-reaction (Claus and Davidsen, Ann. 1891, 265, 346) or from 3-chloro-6-nitro-*p*-toluic acid (Claus and Böcker, *l.c.* 359). Flat needles, m.p. 187°. $\text{BaA}'_2 + 4\text{H}_2\text{O}$, small needles.

2:6-Dichloro-p-toluic acid; from 6-chloro-2-nitro-*p*-toluic acid or 2:6-diamino-*p*-toluic acid (Claus and Böcker; Claus and Beynen,

Ann. 1891, 266, 239). Leaflets, m.p. 186°-188°. $\text{BaA}'_2 + 4\text{H}_2\text{O}$, small needles.

o-Dichloro-*p*-toluic acid, m.p. 151°-158°, has a chloride, m.p. 45°, and an ethyl ester, m.p. 46° (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2212).

o-Trichloro-*p*-toluic acid; prepared from its chloride, which is obtained by chlorinating *p*-toluoyl chloride (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2214). Minute plates, m.p. 197°.

Tetrachloro-*p*-toluic acid; by oxidising tetrachloro-*p*-xylene with nitric acid and potassium permanganate (Rupp, Ber. 1896, 29, 1628). Needles, m.p. 212°.

2-Bromo-*p*-toluic acid; by oxidising 2-bromocymene (Landolph, Ber. 1872, 5, 268), 2-bromo-*p*-xylene (Jannasch and Dieckmann, Ann. 1874, 171, 83), or bromo-*p*-ethyltoluene (Morse and Remsen, Ber. 1888, 11, 225) with chromic acid mixture; by keeping a mixture of *p*-toluic acid and excess of bromine for 12 hours in the cold (Brückner, Ber. 1876, 9, 407); from 2-bromo-*p*-toluidine via the nitrile Claus and Kunath, J. pr. Chem. 1889, (2) 31, 487). Thin needles or laminae, m.p. 203.5°-204°. $\text{CaA}'_2 + 3\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, hair-like needles.

Nitrile; small needles, m.p. 44° (C. and K.).

3-Bromo-*p*-toluic acid; from 3-bromo-*p*-toluidine via the nitrile (C. and K.). Needles, m.p. 140° (C. and K.) or leaflets, m.p. 196°; by oxidation of bromocymene, obtained by the hydrolysis of β -bromocymene sulphonic acid (Kelbe and Koschnitzky, Ber. 1886, 19, 1731). $\text{NaA}' + 3\text{H}_2\text{O}$, needles; $\text{KA}' + 4\text{H}_2\text{O}$, nodules; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 6\text{H}_2\text{O}$, small leaflets.

Chloride; needles, m.p. 120° (C. and K.).

Nitrile; needles, m.p. 47° (C. and K.).

Amide; sublimes in needles, m.p. 137 (C. and K.).

o-Bromo-*p*-toluic acid; by the action of bromine on a bromoform solution of *p*-toluic acid (Zalkind, J. Russ. Phys. Chem. Soc. 1914, 46, 508). Plates with a vitreous lustre, m.p. 223° (Z.).

Nitrile; by bromination of *p*-toluonitrile at 200°. Prisms with a pungent odour, m.p. 115°-116° (Banse, Ber. 1894, 27, 2169).

Methyl-ester; vitreous needles, m.p. 53°-53.5°, b.p. 160°-161°/17 mm. (Z.).

2:3-Dibromo-*p*-toluic acid; from 3-bromo-2-nitro-*p*-toluic acid (Claus and Herbabny, Ann. 1891, 265, 375). Needles, m.p. 194°(?).

2:5-Dibromo-*p*-toluic acid; by oxidising 6-dibromo-*p*-xylene with chromic acid in presence of acetic acid (Schultz, Ber. 1885, 18, 1762); from 5-bromo-2-amino-*p*-toluic acid (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 308). Needles m.p. 195° (S.), 200°-201° (F. and C.).

$\text{NaA}' + 7\frac{1}{2}\text{H}_2\text{O}$, large tables (C. and H.); $\text{CaA}'_2 + 4\text{H}_2\text{O}$, long needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, long thin needles.

Ethyl-ester; long needles, m.p. 49°, b.p. about 310° (S.).

Chloride; needles, m.p. 60° (Claus and Herbabny).

2:6-Dibromo-*p*-toluic acid; from 2:6-dibromo-*p*-toluidine via the nitrile (Claus and Seibert, Ann. 1891, 265, 378). Silky needles, m.p. 235°-236°. $\text{NaA}' + \text{H}_2\text{O}$, fine needles; $\text{KA}' + 1\frac{1}{2}\text{H}_2\text{O}$, silvery needles.

Nitrile; large glistening needles, m.p. 49° (C. and H.).

Amide; small needles, m.p. 117° (C. and S.).

Chloride; needles, m.p. 86° (C. and S.).

Ethyl-ester; vitreous needles, m.p. 79°-80° (C. and S.).

3:5-Dibromo-*p*-toluic acid; from 3:5-dibromo-*p*-toluidine via the nitrile (Claus and Herbabny, Ann. 1891, 265, 378). Needles, m.p. 182°.

Nitrile; large silky needles, m.p. 156° (C. and H.).

Amide; leaflets, m.p. 148° (C. and H.).

3-Chloro-6-bromo-*p*-toluic acid; together with 2-chloro-5-bromo-*p*-toluic acid by heating 3-chloro-6-bromocymene with dilute nitric acid (Plancher, Gazz. chim. ital. 1893, 23, ii. 73; cf. Willgerodt and Wolfen, J. pr. Chem. 1889, (2) 39, 409). The mixture is separated by crystallisation from ligroin. Fibrous crystals, m.p. 187°-188° (P.), 186° (W. and W.).

5-Chloro-2-bromo-*p*-toluic acid; from 5-chloro-2-amino-*p*-toluic acid (Claus and David-son, Ann. 1891, 265, 347). Needles, m.p. 192°-193°. $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, needles.

2-Nitro-*p*-toluic acid; by treating cymene with concentrated nitric acid (Noad, Ann. 1847, 63, 297; cf. Fittig, *ibid.* 1874, 172, 309); by nitrating *p*-toluic acid at 0° (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; cf. Fittig and Ramsay, Ann. 1873, 168, 251).

Large monoclinic prisms, m.p. 189°-190° (Ahrens, Zeit. f. Chem. 1869, (2) 5, 104). Yields 6-amino-3-hydroxy-*p*-toluic acid on electrolysis its solution in sulphuric acid.

$\text{CaA}'_2 + 3\text{H}_2\text{O}$; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, needles (A.); $\text{CuA}'_2 + 7\text{H}_2\text{O}$, blue needles (Noyes, Amer. Chem. J. 1888, 10, 483); $\text{Cu}_2\text{A}'_4(\text{OH})_2$; $\text{Cu}_2\text{A}'_4(\text{OH})_2$ aq. (Noyes, *ibid.* 472).

Nitrile; by nitrating *p*-toluonitrile (Banse, Ber. 1894, 27, 2162). Long yellow needles, which sublime, m.p. 107° (Noyes).

Amide; long needles, m.p. 165°-166° (Fileti and Cairoli, Gazz. chim. ital. 1892, 22, ii. 392); formed also by nitrating *p*-toluamide at 0° (van S.).

Chloride; b.p. 185°/36 mm. (Soderman and Johnson, J. Amer. Chem. Soc. 1925, 47, 1390).

Methyl-ester; crystals (Noad), formed also when methyl-*p*-toluate is nitrated at 0° or 20° (van S.); ethyl-ester, yellow crystals (Noad).

3-Nitro-*p*-toluic acid; by heating the nitrile with hydrochloric acid (D 1:17) for 8-10 hours (Niemientowski and Rozański, Ber. 1888, 21, 2993; Noyes, Amer. Chem. J. 1888, 10, 476); in small yield by oxidising 3-nitro-*p*-xylene with potassium ferricyanide and potassium hydroxide (Noyes).

Long needles or monoclinic pillars which sublime (Nimentowski, Rozański and Haushofer, Ber. 1888, 21, 1994), m.p. 161° (N. and R.), 164°-165° (corr.) (Noyes). When warmed with mixed acids it yields 2:3- and 2:5-dinitro-*p*-toluic acids.

$\text{NaA}' + 6\text{H}_2\text{O}$, large tables (Claus and Joachim, Ann. 1891, 266, 210); $\text{KA}' + 6\text{H}_2\text{O}$, large tables (C. and J.); CaA'_2 , anhydrous (N. and R.) + 2H₂O (Noyes); $\text{BaA}'_2 + 4\text{H}_2\text{O}$ (N. and R.), + 5H₂O (Noyes), glistening leaflets; $\text{CuA}'_2 + \text{H}_2\text{O}$, greenish-blue tables; AgA'_2 , needles.

Nitrile; from 3-nitro-*p*-toluidine by the

Sandmeyer reaction (Leuchart, Ber. 1886, 19, 175; Glock, *ibid.* 1888, 21, 2662; Weise, *ibid.* 1889, 22, 2429; Noyes, *l.c.*; Niemantowski, J. pr. Chem. 1889, (2) 40, 4; Ber. 1888, 21, 1535, 1902). Needles, m.p. 99° (G; W.), 100° (Noyes), 99.8° (Bogert and Hoffman, J. Amer. Chem. Soc. 1905, 27, 1293). It does not form an imino-ether when treated with alcoholic hydrochloric acid (Pinner, Ber. 1890, 23, 2919).

Amide; long hair-like needles, m.p. 152°–153° (N. and R.; cf. Weise, Ber. 1889, 22, 2430).

Chloride; small needles, m.p. 157° (C. and J.).

Some nitrotoluic acids of unknown orientation have been described by Ahrens (Zeit. f. Chem. 1869, (2) 5, 103); Fittica (Ber. 1874, 7, 1357); Ann. 1874, 172, 316); Landolph (Ber. 1872, 5, 937).

2:3-Dinitro-*p*-toluic acid; see below. Glistening rhombic prisms, m.p. 249°, more sparingly soluble than the 2:5-acid. With hydrochloric acid at 265° it yields 2:3-dinitrotoluene.

$\text{CaA}'_2 + \text{H}_2\text{O}$ (R.), or $+1\frac{1}{2}\text{H}_2\text{O}$ (C. and J.), long leaflets; $\text{BaA}'_2 + 3\text{H}_2\text{O}$ (C. and J.) or $+4\text{H}_2\text{O}$ (R.).

2:5-Dinitro-*p*-toluic acid; together with the 2:3-acid by treating 3-nitro-*p*-toluic acid with a mixture of 3 parts of sulphuric acid in 3 parts of nitric acid (D 1.51) (Rozafski, Ber. 1889, 22, 2675; Claus and Joachim, Ann. 1891, 266, 211). Fine needles, m.p. 188° (R.), or small glistening pillars, m.p. 194° (C. and J.). Hydrochloric acid at 250° yields 2:5-dinitrotoluene.

$\text{NaA}'_2 + 3\text{H}_2\text{O}$, yellow glistening scales; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, reddish-brown glistening leaflets; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, fine yellow needles, or $+2\text{H}_2\text{O}$ (C. and J.).

2:6-Dinitro-*p*-toluic acid; by nitrating *p*-toluic acid or its methylamide at the ordinary temperature (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; cf. Brückner, Ber. 1875, 8, 1678); by nitrating 2-nitro-*p*-toluic acid with mixed acids (Cl. and J.); by oxidising 2:6-dinitro-*p*-tolualdehyde with potassium permanganate (Gattermann, Ann. 1906, 347, 347).

Yellow plates which sublime, m.p. 157°–158°. $\text{KA}'_2 + 2\text{H}_2\text{O}$; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, thick red prisms; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, fine needles; AgA' .

3:5-Dinitro-*p*-toluic acid; by heating the corresponding amide with concentrated hydrochloric acid at 220°–230° for 8 hours (Claus and Beysen, Ann. 1891, 266, 226). Slender plates or prisms, m.p. 226°, subliming in needles. $\text{BaA}'_2 + \text{H}_2\text{O}$, yellow pillars.

Amide; by boiling the nitrile with 60 p.c. sulphuric acid. Thin yellow needles, m.p. 255°–257°.

Nitrile; from 3:5-dinitro-*p*-toluidine. Golden-yellow needles, m.p. 103° (C. and B.).

2:3:5-Trinitro-*p*-toluic acid; by oxidising 2:3:5-trinitro-*p*-xylene. Lustrous white lamellae, m.p. 230°–231°, giving a brownish-red coloration with alkali hydroxide.

Methyl-ester, white needles, m.p. 114°–115°; *ethyl-ester*, colourless prisms, m.p. 87°–88° (Gina, Gazz. chim. ital. 1922, 52, i. 183).

ω-Chloro-2-nitro-*p*-toluic acid; by nitration of *ω*-chloro-*p*-toluic acid (Einhorn and Papastavros, Ann. 1900, 310, 200). Yellow needles, m.p. 180°.

2-Chloro-3-nitro-*p*-toluic acid; in small

quantity together with two isomeric acids, by nitrating 2-chloro-*p*-toluic acid (Claus and Böcher, Ann. 1891, 265, 362). Plates, m.p. 211°. CaA'_2 , glistening needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, rosettes.

2-Chloro-5-nitro-*p*-toluic acid; by hydrolysis of the nitrile derived from 2-chloro-5-nitro-*p*-toluidine (Claus and Böcher); by nitration of 2-chloro-*p*-toluic acid (Claus and Böcher); from 2-nitro-5-amino-*p*-toluic acid (Claus and Beysen, Ann. 1891, 266, 234). Needles, m.p. 164°–185°. $\text{KA}'_2 + \frac{1}{2}\text{H}_2\text{O}$, glistening leaflets; CaA'_2 , needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$; CuA'_2 , green precipitate.

Nitrile; tables or smooth pillars, m.p. 157° (Claus and Beysen).

2-Chloro-6-nitro-*p*-toluic acid; together with the 5-nitro- and 3-nitro-derivatives by nitrating 2-chloro-*p*-toluic acid (Claus and Böcher); from 2-nitro-6-amino-*p*-toluic acid (Claus and Beysen). Fine silky needles, m.p. 159°. CaA'_2 , needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, pillars.

3-Chloro-2-nitro-*p*-toluic acid; by nitrating 3-chloro-*p*-toluic acid with nitric acid (D 1.48) in the cold (Claus and Davidsen, Ann. 1891, 265, 347). Needles, m.p. 192°. $\text{MgA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles.

3-Chloro-6-nitro-*p*-toluic acid; by boiling 3-chlorocymene or 3-chloro-6-nitrocymene with nitric acid (D 1.39) (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 312); by nitration of 3-chloro-*p*-toluic acid with nitric acid (D 1.5 (Claus and Davidsen, J. pr. Chem. 1888, (2) 39, 495; Ann. 1891, 265, 341). Needles, m.p. 180°–181°. $\text{MgA}'_2 + 8\text{H}_2\text{O}$, large triclinic tables (Claus, Davidson and Beckenkamp, Ann. 1891, 265, 342).

$\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles, or $+3\text{H}_2\text{O}$ (C. and D.).

Ethyl-ester; tables or needles, m.p. 60°.

Nitrile; from the amine. Long needles, m.p. 93° (C. and D.).

ω-Chloro-2-nitro-*p*-toluic acid; by heating *p*-cyanobenzyl chloride with fuming nitric acid for $\frac{1}{2}$ hour at 100° (Banse, Ber. 1893, 27, 2168). It melts at 140°–141°. BaA'_2 , leaflets; AgA' , precipitate.

Amide; by keeping a mixture of *p*-cyanobenzyl chloride, potassium nitrate, and sulphuric acid for 24 hours. Microscopic needles, m.p. 125° (B.).

Nitrile; by treating a well-cooled solution of *p*-cyanobenzyl chloride in sulphuric acid with potassium nitrate. Prisms, m.p. 84° (B.).

3-Chloro-2:6-dinitro-*p*-toluic acid; by nitrating 3-chloro-2-nitro-*p*-toluic acid or 3-chloro-6-nitro-*p*-toluic acid (Claus and Davidsen, J. pr. Chem. 1889, (2) 39, 496; Ann. 1891, 265, 349). Small glistening needles, m.p. 233°. $\text{BaA}'_2 + \text{H}_2\text{O}$, large vitreous prisms.

Ethyl-ester, m.p. 71°.

2-Bromo-5-nitro-*p*-toluic acid; from 5-nitro-2-amino-*p*-toluic acid (Claus and Beysen, Ann. 1891, 266, 234). Needles, m.p. 181°.

2-Bromo-6-nitro-*p*-toluic acid; from 6-nitro-2-amino-*p*-toluic acid (C. and B.). Small needles, m.p. 181°. BaA'_2 , flat needles.

2-Bromonitro-*p*-toluic acid; by nitrating 2-bromo-*p*-toluic acid (Landolph, Ber. 1872, 5, 268). Needles, m.p. 170°–180° (decomp.). $\text{BaA}'_2 + \text{H}_2\text{O}$, needles.

3-Bromo-2-nitro-*p*-toluic acid; in small quantity, together with the 6-nitro-isomide, by

nitration 3-bromo-*p*-toluic acid (Claus and Herbabny, Ann. 1891, 265, 368). The acids are separated by means of their magnesium salts. The free acid forms fine needles, m.p. 214°, not volatile with steam. $\text{MgA}_2 + 3\frac{1}{2}\text{H}_2\text{O}$, leaflets; $\text{BaA}_2 + 4\text{H}_2\text{O}$, tables.

3-Bromo-5-nitro-*p*-toluic acid; by hydrolysis of the nitrile obtained from the corresponding amine (C. and H.). Small needles, m.p. 206°.

Nitrile; citron-yellow needles, m.p. 130°.

Amide; glistening needles, m.p. 171° (C. and H.).

3-Bromo-6-nitro-*p*-toluic acid; by boiling 3-bromocymene with nitric acid (D 1-29-1-39) (Fileti and Crosa, Gazz. chim. ital. 1886, 16, 297); or better, by boiling 3-bromo-6-nitrocymene with 15 times its weight of nitric acid (D 1-39) for 8 hours (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 300); by nitrating 3-bromo-*p*-toluic acid (C. and H.). Thin tables, m.p. 203°. When heated with alcoholic ammonia at 180°, it yields 6-nitro-3-amino-*p*-toluic acid.

$\text{NaA} + 4\frac{1}{2}\text{H}_2\text{O}$, plates; $\text{KA} + \text{H}_2\text{O}$, needles; $\text{MgA}_2 + 8\text{H}_2\text{O}$, large tables; $\text{CaA}_2 + 5\text{H}_2\text{O}$, needles or prisms; $\text{BaA}_2 + 4\text{H}_2\text{O}$, long needles (F. and C.), or $+5\text{H}_2\text{O}$ (C. and H.).

Ethyl-ester; glistening needles, m.p. 61° (C. and H.).

Chloride; leaflets, m.p. 60° (C. and H.).

Amide; needles, m.p. 191° (C. and H.).

Nitrile; needles, m.p. 132° (C. and H.).

Chlorobromonitro-*p*-toluic acid; by heating chlorobromo-*p*-toluic acid (m.p. 186°) with 5-6 parts of fuming nitric acid (Willgerodt and Wolfen, J. pr. Chem. 1889, (2) 39, 411). Needles which sublime, m.p. 220°. $\text{BaA}_2 + \text{H}_2\text{O}$.

2-Amino-*p*-toluic acid; by reducing 2-nitro-*p*-toluic acid with tin and hydrochloric acid (Ahrens, Zeit. f. Chem. 1869, (2) 5, 104). Long hair-like needles, m.p. 164°-165°.

$\text{BaA}_2 + 1\frac{1}{2}\text{H}_2\text{O}$; CuA_2 , green crystalline precipitate; hydrochloride; platinochloride (Cahours, Ann. 1859, 109, 17).

Nitrile; by reducing ω -chloro-2-nitro-*p*-toluonitrile with tin and hydrochloric acid (Banse, Ber. 1894, 27, 2163). Prisms, m.p. 81°-82°.

Acetyl-derivative; m.p. 267°-270° (decomp. (Kunkell, Ber. deut. pharm. Ges. 1911, 21, 419).

Diethylaminoethyl ester (Soderman and Johnson, J. Amer. Chem. Soc. 1925, 47, 1390).

3-Amino-*p*-toluic acid; from the nitrile (Niementowski, J. pr. Chem. 1889, (2) 40, 15); by reduction of 3-nitro-*p*-toluic acid with tin and hydrochloric acid (Niementowski and Rozański, Ber. 1888, 21, 1997; Noyes, Amer. Chem. J. 1888, 10, 479). Needles, m.p. 177° (decomp.). $\text{CaA}_2 + 2\text{H}_2\text{O}$, scales; $\text{BaA}_2 + 4\text{H}_2\text{O}$, leaflets (Noyes).

Formyl-derivative; long silky needles, m.p. 183°-187° (Niementowski).

Acetyl-derivative; needles, m.p. 183° (Niementowski).

Amide; by boiling the nitrile for 2-3 hours with dilute aqueous potassium hydroxide (Niementowski). Very thin plates, m.p. 146°-147°.

ω -Amino-*p*-toluic acid; by heating *p*-carboxybenzylphthalamic acid with concentrated hydrochloric acid for 3 hours at 200°

(Günther, Ber. 1890, 23, 1060). Yellow scales. Hydrochloride, long needles or trimetric prisms; platinochloride, yellow amorphous substance (G.).

2:3-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-acid with tin and hydrochloric acid (Claus and Joachim, Ann. 1891, 266, 216). Thin needles, m.p. 192°. It yields red flocks with ferric chloride (Kehrmann, Ber. 1889, 22, 1984). BaA_2 , reddish-yellow plates.

2:5-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-compound with tin and hydrochloric acid (C. and J.). Glistening needles, m.p. 240° (decomp.).

2:6-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-compound with tin and hydrochloric acid (C. and J.; Marckwald, Ann. 1893, 274, 357). Silky needles, m.p. 212°. Nitrous acid yields an intense yellow coloration. BaA_2 , glistening leaflets; sulphate $+3\text{H}_2\text{O}$, yellow needles (M.).

Methyl-ester; brown crystals with a peculiar fluorescence, m.p. 129° (Kauffmann and Weissel, Ann. 1912, 393, 1).

Diacetyl-derivative; colourless needles, m.p. above 280° (K. and W.).

5-Chloro-2-amino-*p*-toluic acid; by reducing the corresponding nitro-derivative (Claus and Davidsen, Ann. 1891, 265, 346). Needles, m.p. 220°.

5-Bromo-2-amino-*p*-toluic acid; tables, m.p. 186°-187° (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 307).

5-Nitro-2-amino-*p*-toluic acid; by reducing an ammoniacal solution of 2:5-dinitro-*p*-toluic acid with hydrogen sulphide (Claus and Beysen, Ann. 1891, 266, 232). Long yellowish-red pillars or needles, m.p. 220° (decomp.). BaA_2 , yellowish-brown plates or prisms.

6-Nitro-2-amino-*p*-toluic acid; by reducing 2:6-dinitro-*p*-toluic acid with ammonium sulphide, or with stannous chloride and alcoholic hydrochloric acid (C. and B.). Citron-yellow needles which sublime, m.p. 214°.

$\text{NaA} + \frac{1}{2}\text{H}_2\text{O}$, yellow silky needles; $\text{MgA}_2 + 5\text{H}_2\text{O}$, yellow crystals; CaA_2 , deep yellow pillars; $\text{BaA}_2 + 4\text{H}_2\text{O}$, golden-yellow leaflets.

6-Nitro-3-amino-*p*-toluic acid; by heating the corresponding bromonitro-*p*-toluic acid with alcoholic ammonia at 180° (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 303; cf. Niementowski, J. pr. Chem. 1889, (2) 40, 27). Long silky needles, m.p. 235°-236°. When heated with hydrochloric acid at 150°, it yields 6-nitro-*m*-toluidine.

2-Nitro- ω -amino-*p*-toluic acid; by heating 2-nitrocyanobenzylphthalimide with hydrochloric acid and acetic acid for 3 hours at 150° (Banse, Ber. 1894, 27, 2166). Pearly leaflets, m.p. 243° (decomp.). Hydrochloride, needles, m.p. 249°-250° (decomp.).

p-Toluic sulphinide, 'Methylsaccharin'; obtained similarly to saccharin (Randall, Amer. Chem. J. 1891, 13, 269); by heating 3-sulphonamino-*p*-toluic acid at 200°-220° for 3 to 4 hours (Weber, Ber. 1892, 25, 1737; B. A. S. F., D. R. P. 48583 of 1889); by hydrolysis of *p*-cyanotoluene *m*-sulphonamide with caustic alkalis (B. A. S. F., D. R. P. 48563 of 1889; cf. Basler Chem. Fabr., D. R. P. 122567 of 1900). Long fine needles $+1\frac{1}{2}\text{H}_2\text{O}$, which

lose the water of crystallization at 190°, and then sublimes gradually with decomposition. It melts at 249° (R.) or 246° (W.) and possesses an intensely sweet taste, but a bitter after-taste. On heating with a mixture of potassium hydroxide and potassium hypochlorite, followed by acidification of the product with acetic acid, *p*-toluidine 3-sulphonic acid is obtained. *Barium salt* + 5H₂O, triclinic crystals; *Calcium salt*, opaque white needles; *Silver salt* + 1½H₂O, colourless diamond-shaped crystals.

Ethyl imide: crystals, m.p. 106°; *methyl imide*, m.p. 153° (W.).

For the sulphonic acids, etc., of toluic acid, see Flesch (Ber. 1873, 6, 480); Bechler (J. pr. Chem. 1873, (2) 8, 170); Fittig (Ann. 1874, 172, 329); Iles and Remsen (Ber. 1878, 11, 230); Fischli (Ber. 1879, 12, 616); Hall and Remsen (Ber. 1879, 12, 1433); Remsen and Burney (Amer. Chem. J. 1880-1, 2, 411); Moyer and Baur (Ann. 1883, 220, 18); Kelbe and Baur (Ber. 1883, 16, 2565); Remsen and Emerson (Amer. Chem. J. 1886, 8, 264); Weinreich (Ber. 1887, 20, 982); Randall (Amer. Chem. J. 1891, 13, 258); Holmes (*ibid.* 1891, 13, 380); Weber (Ber. 1892, 25, 1741); Lyman (Amer. Chem. J. 1894, 16, 513); Meldrum and W. H. Perkin (Chem. Soc. Trans. 1908, 93, 1419; B. A. S. F., D. R. P. 48583 of 1889; Basler Chem. Fabr., D. R. P. 122567 of 1900; Jacobsen (Ber. 1878, 11, 895; 1881, 14, 39, 2355); Iles and Remsen (Amer. Chem. J. 1880-1, 1, 41); Jacobsen and Wierss (Ber. 1883, 16, 1959).

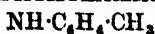
F. M. R. and J. S. H. D.

o-TOLYGLYCINE. Formed by heating *o*-toluidine with an aqueous solution of sodium chloroacetate (Friswell, Eng. Pat. 18149 of 1907).

TOLYLENE-DIAMINES. *Diamino-toluenes* v. AMINES.

TOLYLENE RED v. AZINES.

***p*-TOLYL- α -NAPHTHYLAMINE**



obtained by heating α -naphthylamine with *p*-toluidine and iodine, or α -naphthol with *p*-toluidine, or α -naphthylamine hydrochloride with *p*-toluidine. M.p. 78.5°, b.p. 230°/10 mm. The tolylnaphthylamines are described in Vol. IV., pp. 437, 451.

1-*p*-TOLYNAPHTHYLAMINE 8-SULPHONIC ACID. Prepared by heating 1-naphthylamine 8-sulphonic acid with *p*-toluidine in an autoclave at 150°, with or without hydrochloric acid or benzoic acid (Farb. f. F. Bayer & Co., D. R. P. 71168; Kalle & Co., D. R. P. 170630).

TOLYPYRIN, TOLYSAL, v. SYNTHETIC DRUGS.

TOMATO, *Solanum Lycopersicum* (Linn.) or *Lycopersicon esculentum vulgare*. A Peruvian plant now largely cultivated in many parts of the world for its fruit, which is esteemed as a vegetable. Several species and many varieties are known, differing greatly in size, shape, and colour of fruit.

König gives as the average composition—

Water	Protein	Fat	Sugar	Other extract	N-free	Crude fibre	Ash
93.4	1.0	0.2	3.5	0.5		0.8	0.6

About half the total nitrogen is present as true proteids.

Passerini (Staz. Sper. Agrar. 1891, 18, 545) found the fresh fruit to consist of skin 1.3 p.c., pulp and juice 96.2 p.c., and seeds 2.5 p.c., and the pulp to contain two colouring matters—a yellow amorphous substance and a red crystalline compound—both insoluble in water, but soluble in amyl alcohol or ether, and bleached by chlorine. He attributes the acidity to citric acid, which he estimates as forming about 9 p.c. of the total dry matter of the whole fruit. The ash he found to contain—

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂	Cl
59.5	6.0	1.3	3.1	0.2	12.9	3.5	0.3	19.1

Albahary (Compt. rend. 1907, 145, 131) found in the fresh fruit—

Water	Protein	Fat	Carbo- hydrates	Malic acid	Citric acid	Oxalic acid	Ash
93.5	1.0	0.2	3.6	0.49	0.15	0.001	0.74

Traces of tartaric and succinic acids were also detected.

Stüber (Zeitsch. Nahr. Genussm. 1906, 11, 578) obtained somewhat similar results, but states that citric acid was the chief cause of the acidity (amounting to about 0.5 p.c. citric acid), and that he could not detect malic, tartaric, or succinic acids. The presence of citric acid may be detected by the formation of its triphenacyl ester.

The juice of tomatoes was found by Passerini (*l.c.*) to have a sp.gr. 1.01833 at 15°, to contain 2.44 p.c. of dry matter, of which rather more than ½ was protein, ¼ ash, and a little more than half carbohydrates and acids.

Other analyses of the juice were made by Stüber (*l.c.*), who found water 95.1, nitrogen 0.093, ash 0.56, total sugars, after inversion, 2.15, acidity (as citric acid) 0.65 p.c. The red colouring matter of the tomato was investigated by Arnaud (Compt. rend. 1886, 102, 1119), who believed it to be identical with carotin C₄₀H₅₆; Montanari (Chem. Zentr. 1905, i, 544) concluded that it had the composition C₅₅H₇₄; Willstätter and Escher (Zeitsch. physiol. Chem. 1910, 64, 47), who name it *lycopene*, find that it had the molecular composition C₁₁H₁₆, the same as that which Willstätter and Mig (Annalen, 1907, 355, 1) have ascribed to carotin. It, however, differs in its properties from that substance. It crystallises from light petroleum or a mixture of alcohol and carbon disulphide in dark, carmine-red, felted prisms; it melts at 168°–169° (corr.), but is less soluble in ether, alcohol, carbon disulphide, or light petroleum than carotin. It absorbs oxygen much more readily than does carotin, and forms a di-iodide C₄₀H₅₆I₂, a dark green, gelatinous, insoluble substance.

The leaves and stems of tomatoes were examined by Passerini (Staz. Sper. Agrar. 1893, 20, 471), who found in the fresh substance—

	Total dry matter	
Stems	8.8-9.9	1.6-2.0
Leaves	11.6-14.6	1.6-3.2
The ash contained—		

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	MnO	P ₂ O ₅	SO ₂	SiO ₂	Cl
Stems 25.0	11.1	3.2	7.9	0.5	—	0.3	4.7	0.0	1.4	1.4
Leaves 2.0	1.4	3.1	0.0	0.1	0.05	1.4	12.3	3.3	1.6	—

Lithium, boron, and copper were also present in the ash of the stems.

Salicylic acid occurs naturally in tomatoes although in very small quantity. Pellet (Ann. Chim. anal. 1907, 12, 10) considers that the presence of 10 mgm. of salicylic acid in 1 kilog. of tomatoes should not be regarded as proof of adulteration.

Tomatoes are often canned. American analyses (Bill. 28, U.S. Dept. of Agric.) give, as the mean of 19 samples—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94.0	1.2	0.2	3.5	0.5	0.6

In the ash was included about 0.1 p.c. common salt. Tomatoes are largely used in the preparation of sauces and chutneys, in some of which the red colour is enhanced by the addition of eosin (König).

Air-dried tomato seeds give a yield of about 25 p.c. oil when extracted with ether, and about 18 p.c. when the seeds are pressed. Sp.gr. (average), 0.9190; refractive index at 25°, 1.4722; iodine No. (Hanūs), 122.5; sapon. No., 189.5; Reichert-Meißl No., 0.26; Polenski No., 0.55; acetyl value, 14.2; insol. fatty acids, p.c. 98.5; soluble fatty acids, 0.52; unsat. (liquid) acids, p.c. 78.5; sat. (solid) acids p.c. 16.4 (Jamieson and Bailey, J. Ind. Eng. Chem. 1919, 11, 850). The antiscorbutic value of fresh and canned tomatoes has been studied by Delf (Bio-Chem. J. 1924, 18, 674; Chem. Soc. Abstr. 1924, 126, i. 902). H. I.

TONITE v. EXPLOSIVES.

TONKA BEAN. *Tonquin bean* (Fève tonka, Fr.; *Tonkabohnen*, Ger.). The seed of the fruit of the leguminous tree *Dipterix odorata* (Willd.) which inhabits Guiana and Venezuela. Each pod contains a single seed, which is about 2 ins. long and $\frac{1}{2}$ in. wide. It has a dark-brown colour, is deeply wrinkled externally, and characterised by an agreeable odour and bitter aromatic taste. The tree flourishes in the forests of the Caracas district of Venezuela. The first crop of beans is gathered when the tree is three years old, but a full crop is not obtained until two years later. The fruit bears some resemblance to a small mango, and contains the odorous bean in its centre. The seed of *D. oppositifolia* (Willd.), the so-called English Tonka bean, has similar properties to that of *D. odorata*, but it is smaller and darker in colour.

Besides sugar, gum, malic acid, and woody fibre, tonka bean contains fixed oil and about 1.5 p.c. of coumarin (Boullay and Boutron-Charlard, J. Pharm. Chim. 11, 480). It is to the presence of coumarin that the odour and taste of the seed are due, and crystals of this compound often occur as an efflorescence on commercial specimens. To extract the coumarin, the finely-chopped beans, according to Gössmann, are heated for some time nearly to boiling with an equal bulk of 80 p.c. alcohol; the whole is then filtered and the residue again heated in the same manner; the extracts are mixed together, and the alcohol removed by distillation until the residue becomes turbid, when it is mixed with four times its volume of water, which precipitates the coumarin in somewhat impure crystals. Adhering fat may be removed by heating the mixture to boiling, and filtering through a

moistened filter. On cooling, the crystals which re-dissolve in the hot liquid again separate, and they may be further purified, if necessary, by treatment with animal charcoal (Annalen, 98, 86), v. COUMARIN.

Tonka bean is used to flavour tobacco, and especially snuff, as an ingredient of sachet powder, and in alcoholic solution as a flavouring essence.

TOPAZ (*Topaze*, Fr.; *Topas*, Ger.). A gemstone composed of aluminium fluo-silicate $(\text{AlF})_2\text{SiO}_4$ crystallised in the orthorhombic system. As shown by S. L. Penfield and J. C. Minor (Amer. J. Sci. 1894, 47, 387) the fluorine (15.48–20.37 p.c.) is replaced isomorphously by hydroxyl (0.18–2.50 p.c., as shown by analyses), so that the formula becomes $[\text{Al}(\text{F},\text{OH})]_2\text{SiO}_4$; and, chemically, a fluor-topaz and a hydro-fluor-topaz may be distinguished. Although these two varieties show slight differences in sp.gr. (3.574 in the former, and 3.523 in the latter), and in optical constants, the distinction is of no practical importance. The mineral is very resistant to acids, and water is expelled only at an intense heat. Topaz usually occurs as crystals in granitic and gneissose rocks, and is often associated with tin-ore. An important character is the presence of a perfect cleavage in one direction, perpendicular to the prism. The crystals may be dull and opaque, or more often clear and transparent, and colourless, bluish, greenish, yellow, or pink. The sherry-yellow crystals from Brazil become pink when heated ('burnt topaz'). Most of the gem material comes from Brazil and Russia, but it is also found in many other countries. Colourless topaz, when faceted, is sometimes mistaken for diamond, and much yellow quartz ('Spanish topaz,' 'Scotch topaz,' 'occidental topaz') is passed off as topaz. The more valuable yellow corundum, on the other hand, is known as 'oriental topaz.' The distinguishing characters of these are shown in the following table:—

	Topaz	Quartz 'Occidental topaz'	Corundum 'Oriental topaz'
Comp.	$(\text{AlF})_2\text{SiO}_4$	SiO_2	Al_2O_3
Cryst.	Orthorhombic	Rhombohedral	Rhombohedral
Sp.gr.	3.55	2.65	4.0
H.	8	7	9
Refr.			
Indices	1.61–1.63	1.54–1.55	1.76–1.77

L. J. S.

TOPAZ, ORIENTAL, v. CORUNDUM.

TOPAZ, SCOTCH, v. CAIRNGORM.

TOPAZ, SPANISH, v. CAIRNGORM.

TOPE-LIVER OIL. According to Chapman (Analyst, 1922, 203), the oil obtained by steaming the livers of the tope (*Galeus galeus*, family *Carchariidae*), found on all the coasts of the British Isles, has the following characteristics:—

Specific gravity (15°/15°)	0.9249
Iodine value (Wijs)	152.2
Saponification value	195.1
Unsaponifiable matters	1.14 p.c.
Refractive index at 15°	1.4803
at 20°	1.4778
Specific dispersion ($n_{\text{H}\beta} - n_{\text{H}\alpha}$)	0.0101
Brominated glycerides	42.5 p.c.
Insoluble in ether	

It is a pale-coloured oil, having a strong but not unpleasant odour, and is very similar to cod-liver oil. It is used* medicinally by local fishermen and in the dressing of leather.

TORBANITE or TORBANEHILL MINERAL v. PARAFFIN.

TORBERNITE or CUPRO-URANITE (*Kupferuranit*, Ger.). A mineral consisting of hydrated phosphate of uranium and copper



It crystallises as square (tetragonal) plates which possess a perfect micaceous cleavage with pearly lustre, parallel to their surface. The colour is bright grass-green, which distinguishes cupro-uranite at a glance from the closely-allied mineral autunite (*q.v.*) or calco-uranite. Sp.gr. 3.5; H. 2½. It is a mineral of secondary origin, occurring in the upper portion of lodes containing pitchblende and copper ores, and sometimes as an incrustation on the joint faces in granite. Fine specimens have been found at Gunnislake, Grampound Road, and Redruth in Cornwall. Other localities are Joachimsthal in Bohemia, Johanngeorgenstadt in Saxony, Sabugal in Portugal, Mount Painter in South Australia, Katanga in Belgian Congo, &c. To a limited extent the mineral has been mined, together with autunite, as a source of uranium and radium. L. J. S.

TORMENTILLA. The underground stems of *Potentilla Tormentilla* (Neck.) have been occasionally substituted for those of rhubarb in medicine. They contain from 5 to 6 p.c. of tannin, giving a dark-green precipitate with ferrous sulphate, bluish-red with ferric acetate; is also precipitated by gelatin and by tartaric acid (Stenhouse) (v. TANNINS).

TORREFACTION. Roasting ores in order to expel volatile substances, e.g. sulphur, arsenic, &c.

TOSCA. v. TUFF.

TOULOUOUNA or TULUCANA OIL. An oil obtained by pressing the kernels of *Caraia tuianensis* (Aubl.), v. CARAPA OIL.

TOULOURON OIL. A brown oil obtained from *Papirus Latro*. Used in Senegal as a remedy for rheumatism.

TOURMALINE (*Turmalin*, Ger.; from the Anglose *turamali*). A complex boro-silicate of aluminium, together with variable and mutually replaceable amounts of ferrous oxide, magnesia, and alkalis. As chemical types there may thus be distinguished iron-tourmaline, magnesian tourmaline, and alkali-tourmaline. Analysis shows: SiO_2 , 35-38; TiO_2 , 0-1; B_2O_3 , 9-11; Al_2O_3 , 30-42; Cr_2O_3 , 0-10 (rarely); Fe_2O_3 , 1-8; FeO , 0-17; MnO , 0-2; MgO , 0-1; CaO , 0-2; Na_2O , 0-2; K_2O , 0-2; Li_2O , 0-1; I_2O , 1-4; F, 0-1 p.c. Many different formulae have been suggested. Penfield and Foote (1899) regard the several varieties as salts of the hypothetical aluminoboro-silicic acid



With these wide differences in chemical composition, the sp.gr. ranges from 3.0 to 3.2, and the refractive indices (Na) = 1.6123-1.6155, = 1.6318-1.6354 (E. A. Welfing, 1900), but there are only very slight variations in the

by Penfield and Foote to the mass effect of the large acid radicle). The crystals are rhombohedral-hemimorphic, there being a different development of faces at the two ends. The habit is almost invariably prismatic, with deeply-grooved prism faces, the striations being parallel to the edges of the prism; the cross-section of the prism is triangular with straight or curved outlines. These peculiarities of form render tourmaline a mineral readily recognisable. As a consequence of the hemimorphism the crystals are pyroelectric. The material ranges from colourless to jet-black in colour, and may be any shade of red, yellow, green, or blue. In one and the same crystal there are often striking contrasts in the differently coloured zones. The more darkly coloured crystals are strongly dichroic, the ordinary ray vibrating perpendicularly to the principal axis being almost completely absorbed. On this property depends the use in polarising apparatus (e.g. the well-known tourmaline-tongs) of tourmaline plates cut parallel to the principal axis of a crystal.

Common black tourmaline (*schorl*) is of abundant occurrence in granite and metamorphic rocks, and is a frequent associate of tin ores. Coloured tourmalines are much used in jewellery, either as clear faceted stones or, when cloudy, as beads (H. 7½). The red is often called *rubellite*, and the blue *indicolite*, whilst fanciful names such as 'Brazilian emerald,' 'Siberian ruby,' &c., are also sometimes used. Within recent years large quantities of gem material have been quarried from the pegmatites of California, Madagascar, and the Usakos district, South-West Africa.

L. J. S.

TOUS-LES-MOIS is a species of arrowroot procured from the tubers of *Canna edulis* (Ker-Gawl. nat. ord. *Marantaceae*). The starch is obtained in the same manner as other descriptions of arrowroot. Under the microscope the granules show themselves to be unusually large, measuring from 0.0015 to 0.0037 inch in length and from 0.001 to 0.0027 in breadth; broad, flat, ovate. The hilum is situated at the narrow extremity, and the rings are very close, firm, and regular.

Tous-les-mois is used in admixture with cocoa preparations and as a food for infants, for which latter purpose it is bleached. V. STARCH.

TOXICODENDROL. The active principle of the 'Poison Ivy' (*Rhus Toxicodendron* Linn. and *R. venenata* [DC.]), is an oily substance possessing intensely irritating properties, found in all parts of the plant, the fruits giving 3.6, the leaves 3.3, and the stem 1.6 p.c. The degree of activity varies in the case of different persons; in some cases 1 mgm. produced hundreds of vesicles, and even 100 mgm. proved active in one case. The vesicant action was not immediate, a period of 24 hours to 7 or 9 days elapsing before the eruption appeared (Pfaff, J. Soc. Chem. Ind. 1897, 1037).

The poisonous substance is probably a glucoside; it is decomposed by acids yielding gallic acid, fisetin, and rhamnose. Cases of poisoning are said to be best treated with potassium permanganate* (Acree and Syme, Amer. Chem. J. 1906, 301).

The 'poison oak' (*Rhus diversiloba*, T. & G.) which is very similar in appearance to *R. toxicodendron*, has been examined chemically

by McNair (J. Amer. Chem. Soc. 1916, 38, 1417), who finds that the leaves and branches contain a substance of which the alcoholic extract is poisonous. The poisonous material is not, however, a glucoside of fisetin, rhamnose, and gallic acid, since none of these substances is produced on hydrolysis. Fisetin, rhamnose, and gallic acid are found in non-poisonous species of *Rhus*, and the natural glucoside of these substances is non-toxic.

TOXINS and ANTITOXINS.

TOXINS.

Infective diseases of man and animals, that is diseases which are contagious, infectious, or transmissible by inoculation, are caused by pathogenic (i.e. disease-producing) living organisms which are parasitic on or in the individual attacked. The parasitic organisms may be minute vegetable ones, principally bacteria, minute animal protozoa, or higher and large forms such as moulds, insects, and worms. The bacteria, and presumably also the protozoa, as a rule produce their deleterious effects principally by means of substances which are poisonous to the host, and which are elaborated by, or are derived from, the parasitic organisms. Even the larger parasites, such as worms, though acting mechanically and in other ways, may also elaborate poisonous substances.

In the early days of bacteriology, under the influence of the work of Panum, Selmi, Nencki and others on the products of putrefaction attempts were made to isolate from the cultures of the pathogenic organisms and from the tissues of the disease-stricken patients nitrogenous bodies of a basic and alkaloidal nature similar to the ptomaines of putrefaction, and Brieger in particular isolated such substances as typhotoxine from cultures of the typhoid bacillus and tetanine from the tissues of a case of tetanus (see art. PTOMAINES). It was soon found, however, that such basic substances are not, as a rule, the essential or specific toxic agents of the pathogenic bacteria, and some of those described by Brieger are quite likely artifacts, due to the methods of extraction employed.

The specific toxic agents of the bacteria, or *toxins*, as they may conveniently be termed, are substances of complex composition, which, so far as they have been investigated, seem occasionally to be protein in nature, or to be allied to the proteins or to the enzymes. The whole subject of the nature of toxins is still in a very indeterminate condition, so that any views expressed here must be regarded as tentative. In some instances the toxin appears to be a substance *sui generis*, in others it may be proteose in nature (tox-albumose), and in others it may be albuminous (tox-albumin). Of late, the conception has been gaining ground that toxins and other 'antigens' (v. *infra*, under *Antitoxins*) may be lipid substances or lipid-protein complexes. The toxin may be an excretory product, as it were, of the micro-organism, e.g. tetanus toxin (S. Martin), or may be formed by the action of enzymes, excreted by the micro-organism, on the constituents of the culture medium or of the tissues, e.g. anthrax toxin, or it may be a mixture of these two, e.g. diphtheria toxin (S. Martin), or it may be a protein or other con-

stituent of the bacterial cells themselves, e.g. typhoid toxin. Toxins which are excretory products, or are formed by the action of the organism on the culture medium, are termed *exo-toxins* or simply *toxins*, e.g. diphtheria, tetanus, and botulism toxins; those which are intimately associated with the bacterial cells are termed *endo-toxins*; the toxins of the majority of pathogenic bacteria belong to the latter class. The term toxin has also been extended so as to include various toxic bacterial extracts, such as tuberculin, the toxic proteins, &c., which are found in the higher plants and animals, e.g. abrin and ricin of the jequirity and castor-oil beans respectively, substances like eel serum, which is toxic on injection into other animals, and snake venom.

The bacterial *exo-toxins* may be prepared by cultivating the organisms in a suitable fluid culture medium under appropriate conditions for 1-4 weeks, and then filtering the fluid culture through a Pasteur-Chamberland porcelain, or a Berkefeld, filter. The filtrate is more or less toxic, and may be termed the toxin broth, the actual toxin contained in it may be concentrated in various ways, but extraction in a pure condition is at present impossible, owing to the difficulty of separating it from the constituents of the culture medium. Bacterial *endo-toxins* may be obtained by growing the organisms on a solid culture medium and extracting the bacterial mass with weak alkalis, &c., or by grinding up the bacterial paste in a mechanical disintegrator, such as Macfayden and Rowland's or Barnard's, and subsequent filtration through a porcelain filter (Proc. Roy. Soc. 1912 and 1911).

The bacterial toxins generally are unstable bodies, disappearing, or being converted into non-toxic modifications, on keeping, and destroyed by light, warming to 60°-70°, by acids, alkalis, and oxidising agents, and by digestive enzymes; owing to the last-named fact, the toxins usually are not toxic when taken by the mouth, but only on inoculation. They are much more stable in the dry condition than when in solution. They are insoluble in and are precipitated by strong alcohol, and are precipitated on saturation of their solutions with ammonium sulphate. Diphtheria and tetanus toxins dialyse very slightly through parchment, and they will pass through a gelatin-coated porcelain filter, which does not permit of the passage of serum albumin, suggesting that their molecules are smaller than those of the latter (Brodie, Journ. Path. and Bacter. 1897). They are probably levorotatory. The 'toxin,' in some instances at least, may contain more than one toxic constituent.

Diphtheria toxin was first investigated by Löffler. By precipitating broth cultures of the diphtheria bacillus with alcohol, he obtained a white toxic powder which he classed among the enzymes (Deut. med. Woch. 1890, Nos. 5 and 6). Roux and Yersin, by the cautious addition of calcium chloride, obtained the toxin entangled with the precipitate of calcium phosphate which comes down, and similarly regarded it as an enzyme (Ann. Inst. Pasteur, iii.). Brieger and Fränkel concluded that the toxin is a protein ('tox-albumin'); they found that it is precipitated by ammonium sulphate, but not by magnesium

sulphate, contains a relatively high percentage of sulphur and gives the biuret and Millon's reactions (Berl. klin. Woch. 1890, 241, 1133).

Brieger and Fränkel's method of preparing the diphtheria toxin was to saturate broth cultures with magnesium sulphate at 30°, filter from the precipitated globulin, &c., saturate the filtrate with ammonium sulphate at 30°, wash and dissolve the precipitate, dialyse to remove as much adherent salts as possible, and remove remaining traces of ammonium sulphate by the cautious addition of barium chloride; evaporate the filtrate to half the volume *in vacuo* at 40°, and precipitate with absolute alcohol. The precipitate was collected, redissolved, and precipitated with alcohol 6-8 times. Ultimate analysis gave the following figures: C 45.35, H 7.13, N 16.33, S 1.39, O 29.80.

Brieger and Boer subsequently prepared the diphtheria toxin in as pure a form as it has yet been obtained by precipitating broth cultures with a 1 p.c. solution of zinc sulphate or chloride. The precipitate of the zinc double salt is washed with feebly alkaline water and decomposed with carbon dioxide. The purified product gave the xanthoproteic, biuret, Adamkiewicz's, and Millon's reactions. A litre of broth culture gave about 3 grm. of the zinc double compound (Zeitsch. Hygiene, xxii. 267).

Sidney Martin isolated from diphtheritic membrane and from the spleen and other organs of diphtheria cadavers proteoses, chiefly deutero-albumose, and from the membrane alone an organic acid which was not identified. The latter is a yellowish amorphous body, becoming deep brown with alkalis, and is soluble in water and absolute alcohol, but not in ether, chloroform, or benzene. The proteoses were extracted by placing the minced tissues in absolute alcohol until the ordinary proteins were coagulated and rendered insoluble, extracting with water, and precipitating this extract with alcohol many times. Similar proteoses were obtained from cultures in alkali-albumin of the diphtheria bacillus (Brit. Med. Jour. 1892, i.).

Ehrlich concluded that the diphtheria 'toxin' contains two or more toxic constituents, as well as non-toxic bodies, 'toxoids,' derivatives, or degradation-products, of the toxin (*v. infra*, under *Antitoxins*).

Warden, Connell and Holly regard diphtheria toxin as a fat complex derived from dead and disintegrating bacilli in an emulsified or colloidal form which then becomes adsorbed upon colloidal particles in the broth culture medium, forming, with electrolyte, an adsorption entity constituting toxin (Journ. of Bacteriology, vi. 1921, p. 103).

Tetanus toxin was obtained in a somewhat concentrated form by Kitasato from anaerobic broth cultures of the tetanus bacillus (which produces lock-jaw), and he gave a detailed account of the action of heat and of a number of chemical reagents on the toxin broth (Zeitsch. Hygiene, x. 267). Brieger and Cohn precipitated veal-broth cultures by saturation with ammonium sulphate (*ibid.* xv. 1). The toxin formed a flocculent precipitate which floated; it was purified by redissolving, precipitating the protein with basic lead acetate, removing other soluble impurities by dialysis, and finally pre-

cipitating the dialysed solution with alcohol. Thus prepared, the tetanus toxin formed pale yellow, odourless, easily soluble scales, having a gummy taste; the solution was feebly laevorotatory. It contained only a trace of ash, did not give the Millon's and xanthoproteic reactions, and gave no precipitate with potassium ferrocyanide and acetic acid, nitric acid, or mercuric chloride. Boiled with ferric chloride it gave no red colour. With copper sulphate and sodium hydroxide it gave a slight violet colour. It contained no phosphorus and only a trace of sulphur, and ultimate analysis gave the following figures: C 52.08, H 8.1, N 15.71 (Brieger, Zeitsch. Hygiene, xix. 101). Subsequently, Brieger and Boer obtained the toxin by the method employed by them for isolating the diphtheria toxin (*vide ante*). On these facts Brieger considered that the tetanus toxin is not a true protein.

Hayashi, however, employing the Brieger-Boer method, or a modification of it, came to the conclusion that the tetanus toxin is a protein, and is a primary proteose (Arch. f. exper. Pathol. xlvii. 9). S. Martin also isolated proteoses, chiefly deutero-albumose, from the spleen of a cadaver, but they did not induce tetanic convulsions on inoculation. Tetanus cultures contain methyl-mercaptan and other sulphur compounds (Nencki, Monatsch. x.); but Fermi and Pernossi were unable to extract any basic substance from them (Zeitsch. Hygiene, xvi. 385). Besides the convulsive constituent, 'tetano-spasmin,' the toxin broth also contains a substance, 'tetano-lysin,' which is a solvent for red-blood corpuscles. The purified tetanus toxin is probably the most toxic substance known, less than 0.5 mgrm. being a fatal dose for a man.

Anthrax toxin. Hankin obtained proteoses from cultures of the anthrax bacillus, and Brieger and Fränkel a tox-albumin from animals dead of anthrax. Marnier, by precipitating cultures with ammonium sulphate, isolated a toxic substance which he considered to be neither protein nor basic (Ann. Inst. Pasteur, ix. 533). S. Martin (*loc.*) obtained both from cultures in alkali albumin, and from animals dead of anthrax, proteoses, chiefly deutero-albumose, and a nitrogenous basic substance, both of which were toxic. The toxins are formed mainly by the action on the culture medium of enzymes excreted by the bacillus. Endo-toxins may also be formed.

The toxins of the majority of other pathogenic bacteria are endo-toxins. That is to say, if the organisms be grown in a fluid medium, the filtrate is almost non-toxic, but the dead and disintegrated bacterial cells yield toxic substances. Toxins of protozoan organisms are not known with certainty.

Tuberculin. The original or old tuberculin of Koch is obtained by boiling, concentrating over a water-bath and filtering glycerin broth cultures of the tubercle bacillus. It is toxic to healthy animals only in large doses, but minute doses cause considerable disturbance in tuberculous patients and animals, and this reaction is made use of for the detection of tuberculous infection. It contains small quantities of proteoses, extractives, and salts, and traces of basic bodies. Small quantities of an acid

substance, probably teraconic acid, possibly derived from the bacillar cells, are also present in cultures of the tubercle bacillus. Other tuberculous and bacterial extracts have been prepared.

It must be clearly recognised that in those cases in which the toxin is supposed to be protease or other protein, the latter may be merely constituents of the culture medium by which the toxin is entangled or adsorbed.

[On toxins, &c., see Oppenheimer in Kolle and Wassermann's *Handbuch der Pathogenen Mikroorganismen*, vol. i. (Bibliog.); Vaughan and Novy, *Cellular Toxins*, 1902 (Bibliog.); S. Martin, *Man. of Gen. Pathology*, 1904, and *Reps. Med. Off. Loc. Gov. Bd.* 1889-1900; also various papers in the *Ann. Inst. Pasteur*; *Zeitsch. Hygiene, Centr. Bakteriol.* Abstracts also in chemical journals.]

Snake venom. Poisonous snakes are divided into two groups, the colubrine and viperine. The venom, which is secreted by glands in connection with the mouth, may be limpid or syrupy, pale yellow, orange or greenish in colour, odourless and tasteless, sp.gr. 1.04 (rattlesnake), 1.11 (cobra), 1.08 (Russell's viper). Microscopically, it contains few elements, and when dry resembles dry albumin. The reaction of the pure venom is acid; it contains C, H, O, N, and S in the proportions found in proteins, gives the protein reactions, is precipitated with alcohol, ammonium sulphate, sodium chloride, and coagulates on heating. Viperine venoms lose their toxicity on heating to 80°-85°, but colubrine venoms require to be heated to 120° to destroy their toxicity. The active toxic substances of venom are coagulable proteins (globulin), proteases, toxins allied to bacterial toxins, and Faust has separated a non-nitrogenous toxic substance, *ophiotoxin*. The proteases are chiefly proto- and hetero-protease. The venoms are complex mixtures containing some, but not in any venom all, of the following active substances: 1. *Neurotoxins* acting on (a) respiration, (b) heart, (c) muscle, particularly the diaphragm; 2. *Cytolysins*, solvents for (a) blood corpuscles, (b) vascular endothelium, (c) other cells; 3. *Fibrin ferment* inducing blood-clotting, and others. The venoms thus produce paralysis of voluntary muscles and of the heart and respiration, solution of the red- and white-blood corpuscles and hæmorrhages, and the blood may be either fluid or coagulated in the vessels, and the bodies of the dead putrefy rapidly owing to the destruction of the anti-bacterial properties of the blood. The venom is most active when injected into a blood-vessel, whereas in the subcutaneous tissues it may take some time to act: it is also readily absorbed from the eye. Taken by the mouth, provided there are no cracks or ulcers, colubrine venom is harmless, but viperine venom may cause gastritis, &c., and even death. The hæmolysins which cause solution of the red corpuscles are of the nature of 'amboceptors,' requiring a 'complement' (c. *infra* under *Bactericidal sera*) to activate them. In some cases the venom alone can hæmolyse washed red corpuscles *in vitro*, e.g. man, dog, &c., in others it has no action on washed corpuscles but becomes active on the addition of serum. Some corpuscles, therefore, contain the activating 'complement,' others do

not, and, hence, are not hæmolyzed when washed. Kyes, Sachs, Flexner, and Noguchi have shown that lecithin and lecithides in the corpuscles are the complement-like activators of the hæmolytic amboceptors. A venom which is inactive on washed corpuscles becomes active on the addition of lecithin or even of oleic acid or other fatty acids and soaps.

By the cautious treatment of an animal with increasing doses of venom an antitoxin ('antivenin') is formed which has the power of neutralising the particular venom.

The venom of scorpions (against which an antitoxin can be prepared) and spiders is probably protein in nature; of mosquitos and gnats it may be the products of certain bacteria or moulds present in the oesophageal sacs; of bees a protein-free organic base. The formic acid present in the 'venom' of ants, bees, &c., is probably not the active toxin. Many fish are also poisonous by their bites or by spines connected with special glands. Toads and salamanders have acid and basic poisons in the skin glands. Jelly-fish and sea-anemones have stinging glands. Extracts of intestinal worms may be toxic.

[On snake venom, see Martin and Lamb in Allbutt and Rolleston's *System of Med.* vol. ii. pt. ii. (Bibliog.); *Sc. Memoirs of the Gov. of India*, Nos. 1, 3, 4, 5, 7, 10, 16, 17; Faust, *Die Tierischen Gifte* (Braunschweig, 1906, Bibliog.); Noguchi, *Journ. Exper. Med.* viii. and ix.; and *Snake Venoms* (Smithsonian Inst. Publication); Calmette, *Venoms and Venomous Animals* (Bale). On other animal toxins, see Castellani and Chalmers, *Manual of Tropical Med.* (Bibliog.).]

ANTITOXINS.

It is a remarkable fact that proteins on injection into a suitable animal (the domestic mammals generally) give rise to the formation of 'anti-bodies'—substances having properties in some way opposed to those of the proteins injected—which accumulate in the blood of the treated animal. This property of generating anti-bodies, according to Abderhalden, is characteristic of the animal body and is most active against injected cells, proteins, and allied substances. The substance which generates the anti-body is termed the 'antigen.' Antigens, with certain doubtful exceptions, seem to be proteins or substances related to proteins, or possibly lipoids or lipid-protein complexes. Hence mineral poisons, alkaloids, carbohydrates, &c., form no anti-bodies. If a protein such as human serum is injected into a rabbit, the serum of the treated rabbit gives a white precipitate when mixed with human serum, and to a less extent with apes' serum, but with no other sera—a specific 'precipitin' for human serum has been formed. By this means bloodstains, flesh, &c., can be identified with great certainty. By injecting an enzyme, such as rennin, anti-enzyme is formed which inhibits the action of the enzyme; by injecting red-blood corpuscles 'hæmolysin,' solvent for red-blood corpuscles, is formed. If a poisonous protein is injected (in properly graduated doses so as to avoid killing the animal), such as ricin or snake venom, an anti-body is generated which completely neutralises the poisonous

action of the substance injected. The same is the case with toxins like diphtheria and tetanus toxins. By repeated injections of a horse with increasing doses of the toxin, the animal becomes less and less susceptible, so that it can finally tolerate huge doses of the toxin without harm, and coincident with the development of this insusceptibility antidotal substances appear in its blood, and may be obtained in the blood-serum by bleeding the animal and allowing the blood to clot. The antidotal or neutralising substance to toxin is termed antitoxin; it is a fairly stable substance, and by obtaining and bottling the serum aseptically it may be preserved, and is employed to treat the respective disease in man.

The antitoxic serum contains a variable amount of the antitoxic constituent and for therapeutic use must be standardised.

The antitoxic constituent is probably protein (globulin) in nature, or at least is associated with the globulin constituent of the serum. The globulin content of the blood of antitoxin-yielding horses is frequently higher than normal, and the antitoxin may be precipitated by saturation of the serum with magnesium sulphate, or by partial saturation with ammonium sulphate; it comes down with the eu-globulin fraction of the serum globulin.

Brieger and Boer (*l.c.*) separated the antitoxic constituent by the following methods: (a) 4 grms. of potassium iodide or chloride are added to 10 c.c. of the antitoxic serum diluted with an equal quantity of distilled water. After solution, 4-5 grms. of finely-powdered sodium chloride are added, the mixture is kept at 30°-37° for 18-20 hours, and the precipitate (0.4 gm.) is collected; it is the antitoxic portion of the serum with a slight admixture of protein and salts.

(b) The proteins of the antitoxic serum are precipitated with basic lead acetate containing a trace of ammonia, the precipitate is filtered off and the filtrate is saturated with ammonium sulphate. The precipitate is collected and redissolved, the solution is dialysed, and evaporated to dryness. A light powder is obtained (0.06 gm. from 10 c.c. serum) which contains the antitoxic constituent.

(c) 10 c.c. of the serum are diluted with 50 c.c. of distilled water, and 20 c.c. of a 1 p.c. solution of zinc sulphate or chloride are added. The precipitate is collected, dissolved in feebly alkaline water, and the zinc compound is decomposed with carbon dioxide. The antitoxic constituent is present in solution when the precipitant is zinc chloride, but is entangled in the zinc carbonate precipitate when the precipitant is zinc sulphate.

Homer has elaborated a very exact method by partial saturation of the serum with sodium chloride and ammonium sulphate, whereby practically the whole of the antitoxin may be concentrated and recovered from a weak antitoxic serum (*Journ. of Hygiene*, 1918, 22, 51); also MacConkey, *ibid.* 1924, 22, 413.

Anti-venin, the antidotal serum for snake-bites, is a truly antitoxic serum.

In the case of pathogenic micro-organisms which do not form an exo-toxin, an antidotal anti-serum can also be prepared by the injection of the bacterial cells, first killed cultures, and sub-

sequently the living organisms, but such serums are not nearly so potent as the antitoxic serums produced by exo-toxins, and many are practically useless for treating the respective diseases, e.g. typhoid and cholera serums. The principal action of such an anti-serum is bacteriolytic, i.e. it brings about solution of the micro-organism.

In this bacteriolytic reaction (and similarly in the solution of red-blood-corpuscles by a 'hemolytic' serum) two protein substances seem to be concerned. The fresh anti-serum is solvent for bacteria, but not the old, nor the heated (to 56°C.) anti-serum. The two latter may be rendered active again by the addition of fresh normal serum. That is to say, by injection of the bacteria (or blood corpuscles), a new and relatively stable substance is formed, which reacts with an unstable normal constituent of the serum, the two together bringing about bacteriolysis (or hemolysis). To the former, the name of 'immune body' or 'amboceptor,' to the latter, 'alexin' or 'complement,' is given.

Specificity is the distinguishing feature of the anti-bodies; the anti-body produced by an antigen always reacts most actively with this particular antigen.

The formation of anti-bodies is usually explained by Ehrlich's 'side-chain theory.' This supposes that the protoplasmic molecules of the cells of the animal have an affinity for the substance injected (the 'antigen') which gives rise to the anti-body, so that the antigen becomes incorporated with the protoplasm. The union of the antigen with the protoplasm is assumed to be brought about by the combination of atomic groups comparable to the side-chains of a ring nucleus, those of the protoplasmic molecule being termed 'receptor groups,' those of the antigen 'haptophore' (=binding) groups. The poisoning caused by a toxin is thus due to the union of the toxin with the protoplasm by the combination of the haptophore groups of the toxin with the receptor groups of the protoplasm. Should the animal's protoplasm not possess receptor groups having an affinity for the haptophore groups of the toxin, the toxin would not be poisonous to this animal. This is often the case—a toxin is never poisonous to all animals. Now Ehrlich assumed that the protoplasmic receptor groups fulfil physiological functions in the animal, e.g. nutrition, &c., so that when a toxin becomes united with the protoplasm a defect is created, whereby the latter cannot properly fulfil its physiological functions. Provided the dose of toxin be not too large, recovery ensues, due to the regeneration by the protoplasm of the particular receptor groups involved. This process is repeated again and again, and as a result of the continued stimulation by the numerous doses of toxin, the protoplasm ultimately forms the receptor groups in question in large excess—much more than is necessary simply to repair the damage done. A considerable proportion of the now very numerous receptor groups then becomes detached from the protoplasm, accumulates in the blood, and constitutes the anti-body. The antidotal property of antitoxin is, therefore, due to the fact that it saturates the haptophore groups of

the toxin so that the latter is then unable to combine with the protoplasm.

[On antitoxins, &c., see Ehrlich, *Die Wertbemessung des Diphtherieheilserums*, 1897; *Trans. Jenner Inst. of Prev. Med.* ii.; Croonian Lect. Roy. Soc. Lond. 1900; and *Collected Papers on Immunity*, 1909; Hewlett, *Serum and Vaccine Therapy*, Churchill, 1910 (Bibliog.); Kolmer, *Infection, Immunity and Biologic Therapy* (Saunders, 3rd ed. 1923, Bibliog.)]

Toxin-antitoxin reaction.—The neutralisation of toxin by antitoxin is approximately quantitative, and the toxin and antitoxin unite. This is shown by the fact that if a recently-made mixture of toxin and antitoxin be filtered through a gelatin-coated porcelain filter, the toxin passes through into the filtrate, but not the antitoxin (see *ante*). If, however, the mixture be allowed to stand so that interaction may occur, the toxin can no longer be separated from the antitoxin by this method. The interaction between the two is slow, is retarded by cold, and is hastened by warming (Brodie, *l.c.*; Martin and Cherry, *Proc. Roy. Soc. Lond.* lxxiii.).

The exact nature of the union of toxin with antitoxin, 'the toxin-antitoxin reaction,' has been the subject of much controversy, and three principal hypotheses have been formulated to explain it. Ehrlich held that the union is comparable to the combination of a strong acid with a strong base, i.e. the reaction is a complete one, and there cannot be at the same time in a mixture of toxin and antitoxin, free toxin and antitoxin, together with neutralised toxin. The strictly quantitative relation of toxin and antitoxin supported this view, viz. if 10 equivalents of antitoxin exactly neutralise 10 equivalents of toxin, then 100 equivalents of antitoxin will exactly neutralise 100 equivalents of toxin. But it is found that if 100 fatal doses of toxin (for the guinea-pig) are just neutralised by 100 equivalents of antitoxin, 101 fatal doses of toxin + 100 equivalents of antitoxin is *not* a fatal mixture, and generally 108–116 (sometimes many more) fatal doses of toxin must be added to the 100 equivalents of antitoxin to render the mixture a fatal one (the Ehrlich phenomenon). Ehrlich explained this by supposing that the 'toxin broth' contains not one toxic substance only, but is a mixture of toxin and toxone, the latter being much less toxic than toxin, though requiring as much antitoxin to neutralise it as toxin does. Toxin has, however, a greater affinity for antitoxin than toxone has, so that when more toxin is added to a neutral mixture of toxin broth (containing toxin and toxone) and antitoxin, the toxone-antitoxin complex present is dissociated, and the antitoxin set free then combines with the added toxin, and it is not until the added toxin is more than can be neutralised by the freed antitoxin that the mixture becomes fatal. Ehrlich, in fact, was forced to conclude that toxin broth contains diverse toxic bodies. The second hypothesis, that of Arrhenius and Madsen, while admitting that the union of toxin with antitoxin takes place in definite proportions, regards it as comparable to the neutralisation of a weak base by a weak acid, e.g. ammonia and boric acid, the reaction is incomplete, though resulting in equilibrium, so that free toxin and antitoxin exist in the mixture, together with the toxin-

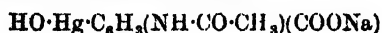
antitoxin complex. The quantity of free toxin would be a function of the relation existing between the initial quantities of the two substances. The Ehrlich phenomenon is quite explicable on this hypothesis, and there is no need to postulate the existence of toxone or other toxic constituents in toxin broth. But other phenomena concerning the neutralisation of toxin by antitoxin do not seem explicable by either of these hypotheses. One of these is what is known as the 'Danysz effect,' which is obtained with many different toxins and their corresponding antitoxins. If a mixture consisting of *a* parts of toxin and *b* parts of antitoxin is exactly neutral, when the whole of the toxin *a* is mixed with the antitoxin; a similar mixture of *a* parts of toxin and *b* parts of antitoxin, prepared by adding the toxin in several fractions to the antitoxin is *still toxic*. This is explained according to Arrhenius and Madsen as being analogous to the neutralisation of chloracetic acid by sodium hydroxide. If equivalent quantities of the acid and base are taken, and only half the acid is added in the first instance to the whole of the hydroxide, the acid is wholly neutralised, leaving half the base free. This then slowly reacts upon the sodium chloracetate forming sodium chloride and glycolate, and the solution ultimately becomes neutral. (Communications from the Nobel Institute, I, iii. 1906). The Danysz effect has its counterpart in the neutralisation of arsenious acid with ferric hydroxide. Bordet maintains that the union of toxin with antitoxin takes place in variable proportions, and resembles the phenomenon of adsorption, similar to the colouring of filter-paper with a dye. Thus, if pieces of filter-paper be placed in a dilute solution of a dye at sufficiently long intervals, the first pieces become distinctly coloured, but the last pieces remain colourless through lack of free dye in the solution. On the other hand, if all the pieces of paper are simultaneously placed in the solution, they all become similarly coloured. Likewise, a mixture of toxin and antitoxin, in which the latter is in insufficient quantity to render the mixture completely innocuous, does not contain, according to Bordet, a certain quantity of free toxin, together with neutralised toxin, but contains only molecules of toxin insufficiently neutralised, because the antitoxin is diffused over all the molecules of toxin, each of which, therefore, fixes an amount of antitoxin too small completely to inactivate it. In a series of mixtures containing increasing quantities of antitoxin for a uniform amount of toxin, each molecule of the latter will, therefore, be united to increasing quantities of antitoxin. The toxicity of the poison will thus become weaker and weaker, and such a series of mixtures will possess all degrees of toxicity. From this conception, reversibility of the toxin-antitoxin combination should exist, and toxin can sometimes be recovered from the toxin-antitoxin complex, showing that it is not destroyed in the interaction. Reversibility can be demonstrated in the case of some antigen-antibody systems, a reversibility which is variable and generally incomplete. On the whole, almost every phenomenon of the toxin-antitoxin reaction seems to be explicable on Bordet's adsorption hypothesis, which is not the case with other hypotheses. Specificity is not explained by

it, nor is it explained by other hypotheses; it may be due to secondary interactions.

[On the toxin-antitoxin reaction, see Ehrlich, Deutsch. med. Woch. 1898; Arrhenius, Immunochimistry (Macmillan Co., 1907), and Quantitative Laws of Biological Chemistry (Bell, 1915), Ergebnisse der Physiol. vii. Jahr., 1908, and Jour. of Hygiene, viii.; Bordet, Ann. Inst. Pasteur. 1899, 1900, 1903; Craw, Jour. of Hygiene, vii., ix.; McKendrick, Proc. Roy. Soc. Lond. B. 1911; Gengou, Jour. State Med. 1912, xx. (Summary and full Bibliog.). Many abstracts in J. Chem. Soc.]

Anaphylaxis. Under certain conditions, an antigen on injection instead of conferring insusceptibility gives rise to increased susceptibility, and this may occur not only with definite toxins but also with proteins, such as egg-white and blood-serum, which are ordinarily innocuous. Thus, if a minute dose of horse-serum be injected into a guinea-pig and three weeks later a second somewhat larger dose be injected, the animal will collapse and probably die in a few minutes. This state of increased susceptibility is known as 'anaphylaxis.' If a course of serum injections be given at intervals not exceeding 14 days, anaphylaxis does not occur. The production of anaphylaxis has been explained as follows: the first serum injection is followed by the formation of an anti-body. This anti-body then reacts with the second dose of serum and in the presence of complement generating a substance, 'anaphylatoxin,' which causes spasm of the bronchial muscles and suffocation. R. T. H.

TOXYNONE. Trade name for sodium m-acetylaminomercuribenzoate



TRACHYTE. A volcanic rock composed mainly of alkali-felspar with usually only small amounts of ferro-magnesian minerals. The presence of the latter give the varieties hornblende-trachyte, augite-trachyte, and mica-trachyte. In mineral and chemical composition they correspond to the coarse-grained plutonic aenities; whilst in appearance they are very like the rhyolites, differing from these in having little or no free silica (when present this is often tridymite rather than quartz). The rock is fine-grained and usually light-greyish in colour. Owing to its more or less cellular structure, it is harsh and rough to the touch, hence the name, from *τραχύς*, rough. Sp.gr. 2.2-2.7; porosity 3-6 p.c.; crushing strength 455-730 tons per square foot. In the normal potash-trachyte the felspar is orthoclase of the sanidine variety, which, besides being present in the groundmass, may form porphyritic crystals sometimes of large size (e.g. on the Drachenfels on the Rhine). In the soda-trachytes anorthoclase and albite are also present. With increasing alkalis there is a passage to phonolite (q.v.). The following analyses are of trachyte from: I, Plateau de l'Angle, Auvergne. II, mica-hypersthene-trachyte, from Monte Amiata, Tuscany (also SO₂ 0.08, Cl 0.01, x 0.33, Li₂O, trace). III, Algersdorf, Midland Mountains of Bohemia (also BaO 0.06, Cl, F, traces: contains sanidine 60, plagioclase 30, augite 5, magnetite 2, sphene 0.8, apatite 0.5 p.c.). IV, 'Piperno' from Arecco quarries, Pianura, Naples (also NaCl 0.19). V, Whitton Hill, Jedburgh, Scotland (Old Red

Sandstone age). VI, Garleton Hills, Haddingtonshire (Carboniferous age).

	I.	II.	II.	IV.	V.	VI.
SiO ₂	63.53	64.76	64.69	61.74	62.44	62.61
TiO ₂	—	0.42	0.31	—	—	—
Al ₂ O ₃	17.81	16.48	18.34	19.24	18.99	18.17
Fe ₂ O ₃	3.92	0.74	—	4.12	3.35	0.32
FeO	—	2.74	3.44	—	1.80	4.25
MnO	—	trace	trace	—	0.25	0.20
CaO	2.31	3.24	1.72	1.14	1.84	2.58
MgO	1.10	1.74	0.50	0.39	1.37	0.74
K ₂ O	5.21	5.49	6.46	5.50	5.02	4.02
Na ₂ O	4.76	2.67	4.61	6.68	2.65	6.49
P ₂ O ₅	—	trace	0.18	—	—	—
H ₂ O	1.16	1.62	0.24	1.12	2.48	0.80
	99.80	100.32	100.57	100.12	100.19	100.18
Sp.gr.	2.64	2.56	2.57	2.59	2.55	2.6

Recent and Tertiary trachytes are found in the Rhenish and Eifel district, Auvergne, central Italy, Canary Islands, &c. These are used on the Continent for building stones, and occasionally for millstones. A variety called locally *piperno* is distinguished by dark flame-like streaks parallel to the lines of flow in a lighter ground; this is from Pianura and Soccavo near Naples, where it is used as a building stone. In the British Isles the trachytes of the Exeter district are of Permian age, and those of the central valley of Scotland of Carboniferous age; these are quarried for road-stones. L. J. S.

TRAGACANTH. *Tragacanthin v. Gums.*

TRASS v. TUFF.

TRAUMATOL v. SYNTHETIC DRUGS.

TRAVERTINE, Calc-sinter, or Calcareous Tufo (*Tuf calcaire*, Fr.; *Kalktuff*, *Tuffstein*, Ger.). A porous, cellular variety of limestone formed by the direct chemical precipitation of calcium carbonate, as the mineral calcite, from calcareous springs. It is of common occurrence in limestone districts, more particularly in those of declining volcanic activity. The liberation of carbon dioxide, on which the precipitation depends, is assisted by the agitation of the water in rapidly-running streams and cascades, and also to a considerable extent by water plants and algae, the material being often deposited around and encrusting reeds, twigs, and mosses. Even in the hot springs at Karlsbad in Bohemia microscopic plants have been found to be important agents in determining the deposition of the calcareous tufo or *Sprudelstein*, which here consists of the mineral aragonite.

The typical locality is at Tivoli, the ancient Tibur, near Rome; hence the name, from the Latin *lapis tiburtinus*, through the Italian *tiburtino* and its corrupted form *travertino*. Here the most important deposit, with a thickness of 500 feet, occupies the site of an ancient crater lake into which issued the sulphuro-calcareous waters of the Acque Albule thermal springs. The material is being deposited under the same conditions at the present day in the Lago di Zolfo in the Roman Campagna. It is also seen in process of formation at the cataracts of the Anio at Tivoli. Travertine is the principal building stone of ancient and modern Rome. The quarries of Barco, on the Anio, furnished the stone for the Colosseum, and those of Fosse the material for St. Peter's church. To supply modern Rome new quarries have been opened at the Villa Adriana below Tivoli. Roman travertine has also been exported, being used,

for instance, for the columns supporting the arched roof of the new (1910) railway station in New York. The stone is whitish or light cream-coloured, porous, and with wavy lines of lamination; sp.gr. 2.35. When freshly quarried it is soft enough to be cut with a saw, but it hardens on exposure (N. Pelati, I Travertini della Campagna Romana, Rome, 1882; P. Zezi, in H. J. Johnston-Lavis's *South Italian Volcanoes*, Naples, 1891, 83).

Similar deposits of travertine are formed by the thermal springs at Clermont and Vichy in the Auvergne, Hieropolis in Asia Minor, &c. Analyses of travertine from Vichy (C. Girard and F. Bordas, C.R., 1891, 132, 1423) show CaCO_3 , 91.71-97.17, MgCO_3 , 1.01-2.10 p.c., with small amounts of carbonates of sodium, potassium, manganese, and iron, sodium phosphate, aluminium sulphate, ferric arsenate (trace to 0.342 p.c.), alumina, silica, insoluble residue, and traces of copper, barium, lithium, and chlorine. In the British Isles small deposits are found in limestone districts, e.g. at Matlock Bath in Derbyshire, Knaresborough in Yorkshire, and it was formerly quarried at Dursley in Gloucestershire and elsewhere as a building stone, but now it is employed only for rock-gardens and aquaria. In all these instances the travertine is of recent formation, but material of the same mode of origin, though now more compacted, is met with in the geological series of sedimentary rocks

L. J. S.

TREACLE *v.* SUGAR.

TREE WAX *v.* *Insect wax*, art. WAXES.

TREHALOSE *v.* CARBOHYDRATES.

TREMOLITE *v.* ASBESTOS AND HORNBLENDE.

TRENT SAND. A sand found in the Trent, Severn, and in other rivers; used for polishing.

TRICALCOL. Trade name for a combination of tricalcium phosphate and albumen.

TRICARBIN (*Glycarbin*). Glyceryl carbonate.

TRIDECOIC or **TRIDECYLIC ACID** $\text{C}_{13}\text{H}_{25}\text{COOH}$ is obtained by the oxidation of methyl tridecyl ketone; it crystallises in thin plates; m.p. 40.5°; b.p. 236° (100 mm.) (Krafft, Ber. 1879, 1668).

TRIDYMITE. One of the three crystalline modifications of native silica, SiO_2 , of much less common occurrence than quartz (*q.v.*) but more frequent than cristobalite (*q.v.*). The crystals have the form of thin hexagonal plates or scales, which are often grouped with a fan-like arrangement or in rosettes. These crystals are, however, pseudo-hexagonal, since, when examined under the polarising microscope, they are seen to be built up of two or more optically biaxial individuals, the symmetry of which is probably orthorhombic. At a temperature of 117° these optical anomalies disappear, and the crystals are then optically uniaxial and truly hexagonal. The hexagonal plates themselves are also twinned together, often in radial groups of three; hence the name of this mineral, from *tridymos*, threefold. Other more complex types of twinning also exist, producing at times pseudocubic forms. The crystals are dull and of a white or greyish colour. They are quite small, usually 1 or 2 mm. across, and only exceptionally as much as $\frac{1}{2}$ cm. Sp.gr. 2.28-2.3; H. 7; mean refractive index (Na) 1.477. In addition

to the much lower sp.gr., the mineral also differs from quartz in being soluble in a boiling solution of sodium carbonate. The crystals are, however, often altered to an aggregate of differently orientated grains of quartz, being, in fact, paramorphs of quartz after tridymite.

Tridymite occurs principally in acid volcanic rocks—rhyolite, andesite, and especially trachyte—the crystals being attached to the sides of cavities in the rock. It is also found in blocks of sandstone and quartzite that have been caught up and baked by lavas. Well-known localities are in trachytes at the Euganean Hills near Padua, the Drachenfels on the Rhine, Mont Dore in Auvergne, &c. At the Cerro San Cristobal, near Pachuca in Mexico, it occurs together with cristobalite in andesite. Other modes of occurrence are: as crystals embedded in opal; in zeolitised Roman tiles at the hot springs of Plombières in France; in fulgurites produced by the fusing of siliceous rocks by lightning; and rarely (as 'asmanite') in meteoric stones and irons. It has also been observed as a furnace product, e.g. in the vitrified walls of zinc muffles, and as fibrous concretionary masses in blast furnaces; and it has been formed by the burning of stacks of straw. It has been produced artificially by a variety of methods, both by wet methods (hot solutions under pressure) and by dry fusion. The silica skeleton obtained by dissolving silicates in blowpipe beads of microcosmic salt consists of tridymite. The best crystals are obtained from quartz in a sodium tungstate fusion. The products are only to be distinguished by their optical characters under the microscope. But the very frequent formation by artificial means unintentionally has only recently been recognised. As noted below, quartz is converted into tridymite at 870° with a considerable increase in volume (16.2 p.c., corresponding to the change in sp.gr. from 2.65 to 2.28). This has an important bearing on the siliceous refractory materials used for furnace linings and silica-bricks. Coarsely powdered quartzite quickly heated to 1400° in presence of a small quantity of a catalyst is converted after five or six hours into almost pure tridymite (Rebuffat, Trans. Ceram. Soc. 1923-24, 23, 14; J. Soc. Chem. Ind. 1924, 43, B. 514).

In addition to the reversible inversion of α -tridymite to β -tridymite at 117° noted above, the heating curve shows a second break at 163°, indicating another inversion β -tridymite \rightarrow β' -tridymite. Here there is no observable change in the optical characters, and the change is perhaps one of degree of symmetry, analogous to α -quartz \rightarrow β -quartz at 575°. At ordinary temperatures quartz is the only stable crystalline modification of silica, but at 870° it passes over into tridymite with an accompanying increase in volume. At 1470° this tridymite is changed into cristobalite, which melts at 1625°. Tridymite is therefore the stable form between the temperatures 870° and 1470°, but the velocity of transformation being slow it can also exist at lower temperatures. In this connection we

¹ C. N. Fenner, *The Stability Relations of the Silica Minerals*, Amer. J. Sci. 1918, 26, 331, 37, also Shepherd, Rankin, and Wright, *ibid.* 1909, 28, 332; C. Johns, *Geol. Mag.* 1906, 3, 118. Ferguson and Merwin, *Amer. J. Sci.* 1918, 46, 417 give the melting-point of tridymite as 1670° and of cristobalite as 1710°.

may recall the frequent occurrence in nature of paramorphs of quartz after tridymite; and also the fact that tridymite is not found in older (pre-Tertiary) volcanic rocks. L. J. S.

TRIFOLIN v. GLUCOSIDES.

TRIGEMIN, TRIPHENIN, v. SYNTHETIC DRUGS.

TRIGONELLINE (*Methyl betaine of nicotinic acid*) $C_7H_{11}NO_3$ is an alkaloid which occurs in the seeds of *Trigonella Foenum-graecum* (Linn.); in ordinary peas (*Pisum sativum* [Linn.]); in hemp seeds (*Cannabis sativa* [Linn.]) (Jahns, Ber. 1885, 18, 2518; Schulze and Frankfurt, *ibid.* 1894, 27, 769; Schulze and Winterstein, Landw. Versuchs. Stats. 1895, 46, 23); in commercial strophanthine and in the seeds of *Strophanthus hispidus* (DC.) and *S. Kombé* (Oliver) (Thoms, Ber. 1898, 31, 271, 404; Karsten, Chem. Zentr. 1902, ii. 1514). Trigonelline has also been found in an animal, the sea-urchin (*Arbacia pustulosa*) (Holtz, Kutscher and Thielmann, Z. Biol. 1924, 81, 57; Chem. Soc. Abstr. 1924, 126, i. 907).

Preparation.—The powdered seeds are extracted with alcohol; after distilling off the latter, lead acetate and caustic soda are added, and the alkaloid is separated by means of potassium bismuth iodide and sulphuric acid. The precipitate is then treated with caustic soda to separate albuminoids, the filtered solution is neutralised with sulphuric acid and precipitated with mercuric chloride. The choline so precipitated is removed by filtration, the filtrate acidified with sulphuric acid, and the trigonelline in the form of its mercury iodide salt is then precipitated. The free base is obtained by decomposing the double salt with a sulphide (see Schulze, Zeitsch. physiol. Chem. 1909, 80, 155).

Trigonelline has also been obtained by treating nicotinic acid with methyl iodide, and the product of the reaction with silver hydroxide (Hantzsch, Ber. 1886, 19, 31); or by the oxidation of nicotine *iso*-methoxyhydroxide, with potassium permanganate (Pictet and Genequand, Ber. 1897, 30, 2117, 2122).

Trigonelline crystallises with one molecule of water, forming colourless, flat prisms of feeble saline taste and neutral reaction. It is hygroscopic, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether, benzene, and chloroform. When heated, it loses its water of crystallisation and dissolves or melts in the latter at 130°. The anhydrous alkaloid darkens when heated at 200°, and melts at 218° (decomp.). When heated with barium hydroxide at 120° trigonelline evolves all its nitrogen as dimethylamine, and when heated with excess of hydrochloric acid, it yields nicotinic acid and a gas, probably methyl chloride (Jahns, Ber. 1887, 20, 2840). It gives the usual reactions of an alkaloid with reagents.

On reduction of trigonelline with hydrogen in presence of platinum black it forms products resembling, but apparently not identical with, those of arecaidine (Winterstein and Weinhegen, Zeitsch. physiol. Chem. 1917, 100, 170).

A *hydrochloride*, *platinohydrochloride*, and two *aurochlorides* $C_7H_{11}NO_3 \cdot HCl \cdot AuCl_3$, m.p. 198°, and $4(C_7H_{11}NO_3) \cdot 3HCl \cdot 3AuCl_3$, m.p. 186° (Jahns, l.c.; Schulze and Frankfurt, l.c.), are known. The ferrocyanide and ferricyanide crystallise in red and yellow prisms respectively (Roeder, Ber.

1913, 46, 3724). For the physiological action of trigonelline, see Kohlrausch, Chem. Zentr. 1909, ii. 465; Zeitsch. Biol. 1911, 57, 273; for its origin, see Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 46 (v. BETAINES).

TRIHIDROXYBENZENE v. PHENOL AND ITS HOMOLOGUES.

TRIKETOHYDRINDENE v. KETONES, INDENE.

TRIKETONES v. KETONES.

TRIMETHOL. Trimethylmethoxyphenol.

TRIMETHYLACETIC ACID v. VALERIC ACIDS.

TRIMETHYLBENZENES v. CUMENES.

TRIMETHYLENE v. PROPYL.

TRIMETHYLHISTIDINE v. BETAINES.

TRIMETHYLHYDROXYBENZENE v. PHENOL AND ITS HOMOLOGUES.

TRIMYRISTIN. Piettre and Roeland (Compt. rend. 1924, 278, 2283; Analyst, 1924, 49, 437) obtained 2 grms. of trimyristin (see Vol. IV., p. 405) by dissolving the fat from one litre of milk in a mixture of ether and alcohol and allowing the solution to cool slowly.

TRINITRIN. Syn. for nitroglycerin.

TRINITROPHENOL v. PICRIC ACID.

TRIONAL (*diethylsulphonemethylethylmethane* or *methyl sulphonol*) $CH_3(C_2H_5)_2C(SO_2C_2H_5)_2$ is prepared, like sulphonol and tetronal, from methyl ethyl ketone and ethyl mercaptan (Fromm, Annalen, 1889, 253, 150; D. R. P. 49073; Frdl. 1887–1890, ii. 521). It forms colourless, odourless, lustrous square tablets, m.p. 76°, soluble in 320 parts of cold water, but more readily so in boiling water, in ether, and in alcohol. It is employed in medicine for the same purposes as sulphonol and tetronal, v. SYNTHETIC DRUGS. For its detection, v. SULPHONAL AND TETRONAL.

TRIPHANE v. SPODUMENE.

TRIPHENIN. *p*-Propionyl-phenetidine, used as an antipyretic.

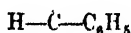
TRIPHENYLMETHANE COLOURING MATTERS.

TERS. This is the generic name of a very large and varied class of artificial dye-stuffs which have been obtained by very different methods. Some of the oldest artificial dye-stuffs belong to this group. Their generic connection was, in many instances, not known until their constitution was fully ascertained. When this had been done, a large number of new dye-stuffs belonging to the same class was prepared by direct synthesis. The members of this group vary more than those of any other in their physical properties; they represent almost every possible shade, and include dye-stuffs suitable for almost every kind of dyeing and printing process. They are applicable to silk, wool, and cotton dyeing; as a rule, they are of very pure and brilliant shades—in fact, the most brilliant of all colouring matters are found amongst them. Many are rather fugitive, especially the older ones—magenta-red and its congeners. It is for this reason that aniline dyes generally have been declared fugitive and unstable by people of hasty judgment. This want of stability is, however, not characteristic of the triphenylmethane group; some of the best and most permanent dye-stuffs belong to it. It may be well to remark at once that resistance to light and other influences seems not to be directly related to the chemical constitution of these substances, as it is frequently observed that of two

dye-stuffs of very similar constitution one may be very fugitive, whilst the other is remarkable for its fastness. The fastness of these and other dye-stuffs also depends to some extent on the manner in which they are applied to the textile fibre.

The members of this family are not, like those of the azo- group, connected by one generic method, by which all of them might be produced from various materials. Nor is it possible to enumerate a number of general synthetic methods which result in their production. The methods applicable are so numerous that no generalisation is possible. The only connecting link between all these dyes is their chemical constitution, which is now well established in almost every case; it is also in this constitution that we find the necessary criteria for the subdivision of the group. Some introductory remarks about the constitution of these dyes are therefore necessary for a complete revision of the subject.

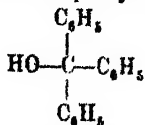
If we consider the constitution of these colouring matters, we observe that there is but one characteristic feature common to them all. This is the presence of an atom of carbon connected by three of its valencies to three aromatic radicles. The compound of the simplest constitutional formula in which this 'central carbon' (as we will henceforth call it) is observed is the hydrocarbon triphenylmethane, the formula of which is $C_{19}H_{15}$.



Triphenylmethane thus becomes the prototype of all the members of this group; it is for this reason that the name of *triphenylmethane colouring matters* was chosen.

Triphenylmethane was first prepared by Kekulé and Franchimont, in 1872, by heating benzylidene chloride with mercury diphenide to 150° (Ber. 5, 907). Its formation has since been observed in numerous reactions. The best method for preparing it consists in treating a mixture of two parts of chloroform and seven parts of benzene with aluminium chloride, until no more hydrogen chloride is given off. The resulting liquid is washed with water and dried. On distillation it yields benzene, diphenylmethane, and triphenylmethane. The last may be purified by crystallisation. This method was indicated by Friedel and Crafts (Ann. Chim. Phys. [vi.] 1, 489). Triphenylmethane is obtained in colourless crystals; m.p. 92° ; b.p. 355° - 359° . It is capable of forming a molecular compound with benzene. Of its derivatives the following three are important on account of their relations to the colouring matters under consideration.

Triphenylcarbinol $C_{19}H_{16}O$ is the tertiary alcohol derived from triphenylmethane:



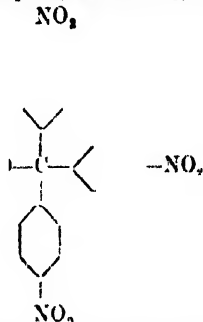
It is easily obtained by oxidising the hydrocarbon by means of chromic acid. It forms

colourless crystals, melting at 159° and boiling at 360° (E. and O. Fischer, Annalen, 194, 271).

In boiling glacial acetic acid it is readily reconverted to triphenylmethane either by hydriodic acid (Tschitschibabin, Ber. 1911, 44, 441) or by trioxymethylene in presence of a small quantity of conc. sulphuric acid (Banda, Anal. Fis. Quim. 1913, 11, 599; cf. J. Chem. Soc. 1914, i. 279). For the use of formic acid for this purpose, see Guyot and Korache (Comp. rend. 1912, 154, 121, and 1913, 156, 1324).

Trinitrotriphenylmethane $C_{19}H_{13}N_3O_6$ is obtained by treating the hydrocarbon with strong nitric acid. Crystals, melting at 203° . Chromic acid transforms it into trinitrotriphenylcarbinol (E. and O. Fischer, *ibid.* 194, 250).

Tri-*p*-nitrotriphenylcarbinol $C_{19}H_{13}N_3O_7$:



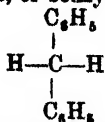
is best crystallised from glacial acetic acid and forms small crystals, melting at 171° - 172° and soluble in alcoholic potash solution with a beautiful reddish-blue colour.

None of the above substances is a colouring matter, nor are they even coloured. But if we reduce trinitrotriphenylcarbinol by adding zinc-dust to its solution in acetic acid, we obtain triaminotriphenylcarbinol, which is identical with pararosaniline. By showing this identity, E. and O. Fischer solved the problem of the constitution of this very important colouring matter. Leucaniline, the reduction product of rosaniline, was shown to be identical with triaminotriphenylmethane. This discovery became the starting-point for very important theoretical and practical work. All the congeners of rosaniline were shown to be derivatives of triphenylmethane or analogous hydrocarbons, and new synthetical methods were devised by which such derivatives could be obtained.

It is quite obvious that not only triphenylmethane, but also all its homologues and analogous hydrocarbons, are parent substances of dye-stuffs. The number of such hydrocarbons indicated by theory is very large, since every one of the three phenyl radicles connected with the central carbon may be replaced by any other aromatic radicle. Every one of the hydrocarbons thus formed is capable of yielding, like triphenylmethane itself, a very large number of colouring matters, as will be seen from subsequent considerations. It thus becomes evident that the theoretical number of possible triphenylmethane colouring matters is almost unlimited. It has, however, been shown that the variation of the aromatic radicles connected with the central carbon is not the only point of importance as regards the variation of the shades and properties of the resulting

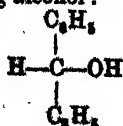
dye-stuffs. The triphenylmethane colouring matters in actual use are the derivatives of a very few hydrocarbons, of which triphenylmethane itself is by far the most important. Tolyldiphenylmethane, ditolyldiphenylmethane, tritolyldiphenylmethane, and naphthyldiphenylmethane are the principal parent substances of a large number of colouring matters, which at present form the object of regular and extensive manufacture, and of several hundred more which have been prepared and patented without coming into general use. The extensive range of shade and general applicability, so characteristic of the colouring matters of this class, and unequalled by any other class of dye-stuffs known, is not so much a result of the variation of the hydrocarbons forming their parent substances, as of the extremely large number of coloured derivatives which may be produced from every one of these hydrocarbons. No other branch of the chemistry of dye-stuffs is so extremely fertile in the synthetical methods at its disposal as this, and every one of these methods forms an easy way for the production of a considerable number of dye-stuffs, which can generally be produced by this one method alone. Many of these methods, both empirical and synthetical, have been patented, and some of these patents are of great value and importance. They are generally 'process' patents, claiming new methods of manufacture; in this respect they form the exact counterpart of the still more numerous 'substance' patents for azo-colouring matters, which, being all based on the same method of work, only claim the novelty of the product obtained by varying the ingredients of the process.

Before entering into the details of the constitution of triphenylmethane dye-stuffs, and the connection of this constitution with the properties of the dyes, we have to describe another substance closely related to triphenylmethane, some of the derivatives of which are dye-stuffs similar to those derived from triphenylmethane itself, whilst others play an important part in the process for the production of triphenylmethane colouring matters. This substance is also a hydrocarbon, derived from methane by replacing only two of its hydrogen atoms by the aromatic radicle phenyl. This hydrocarbon is *diphenylmethane*, or benzyl-benzene $C_{11}H_{12}$:



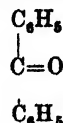
It was discovered by Zincke in 1873 (Annalen, 159, 374), and is best prepared by the method indicated by Friedel and Baisohn (Bull. Soc. chim. [ii.] 33, 337), by adding aluminium chloride to a mixture of 1 part benzyl chloride with 5 parts of benzene. It melts at 26° - 27° , and boils at 261° - 262° . It forms white crystals, possessing an agreeable odour of oranges. Of its derivatives the following are of practical importance:—

Diphenylcarbinol or benzhydrol $C_{11}H_{12}O$ is the corresponding alcohol:



It is prepared by boiling benzophenone with alcoholic potash solution and zinc-dust. It forms white crystals, melting at 67.5° - 68° , boiling at 297° - 298° (Linnemann, Annalen, 133, 6; Zagumenny, *ibid.* 184, 174).

Benzophenone $C_{13}H_{10}O$ is the second product of oxidation of diphenylmethane, to which it stands in the same relation as that which exists between propane and acetone. Benzophenone is the typical ketone of the aromatic series



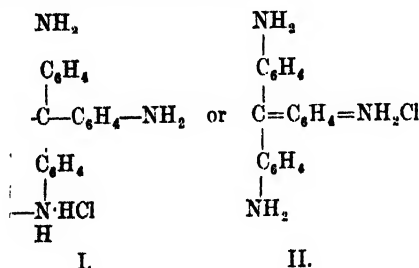
It is prepared by the process which led to its original discovery, by distilling calcium benzoate, or, better still, by distilling a mixture of calcium and zinc benzoate. Another process consists in adding aluminium chloride to a solution of carbonyl chloride $COCl_2$ (phosgene) in pure benzene, or to a mixture of benzene with benzoyl chloride. Benzophenone forms beautiful prismatic crystals, melting at 48° - 48.5° , distilling at 305° (Péligot, Annalen, 12, 41; Chancel, *ibid.* 72, 279; Friedel, Crafts and Ador, Ber. 10, 1854) (*v.* QUINONES).

The amino derivatives of diphenylmethane diphenylcarbinol, and benzophenone, which are of special importance in the chemistry of the triphenylmethane dye-stuffs, will be described subsequently in connection with the dye-stuffs to which they give rise.

The substances mentioned so far, although the parent substances of so many beautiful dyes, are all perfectly colourless. Even triaminotriphenylcarbinol, which is identical with *p*-rosaniline, is perfectly colourless; it only becomes a dye-stuff by being dissolved in an acid, a reaction from which one might infer that *p*-fuchsin, the typical magenta colour, is merely a salt of *p*-rosaniline. This is, however, not the case, although colour-makers are apt to call, for simplicity's sake, the rosanilines 'magenta bases.' In this connection a decision of the U.S.A. Customs Authorities is of interest, in that they upheld the claim of an importer; that rosaniline, not being itself a dye, should be subject to duty (20 p.c. ad. val.) as 'a coal-tar product not being a colour or dye,' and not to the duty (30 p.c. ad. val.) levied upon coal-tar colours or dyes (U.S.A. Cust. decision, Oil Paint and Drug Rep. Nov. 3, 1913, *cf.* J. Soc. Chem. Ind. 1913, 1060). The dissolution of any or either of the aminocarbinols in an acid is invariably accompanied by a condensation in the molecule, and a loss of one molecule of water. The basic triphenylmethane colouring matters are therefore free from oxygen (unless they contain it in the shape of water of crystallisation); if we decompose the salts, by the addition of an alkali, coloured bases are formed, which, however, are very unstable. They take up, at once, one molecule of water, and re-form the original colourless or faintly-coloured carbinol base. If the precipitation is carried out by means of ammonia instead of sodium hydroxide or carbonate, or if ammonia be present in the liquid, the carbinol base is partly or wholly transformed into the corresponding amino compound.

as has been shown by Villiger and Kopetschni, Ber. 45, 2910, and by Nölting and Saas, *ibid.* 46, 952. By this observation it is clearly shown that something more than the presence of the 'central carbon' is necessary for the formation of a triphenylmethane colouring matter. We have, therefore, to consider the constitution of the colouring matters themselves to obtain a knowledge of the chromophoric group of these dye-stuffs. This consideration leads at the same time to an easy and useful classification, to a subdivision into a series of small groups, the members of which show a closer connection in their methods of formation, their physical properties, and their manner of application.

The constitution of parafuchsin is now established beyond any doubt. It may be represented by the following formulæ:



which are practically identical, II. corresponding to the modern way of expressing 'quinonoid' structure. This formulation will therefore be used exclusively in this article to explain the constitution of the dyestuffs to which it refers, whilst formulæ corresponding to I. have been used in the first edition of this work. For alternative formulæ more recently suggested by Kauffmann, see Ber. 1912, 45, 781. For consideration of the salts of triphenylmethane bases which are formed in strongly acid solutions, see Kehrman, Ber. 1918, 51, 468. The formulæ chosen show also the typical constitution of all the congeners of magenta, every one of which may be represented by similar formula, in which either one or more of the phenyl radicles is replaced by other aromatic radicles, or one of the amino groups replaced by hydrogen, or one of the six available hydrogen atoms of the amino groups replaced by radicles of the fatty or aromatic series, or several of these changes introduced at the same time. It will at once be obvious that several thousand different combinations may thus be produced, all colouring matters of different shades, but showing in their properties a general resemblance to parafuchsin. The constitutional formulæ of all these colouring matters have but one thing in common besides the 'central carbon' (which is, as has been said, characteristic not only of these, but also of all the other triphenylmethane colouring matters); this one essential feature is the quinonoid nature of the substance, expressed in the structural formula either by the connection between the central carbon atom and the pentavalent nitrogen (as shown in formula I.), or, as it has become customary of late, by shifting the double valencies in the benzene hexagon and connecting it accordingly with the other parts of the molecule, as shown in formula II. We

have, therefore, a perfect right to claim this invariably present quinonoid configuration as the essential feature of the whole molecule, and as the cause of its being a colouring matter. It forms a part of the chromophoric group of the fuchsin family.

It is, however, important to notice that, no matter how we write the structural formula of *p*-fuchsin or any of its congeners, whether we use the older or the more modern way of expressing the quinonoid nature of the substance, one of the amino groups present is always taking part in the quinonoid chromophoric group and therefore is no longer available as an auxochromic group. To supply this, at least one more amino-group must be present, and this is the reason why only di- or poly-amino derivatives of triphenylmethane can become mother-substances of dye-stuffs belonging to this group. On the other hand, both the amino groups of auxochromic nature, as well as the one entering into the chromophoric part of the molecule, may be replaced by other suitable groups. The hydroxyl group with its tendency to form salts by combining with metallic ions is as important an auxochromic group in the series of triphenylmethane dye-stuffs as in any other. And the quinonoid imino group contained in the chromophore, may, as in other dye-stuffs, be replaced by an oxygen atom acting in similar capacity. Thus we obtain two separate groups of dye-stuffs, the first of which, generally called the *fuchsin group*, is characterised by the presence of nitrogen and the basic nature of its members; the second, called the *aurin group*, by the absence of nitrogen and the phenolic character of the dyestuffs it embraces. In addition to these two groups, a third one, the *phthalein group*, has been established by the common consent of all authors on the subject. This group contains a large number of important dye-stuffs of both basic and acid nature, which have this in common, that they are all derived from phthalic acid and take their 'central carbon' from one of the carboxyl groups of this acid, whilst the other, remaining available, enters the molecule of the dye-stuff and thus renders the latter a true organic acid, which is not necessarily the case amongst the members of the fuchsin and aurin group. Moreover almost all the phthalein dye-stuffs of any practical importance contain, in addition to the typical chromophore of the triphenylmethane colouring matters, an additional one in the shape of the 'pyrone' ring, formed by the elimination of water from certain suitably placed hydroxyl groups of the molecule. This pyrone ring will be easily recognised in the formulæ of the members of the phthalein group to be given subsequently. The fact that only those phthaleins, which contain this pyrone ring, are colouring matters of any practical value, greatly diminishes the number of possibilities for the synthesis of such dye-stuffs, which might be made to form a class of their own, if it had not become customary to treat them as a special division of the triphenylmethane group of colouring-matters.

We now proceed to give a detailed account of these three groups and their various members, of which, however, we shall enumerate only those which are, either scientifically or practically, important. For a complete list we refer the

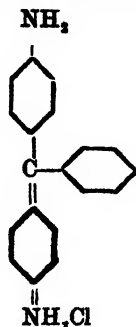
reader to the well-known tables of Schultz and Julius,¹ or the more recent "Colour Index."²

I. THE FUCHSIN GROUP.

(A) Diaminotriphenylmethane derivatives.—

The simplest type of these colouring matters is

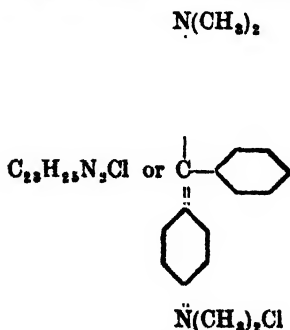
1. Benzaldehyde violet $C_{15}H_{11}N_2Cl$ or



which may be prepared from diaminotriphenylmethane by oxidation. The yields are, however, very poor, and the colour itself is of no great value. Its manufacture has, therefore, never been taken up.

The derivatives of this substance, however, in which the hydrogen of its two amino groups is replaced by various radicles of either the fatty or aromatic series, are of great value and importance. Of these, the oldest, best known, and simplest in its constitution, is

2. Benzaldehyde green. (Syn. *Malachite green*, *New green*, *Victoria green*, *Fast green*, *Diamond green*, *Benzoyl green*, *Benzal green*.)



This product was discovered almost simultaneously by Otto Fischer (1877; Ber. 10, 1625) and O. Döbner (1878; *ibid.* 11, 1236), who prepared it by different methods. For some time it was believed that Döbner's product was different from Fischer's until their identity was finally established. Döbner's process was patented (D. R. P. 4322). Fischer's process found, however, more favour with the majority of manufacturers, and has mostly been adopted.

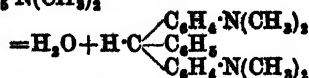
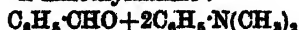
Fischer's process gave bad yields and a poor product at first, until the best method for its manufacture was worked out. It consists in the following operations:—

(a) Manufacture of tetramethyldiaminotri-

¹ *Gustav Schultz und Paul Julius. Tabellarische Uebersicht der künstlichen organischen Farbstoffe* Berlin (Fifth edition, 1914.)

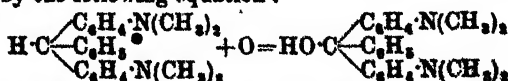
² "Colour Index," published by the Society of Dyers and Colourists, Bradford, 1925-6.

phenylmethane by the action of benzaldehyde on dimethylaniline:



The base obtained in this reaction is generally called 'green leuco base' by the manufacturers. For preparing it one molecule of benzaldehyde is mixed with very little more than two molecules of absolutely pure dimethylaniline, a substance capable of absorbing the water formed in the reaction being added. Dry zinc chloride was originally employed, and is still used by many manufacturers. In quantity it should be equal in weight to the aldehyde employed. Hydrochloric, sulphuric, or anhydrous oxalic acid, or acid sodium sulphate may be used instead of the zinc salt. The mixture is heated in a jacketed still to 100°–110° for about forty-five to forty-eight hours. The product is then transferred to a still, a sufficient quantity of caustic soda is added to make the mixture alkaline to test-paper, and a current of steam is blown through the liquid in order to remove every trace of dimethylaniline and benzaldehyde. The leuco base is not volatile; it remains in the still in the shape of a viscid mass, which solidifies into white crystals after a while. This base is now subjected to the second operation.

(b) Oxidation into green. It is here that great difficulties were encountered in the beginning of the manufacture. Special conditions are required to obtain a good crystallisable dye-stuff. If these are not strictly adhered to, a non-crystallisable green is the result. The latter is different from the crystallisable substance in composition, containing one methyl group less, which is lost in the shape of formaldehyde by a too powerful action of the oxidising agents. The following conditions give excellent results: 33 kilos of leuco base are dissolved in 25 kilos of ordinary hydrochloric acid, and diluted with 200 litres of water; 30 kilos of ordinary acetic acid of 45–50 p.c. are then added. It is necessary that these two acids should be present; neither of them can be replaced by another acid of equal strength. The solution is then oxidised in the cold (in the summer it is advisable to add some ice) with a paste of lead peroxide of known strength. The peroxide should be tested by the oxalic acid method (determination of the CO_2 evolved from an excess of oxalic acid by the peroxide in question), and not by the iodometric method, as the latter gives too high results. Every kind of lead peroxide contains a certain amount of crystalline peroxide, which neither acts on the leuco base, and is therefore quite irrelevant in its oxidation into green, nor on oxalic acid, whilst the iodometric method gives values for both modifications indiscriminately. For oxidising the leuco base the exact quantity of peroxide should be taken, which is indicated by the following equation:

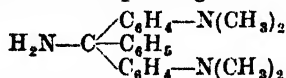


One molecule of active peroxide is, therefore, required for every molecule of the base.

As soon as the peroxide has been added

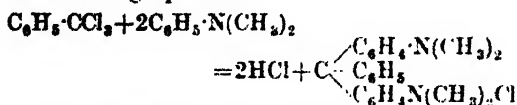
with constant stirring, the liquid turns a deep green. From this liquid the dye-stuff may be separated by various methods; an addition of zinc chloride solution is generally recommended. This, however, precipitates both the crystalline green and the tarry modification which is never quite absent. The following process has given excellent results in the hands of the writer.

The green liquid obtained by oxidation is saturated with common salt. On standing small glittering scales of the lead double chloride of the crystallisable green very soon make their appearance, and are collected on a filter. From the mother-liquor an inferior quality of green may be obtained by adding a solution of sodium sulphate, filtering, and precipitating with zinc chloride and common salt. The crystals of the lead double chloride are dissolved in hot water, and sufficient sodium sulphate is added to precipitate the lead. The liquid is then filtered and precipitated with ammonia. The 'green base' (a mixture of tetramethyl-diaminotriphenyl-carbinol with the corresponding amino derivative



discovered by Villiger and Kopetschni) settles out in the shape of a pink precipitate, which is filtered off and washed. From it the 'green crystals' of commerce may be prepared, either by dissolving it in a hot solution of oxalic acid and allowing the liquid to cool very slowly, or by dissolving it in dilute hydrochloric acid and adding a solution of zinc chloride. Besides these two the iron double salt is also occasionally met with in commerce. The picrate is also sold under the name of 'spirit green.'

Döbner's process.—This consists in heating dimethylaniline with benzotrichloride in presence of metallic chlorides. This process has certain advantages if benzotrichloride is available at a low price. It may be represented by the following equation:



The following proportions are recommended in the patent:

3 parts dimethylaniline,
2 „ benzotrichloride,
1.5 „ zinc chloride.

These are to be heated for three hours to 110° in an enamelled iron vessel with constant stirring. The resulting melt is transferred to a still, and steam is blown through it to remove all excess of trichloride. It is then thoroughly extracted by boiling water. The filtrate is now precipitated by salt, and the precipitate recrystallised from water. The dye-stuff is always obtained in the shape of the zinc double chloride.

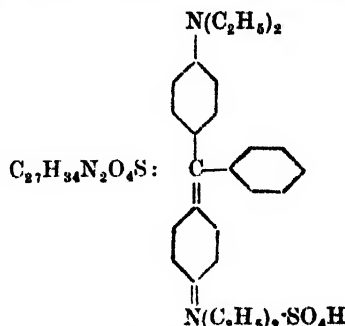
The oxalate of benzaldehyde green forms large plates of an intense grass-green colour, which dissolve easily in hot water. It contains three molecules of oxalic acid to every two of green base.

The zinc double chloride, which has the composition $3(\text{C}_{23}\text{H}_{22}\text{N}_2\text{Cl}) \cdot 2\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, forms green crystals with a fine yellow metallic lustre. It is not quite so easily soluble as the oxalate.

The application of these salts is similar to

that of all the basic dye-stuffs, and need not here be described.

3. Brilliant green. (Syn. *Ethyl green*, *Emerald green*; also all the other names given for the preceding compound, with the addition of the letters G, J, or Y (meaning *gelb*, *jaune*, or *yellow*).



is prepared from diethylaniline by exactly the same process as described for benzaldehyde green. After precipitating the free green base, it is transformed into its sulphate by mixing it with the theoretical quantity of sulphuric acid diluted with its own weight of alcohol. The mixture forms a thick tar at first, but suddenly solidifies into a mass of well-defined crystals.

The shade of this green is considerably yellower than that of the ordinary benzaldehyde green.

4. Victoria green 3 B. $\text{C}_{23}\text{H}_{22}\text{N}_2\text{Cl}_3$. This is a colouring matter prepared from dichlorobenzaldehyde instead of the ordinary benzaldehyde. It is considerably bluer in shade than the ordinary benzaldehyde green. A large number of similarly constituted bluish-greens and greenish-blues is manufactured and sold, especially by the Swiss colour-works.

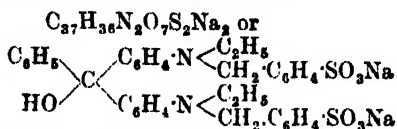
Acid greens. Considerable importance has always been attached by dyers to the sulpho derivatives of basic colouring matters, because these are more easily and evenly dyed on wool than the hydrochlorides and other salts of the bases themselves. Many attempts have, therefore, been made to obtain acid greens. They were at first only partly successful; at present there are, however, several acid greens in commerce, ranging in shade from a yellowish-green to a clear greenish indigo blue. They are very largely used in wool dyeing, especially for mixed shades.

The oldest of these acid greens, which appeared in the market in 1878, was called

5. Helvetia green or Acid green C. It was the sodium salt of the mono-sulpho derivative of the ordinary benzaldehyde green, prepared either by sulphonating the green itself by means of chlorosulphonic acid, or by sulphonating tetramethyldiaminotriphenylmethane and oxidising the resulting colourless acid by means of lead peroxide. Neither of these two methods works satisfactorily. For this reason the product has gradually been abandoned, and replaced by the benzyl derivatives, which are more easily prepared, and at the same time much more brilliant in shade.

6. Benzyl acid greens. In the various attempts to prepare acid greens it was found that the phenyl groups, combined with the central carbon, show little tendency to permit of the introduction

tion of the sulpho group. This reluctance is, indeed, quite characteristic of all triphenylmethane derivatives. It is the cause of the difficulties experienced in preparing sulphonated derivatives of these dye-stuffs. It was, therefore, a happy thought to introduce into the molecule of the green an independent radicle, capable of receiving the sulpho group without influencing more than necessary the shade and other properties of the green. Such a radicle was found in the benzyl group. If we introduce this, instead of methyl and ethyl, into the amino groups of the green, it acts in the manner of a radicle of the fatty series, influencing the shade of the green very little. The C_6H_5 group, however, brought into the molecule as a constituent of the benzyl radicle, is capable of being sulphonated with the greatest facility. Various dye-stuffs have been prepared according to this principle. Of these *Guinea green B* is the simplest. It is the disulpho derivative of diethyl-dibenzyl-diaminotriphenyl-carbinol



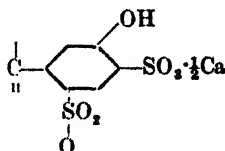
obtained by combining benzaldehyde with two molecules of ethylbenzylaniline sulphonic acid, and oxidising the leuco compound thus obtained. This product was discovered by G. Schultz and Streng, in 1883, and patented (D. R. P. 50782, 1889; Eng. Pat. 7550, 1889). It is an excellent and very useful dye-stuff. *Guinea green B*, which dyes a more yellowish shade, is obtained in the same manner, using *m*-nitrobenzaldehyde instead of the ordinary benzaldehyde, whilst if *o*-chlorobenzaldehyde is used the resulting dye is *Benzyl green B*.

The various shades of *light green* or *acid green* sold by the majority of manufacturers are prepared somewhat differently. Benzaldehyde is combined with two molecules of benzyl-methyl- or benzyl-ethylaniline. The base thus obtained is treated with sulphuric acid, when three sulpho groups enter the molecule, one of which is linked to the phenyl radicle containing no amino group, whilst the two others are combined with the benzyl radicles. The resulting trisulpho derivatives are oxidised in the usual manner, yielding the dye-stuffs in the shape of a very soluble green powder.

7. A curious product, belonging to the class of acid greens, was described by R. Meldola, under the name of *Viridin* (Chem. Soc. Trans. 1882, 187; Ber. 14, 1385). It was prepared by oxidising benzyl-diphenylamine, and sulphonating the resulting green, dissolved in spirit. This green, or a substance very similar to it, had already been prepared by Ch. Girard (Wurtz, Progrès de l'Ind. des Mat. col.; Paris, 1876; p. 134).

8. *Patentblau*, *Patent blue*, a product of the Farbwerke vorm. Meister, Lucius and Brüning, in Höchst-am-Main. This is a dye-stuff closely allied to the acid greens. It was discovered by Hermann, and patented by the Farbwerke (D. R. P. 46384, 1888, and many additional patents; see also Fritsch, Ber. 1896, 29, 2291, and Erdmann, Annalen, 1897, 294, 376). It is prepared by a somewhat complicated method.

m-Nitrobenzaldehyde is combined with two molecules of dimethylaniline. The resulting base is reduced, the amino derivative diazotised, and, by boiling with water, transformed into *m*-hydroxytetramethyldiaminotriphenylmethane. This is sulphonated by treatment with sulphuric acid. The resulting sulpho derivative is oxidised and transformed into a calcium salt, which is delivered into the market. The constitution of the dye-stuff is represented by the following formula:

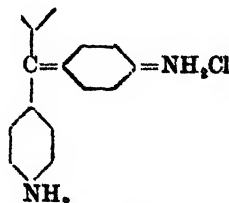


This dye-stuff dyes wool and silk a beautiful greenish-blue of great brilliancy and clearness. Several other dye-stuffs of very similar composition are on the market.

(B) *Derivatives of triaminotriphenylmethane*.—This group contains some of the oldest artificial dye-stuffs, which were prepared by strictly empirical methods. When the constitution of the triphenylmethane group was established, synthetical methods for producing dye-stuffs of this group were gradually introduced. At the present time the old empirical processes hold their own for the production of the old colouring matters, whilst the synthetical methods, which are mostly patented, are used for preparing new dye-stuffs of great beauty and perfection.

The prototype of this group is—

1. *Parafuchsin*, *Paramagenta*, the anhydrochloride of triaminotriphenylcarbinol $C_{18}H_{15}N_3Cl$ the constitution of which is:



It always crystallises with four molecules of water of crystallisation, which should be added to the above formula.

This is the dye-stuff which was used by O. and E. Fischer for the elucidation of the chemistry of this class of substances (O. and E. Fischer, Annalen, 1878, 194, 242; Ber. 11, 1079; 13, 2204). It is one of the oldest artificial dye-stuffs; it was discovered in 1858 by A. W. Hofmann (J. 1858, 351); and re-discovered by Rosenstiehl in 1869 (Bull. Soc. Ind. Mulhouse, 36, 264). For a long time it was considered a substance of merely theoretical interest, because its shade is almost identical

with that of ordinary fuchsin or magenta (see under 2), which is much more easily prepared. At present, however, it is manufactured on a large scale, not as a dye-stuff for sale, but as a raw material for certain blues, which will be mentioned later on.

A large number of reactions have been observed and described which result in the formation of pararosaniline. Of these the following may be mentioned :

(a) Pure aniline heated with carbon tetrachloride yields parafuchsin. This method was used on a manufacturing scale by Monnet and Dury in Lyons.

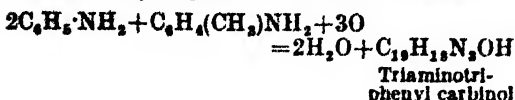
(b) Pure aniline, heated with iodoform, gives a fair yield of parafuchsin hydriodide.

(c) Pure aniline, heated with *p*-nitrobenzyl chloride in the presence of iron filings or iron salts gives a good yield of parafuchsin. This method, or modifications of it, form the substance of Greiff's and Baum's patents (D. R. PP. 15120 and 19304 Grieff, and 14929 Baum).

(d) Pure aurin (rosolic acid), which will be described subsequently, yields parafuchsin if strong ammonia be allowed to act on it for a long time at a high temperature.

(e) It has been shown (v. introduction) that the reduction-product of parafuchsin is paraleuco-aniline, and that the latter is identical with triaminotriphenylmethane. The latter may easily be prepared from triphenylmethane by nitration and reduction, and by various other methods. Attempts have not been wanting to work out a method for the production of parafuchsin from synthetical leucaniline. No good method, however, has hitherto been discovered for this purpose, and all the patents based on this reaction have proved failures. It is very easy to produce a trace of fuchsin in a solution of leucaniline; but no method is known for finishing the reaction.

(f) Mixtures of pure aniline with pure *p*-toluidine yield parafuchsin if subjected to oxidation. This is the usual practical way for the production of parafuchsin. The oxidation may be effected either by arsenic acid or by nitrobenzene. Other oxidising agents—such as mercuric chloride, stannic chloride, &c.—produce the same result, but at a higher cost. The arsenic acid process (which will be described later on) was for some time almost exclusively used for the production of parafuchsin. The chemical reaction which takes place is very simple. Arsenic acid is reduced to arsenious acid. The oxygen which is thus obtained combines with hydrogen of the aromatic bases :



The methyl group of *p*-toluidine is used up for yielding the central carbon around which the other radicles are grouped.

(g) Diaminodiphenylurethane, mixed with aniline and heated with oxidising agents, yields parafuchsin. This synthesis forms the basis of a more modern manufacturing process.

It has already been said that parafuchsin has no advantages over ordinary magenta red for dyeing purposes. It is, therefore, rarely to be met with as a dye-stuff in the market. As a

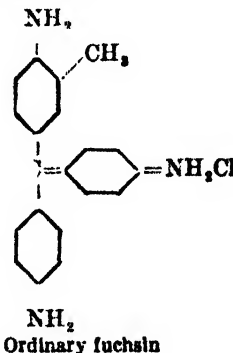
rule the melts are worked up in the same manner as ordinary magenta melts, but the resulting crystals of the pure hydrochloride are redissolved and precipitated in the shape of pararosaniline base by the addition of soda or milk of lime. The base is then used for the production of blues.

Parafuchsin hydrochloride forms small glistening crystals having a metallic green lustre. As a rule, they are very small, much smaller than the crystals of ordinary magenta. Parafuchsin acetate is similar in appearance and crystallises much more easily than the ordinary magenta acetate.

Pararosaniline is important because it is the parent substance of all the various violets, and of some of the blues, which will be described subsequently.

2. Ordinary fuchsin, magenta red, rosein (*rubesine, harmaline, aniline red, azalein, solferino, erythrobenzine*) $\text{C}_{20}\text{H}_{12}\text{N}_2\text{Cl}$, is an article of great importance and of very general application. The latter is due to the fact that it was one of the first artificial dye-stuffs, although not one of the best. A great demand for it has gradually been established, which forces the manufacturers to carry on its production on a large scale, even now, when much better dye-stuffs may be prepared by other methods.

Chemically, this colouring matter may be defined as the higher homologue of parafuchsin, in which one of the phenyl groups has been replaced by a tolyl group :



The product of commerce, though chiefly composed of this substance, invariably contains an admixture of parafuchsin as well as of the higher homologues ($\text{C}_{21}\text{H}_{12}\text{N}_2\text{Cl}$ and $\text{C}_{22}\text{H}_{14}\text{N}_2\text{Cl}$). Like parafuchsin, it contains four molecules of water of crystallisation.

Fuchsin is invariably prepared by oxidising a mixture of aniline with *p*-toluidine and *o*-toluidine. This mixture is generally known as 'aniline for red,' and was originally produced by the nitration and subsequent reduction of a certain fraction of crude benzene, which consisted of benzene and toluene. Sometimes it even contained some xylene; in this case xylylene entered into the composition of 'aniline for red.' At present most of the 'aniline for red' is a mixture of pure aniline with crude toluidine. By the latter we mean the mixture of *o*- and *p*-toluidine which is obtained by the nitration and subsequent reduction of pure toluene. Crude toluidine consists as a rule of 55 p.c. *o*-toluidine and 45 p.c. *p*-toluidine. The quantity of aniline added to crude toluidine

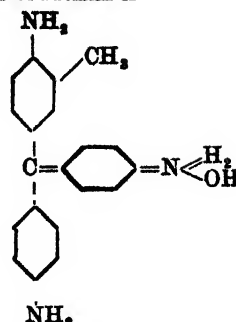
in order to produce the 'aniline oil for red' varies according to the recipes of various manufacturers. As a rule, half of the weight of the toluidine is added. A certain boiling-point (for instance, 188°-200°) and a certain specific gravity (for instance 1.010) are prescribed, and should be strictly adhered to by the aniline oil manufacturer. In some cases an addition of xylidine is necessary in order to produce a product of the desired boiling-point and density. Theoretically, an oil containing equal molecules of the three bases would be required; but for practical work an excess of aniline and o-toluidine is used, because a part of these two compounds escapes the reaction, whilst the p-toluidine is entirely used up.

Of all the methods which in the course of time have been proposed for oxidising this mixture, only two have survived, one of which is also rapidly disappearing. They are known under the names of the *arsenic acid melt* and the *nitrobenzene process*. From a practical point of view they are of equal value, but the arsenic acid melt is being abandoned on account of the poisonous nature of the arsenic compounds required.

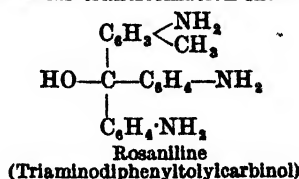
Magenta was originally prepared by Natan-son, in 1856, by heating aniline with ethylene chloride. In 1858 Hofmann observed its formation when allowing carbon tetrachloride to act on aniline. In 1859 Verguin prepared it by the action of stannic chloride on aniline. Verguin's employers, the dyers Renard Frères and Franc, in Lyons, took up its manufacture on a large scale, and invented the name *fuchsin*. Later on a company was formed, under the name of 'La Fuchsin,' for working Verguin's patent. Gerber-Keller invented a process for oxidising aniline by means of mercuric nitrate. The dye-stuff thus obtained was believed to be different from fuchsin, and received the name *azalein*. In 1860 Medlock invented the arsenic acid process, which for a long time was considered the only practical method of manufacturing magenta. His patent was invalidated owing to a clerical error contained in the description. In 1869 Couper described his process for producing fuchsin by the nitrobenzene process. This method, which did not give good results at first, was gradually worked out by various manufacturers, and is now equivalent, if not superior, to the best forms of the arsenic acid process.

Various salts of rosaniline were formerly in commerce. The original fuchsin was the hydrochloride, azalein was the nitrate; whilst magenta and rosein were the names applied to the acetate, produced by Nicholson, the first to manufacture this colouring matter in a practical and rational manner. Gradually the nitrate and acetate disappeared from the market. At present the hydrochloride is the only salt produced, to which, therefore, the original name of fuchsin should be applied. English manufacturers still use the names magenta and rosein for the hydrochloride. A large quantity of the fuchsin manufactured is transformed into rosaniline, which is delivered into the market either under this name or as 'magenta base,' 'red base,' or 'rosein base.' These names are not quite correct, because rosaniline may not strictly be considered as the true base of the hydrochloride of fuchsin.

The true base of fuchsin is



which, in the moment of its formation, undergoes a molecular transformation into



Manufacture of Fuchsin.

1. *Arsenic acid process*.—The properties of the 'aniline oil for red' have already been discussed. The mixture of bases known under this name is transformed into the dye-stuff by heating it with arsenic acid. The latter is prepared by oxidising arsenious acid (white arsenic) by means of nitric acid in closed earthenware pots. The escaping nitrous fumes are condensed in a tower, in which they meet an opposing current of water and air. The nitric acid is thus regenerated, and may be used again. Practically, therefore, the formation of the arsenic acid is accomplished by the oxygen of the air. The arsenic acid solution obtained has a sp.gr. of 1.85-2.3, and contains from 60-75 p.c. of arsenic acid H_2AsO_4 . 1,500-1,700 kilos of this solution are required in order to oxidise 1,000 kilos of 'aniline oil for red.' These quantities of the reagents are introduced into enamelled cast-iron pots, closed by lids; a mechanical stirrer and a tube for the escape of the vapours should be provided. The mixture is then gradually heated to 180°. This temperature should be strictly maintained during the whole operation. If the temperature rise above 190°, the dye-stuff already formed is decomposed. From eight to ten hours are required in order to complete the reaction. During the whole time vapours escape, which should be condensed in a leaden coil connected with the escape tube, and cooled by a current of water. At first the distillate consists chiefly of the water introduced with the arsenic acid. Later on, the water formed in the reaction distils; at the same time some aniline oil goes over. The total quantity of the aniline escaping the reaction is one-third, or even one-half, of the quantity originally used. The melt, which is very thin at first, gradually becomes viscid; at the same time it assumes a brown, metallic lustre. Samples should be taken from time to time. When the melt becomes brittle on cooling, the reaction is finished, and the fire should be drawn. The melt is then at once removed from the pot. In some factories an opening is provided for this purpose in the

lowest part of the pot, which is closed by a lid and screw whilst the heating lasts. As a rule, however, it is preferred to remove the cover of the pot, and to ladle out the melt. The latter is spread on trays made of sheet iron. On cooling, it solidifies into cakes, which are very brittle, and break up into small lumps on being handled.

The crude melt contains the colouring matter in the shape of arsenite, together with an excess of arsenious and arsenic acids, some coloured by-products (*v. infra*), and a large quantity of tarry impurities. In order to obtain the pure dye-stuff, the crude melt is introduced into horizontal wrought-iron boilers, in which an eccentric horizontal stirrer is made to rotate. Water is added, the lid of the boiler is closed, and steam is introduced at a pressure of from four to five atmospheres. After several hours' vigorous stirring, the greater part of the rosaniline arsenite has been dissolved by the water. The liquid is then forced through felt into iron tanks, where it is allowed to cool down to 50°. A sufficient quantity of salt is then added to precipitate the whole of the colouring matter. By the addition of the salt a mutual decomposition takes place. Sodium arsenite is formed, and remains in the liquid, whilst the colouring matter is precipitated in the shape of chloride. It settles out as a thick green tar of metallic lustre, which solidifies into a brittle substance on cooling. The supernatant aqueous liquid is then drawn off, the crude fuchsin is chipped out, and introduced into another extractor, similar to the one used for treating the melt. A very small quantity of soda ash or chalk (about $\frac{1}{2}$ p.c. of the weight of the crude dye-stuff) is added, and a second extraction takes place. The liquid is again forced through felt into large wooden vats, in which some wooden boards are suspended. When the vats are filled, a small quantity of hydrochloric acid and clean butter-salt is added to each vat. In these vats the dye-stuff separates out, in the shape of fine glistening green crystals. The largest crystals are generally deposited near the surface of the liquid. When the crystallisation is finished, the mother-liquor is drawn off, and the crystals are collected and sorted according to their shape and size. The largest crystals are sold under the name of 'diamond fuchsin.'

By-products.—The residues of the first boiling may be subjected to a second extraction; as a rule, some hydrochloric acid is added in this case. A deeply-coloured solution is thus obtained, from which an impure colouring matter may be precipitated by the addition of salt. This colouring matter is sold under various names (*magenta cake, cerise, grenadine, maroon*), and finds a ready market. It dyes a magenta colour, which is less brilliant than the shade obtained with the crystals. A third boiling is sometimes necessary. The colouring matter obtained from this is very impure. It is, therefore, dissolved in weak hydrochloric acid, and some zinc-dust is added, which reduces the magenta contained in the liquid. On precipitating with salt, a colouring matter of a brown shade is obtained, which is sold as 'Nanking,' or 'leather brown.' The black insoluble residue of the third boiling still contains some dark-blue colouring matters of the induline series, which are, however, not worth the trouble of extracting.

The mother-liquors from the crystals contain a yellow colouring matter of great fastness and purity. This substance, known under the name of *phosphine*, belongs to another group of dye-stuffs, being a salt of diaminophenylacridine. For extracting it from these mother-liquors, the latter should be acidified with hydrochloric acid, and some zinc-dust added until all the fuchsin present in the liquid is reduced. The phosphine, which is not so easily reduced by zinc-dust, may then be precipitated by the addition of sodium nitrate. The amount of phosphine formed varies according to the composition of the aniline oil and the temperature of the melt. It is never considerable, and very often the quantity present is so small that it is not worth while to separate it (*v. CHRYSANILINE*, vol. ii. 246).

Recovery of the arsenious acid.—Formerly the residues of the manufacture of magenta were left in the factory yards or thrown into the sea. At present this is not allowed, and the manufacturers are invariably forced to recover their arsenious acid, so as to prevent the poisoning of wells and streams. The recovery, as it is now carried out, is so economical that the value of the arsenious acid obtained covers the cost of working the process. The process, which was worked out by A. Leonhardt, consists in burning the solid residues and using the heat for evaporating the arsenical liquids. The dry residue of the evaporation is introduced into the furnace, and burned along with the solid residues. Care is taken to introduce no more air than is necessary for burning the organic matter. By this precaution a complete volatilisation of the arsenic in the metallic state is obtained. The vapours of arsenic are led into a highly-heated combustion-chamber. Here they are mixed with the necessary quantity of hot air to completely burn the metallic arsenic into arsenious oxide As_2O_3 . The vapours of the latter are then led through condensing chambers similar to those used in the manufacture of white arsenic. In these chambers the arsenious acid is deposited in the shape of a white powder. From time to time the chambers are opened, the arsenic is removed, and used again for the manufacture of syrupy arsenic acid by the aid of nitric acid. A certain stock of arsenic is thus sufficient to carry on the manufacture of fuchsin for an indefinite period.

2. *The nitrobenzene process.*—This process was originally invented by Couper, of Paris; but it was for the first time successfully worked on a large scale by the firm of Meister, Lucius und Brünig, of Höchst-am-Main. Other firms followed in the course of time, and at present this process has practically superseded the one with arsenic acid.

It was originally supposed that the nitrobenzene used in this process enters into the rosaniline formed, after having served as an oxidiser. At present it is generally recognised that the nitrobenzene merely acts as an oxidising agent, and that, in so doing, it is transformed into tarry matters, which are useless and remain in the residues. The nature of the nitro compound used is, therefore, of no influence on the composition of the dye-stuffs obtained. Pure nitrobenzene, or a mixture of nitrobenzene with nitrotoluene, may be used. *o*-Nitrotoluene acts

more easily than any other nitro compound; it has, therefore, been used with advantage by the writer. *p*-Nitrotoluene has little tendency to act as an oxidiser. If, therefore, a mixture of nitrobenzene with the two nitrotoluenes (the so-called 'nitrobenzol for red') be used, the *p*-nitrotoluene escapes with the distillate.

The advantage of the nitrobenzene process consists, therefore, not in an economy of ingredients, but in the fact that by its application magenta free from arsenic may more easily be obtained. The yield in good crystallised fuchsin is slightly larger (if only the aniline used be taken as basis of the calculation) than in the arsenic acid process. This increase of yield pays for the increased price of the oxidising agent. In times when commercial benzene is cheap the process compares favourably with the arsenic acid process, whilst it was at a disadvantage when the prices of benzene were high. At the present time, benzene is so cheap and plentiful that the nitric acid consumed in this process is perhaps a more important item in the calculation of its cost than the benzene. For working this process it is a condition that the manufacture of aniline be carried on in the same works; the distillates are a mixture of aniline and nitrobenzene, which must be returned into the reduction process before they can be used again.

The process is worked with different proportions and in a different manner in different works. It is based on the following facts: aniline and nitrobenzene do not react upon each other; nor does a reaction take place if aniline hydrochloride be added. But if a small quantity of iron chloride be present, a reaction sets in, at a temperature of 160°. If the aniline and aniline salt used are pure, a dyo-stuff of the induline group is obtained; but if *p*-toluidine and *o*-toluidine be present in the necessary proportions ordinary fuchsin is the result of the reaction. The nitro compound, however, attacks the fuchsin already formed, and part of it is therefore decomposed again. For this reason, quantitative yields cannot be obtained. At 190° the action of the nitrobenzene becomes so violent that all the colouring matter is destroyed. The greatest care is, therefore, required in this process, and the temperature should never be allowed to rise over 175°. Cold-air flues, and even arrangements for cooling with water or ice, are therefore invariably provided in connection with the melting-pots. The size of the latter has been constantly increased, because it is easier to keep large vessels at a constant temperature than small ones. Enormous pots, capable of working one or two tons of melt, have been used. Excellent arrangements for stirring should be provided. It is a good plan to make the melting-pots of spherical shape, and to give the stirrer an oblique position in this spherical pot. No water should be present in the mixture, as in this case the nitro compound is simply reduced into aniline by the ferrous chloride, and the reaction stops. The hydrochloric acid used should, therefore, be mixed with the necessary quantity of the aniline and the mixture evaporated until it solidifies into 'aniline salt cake' on cooling. Sometimes the iron chloride solution is added, so that the cake obtained is intimately mixed with the iron salt. This cake is then dissolved

in the rest of the aniline, the nitro compound added, and the mixture heated until the reaction sets in. Other manufacturers prefer to add iron filings or dry ferrous chloride to the mixture of aniline with aniline cake and nitrobenzene. An ingenious patent, taken out by Herran and Chaudé, proposed the use of certain double salts of the general formula $R_2Cl_2 \cdot 2RCl$, such as ferric ferrous chloride, ferric zinc chloride, aluminium zinc chloride, and others. The addition of iron filings, originally proposed by Coupier is not customary at present. Anhydrous zinc chloride, which has also been proposed as a means of starting the oxidising action of the nitro compound, has not proved satisfactory.

The following proportions have been proposed:

100 parts aniline for red,
50 „ nitrobenzene,
3-5 „ iron filings,

and a sufficient quantity of hydrochloric acid to neutralise two-thirds of the aniline (Häussermann). The quantity of nitrobenzene is too large; it may very well be reduced to 40 parts, or even less.

Wurtz gives the following proportions:

38 parts aniline,
17-20 „ nitrobenzene,
18-22 „ hydrochloric acid,
2 „ iron filings.

The following is Coupier's mixture:

67 parts toluidine,
95 „ nitrotoluene,
65 „ hydrochloric acid,
7 „ ferrous chloride.

The large quantity of nitrotoluene proposed in this prescription is due to the fact that only the *o*-nitrotoluene, of which about 50 parts are present in the mixture, acts as an oxidiser. The *p*-nitro compound is recovered in the distillate.

The following proportions were used by the writer in regular factory work:

400 kilos aniline for red,
222 „ hydrochloric acid, 20° Bé.,
247 „ *o*-nitrotoluene,
and the ferrous chloride prepared from
9 kilos iron borings, and
41 „ hydrochloric acid.

Half of the aniline is dissolved in the 222 kilos of hydrochloric acid, the solution of the ferrous chloride is added, and the whole evaporated in a stone still before being mixed with the remainder of the aniline and the nitrotoluene.

The nitrobenzene melt cannot be pushed so far as the arsenic acid melt. When finished it should not solidify into a brittle mass on cooling. It should be still soft, owing to a proportion of uncombined aniline which it still contains. This aniline must be extracted by boiling with a small quantity of dilute hydrochloric acid. After its removal, the melt becomes brittle on cooling. It is worked up in the Leonhardt extractors, in exactly the same manner as described for the arsenic acid melt.

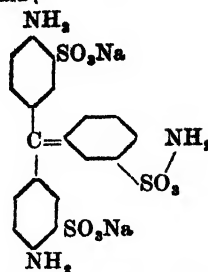
Later improvements.—It has already been said that several synthetical methods have been

proposed for the manufacture of magenta, which met, however, with no success. Gradually, however, improvements have been introduced into the old melting processes, which, being based on theoretical considerations, have given favourable results. The most important of these improvements is the one described in the German patent 53937 (and additional patent) of the Farbwerke vorm. Meister, Lucius und Brüning in Höchst-am-Main, dated November 27, 1889. It consists in replacing, in the nitrobenzene process, the 'aniline for red' by a mixture of diamino-diphenylmethane and aniline. The patents refer only to the production of the diamino-diphenylmethane, which is prepared by first acting with formaldehyde (the well-known 'formalin' of commerce) upon aniline. The methylene-aniline obtained is heated with aniline and aniline hydrochloride, by which means diamino-diphenylmethane is easily formed. If instead of $C_6H_5N:CH_2$, methylene-aniline, any of its higher homologues be heated with the corresponding bases, the homologues of diamino-diphenylmethane are produced. By introducing these bases instead of *p*-toluidine into the magenta melt, very large yields of the dye-stuff are said to be obtained. The dye-stuff prepared by this method is sold under the name of 'Neu-Fuchsin' (new magenta).

Later on a patent was obtained by Cassella & Co., of Frankfurt-am-Main, the essence of which is probably the same. It consists in introducing methyl alcohol into the arsenic acid melt. Formaldehyde is probably thus produced, which is at once transformed into diamino-diphenylmethane. By introducing chlorinated anilines into the pararosaniline melt the chlorine substitution products of rosaniline have been obtained, which are remarkable by being much more bluish in shade than either pararosaniline or ordinary magenta (Cassella & Co., D. R. P. 21923, 1913).

Acid magenta.—The ordinary fuchsin or magenta has been used for dyeing cotton, wool, and silk. But its properties make it necessary to use neutral or very slightly acid baths. This is a considerable drawback to its use on silk or wool, especially in combination with other dye-stuffs which require distinctly acid dyebaths for their successful application. It was, therefore a decided advance to introduce a sulpho derivative of magenta into the market. This step was realised by H. Caro in 1877 (Eng. Pat. 3731, 1877; D. R. P. 2096, Badische Anilin- & Soda-Fabrik). Caro proved that magenta, which shows a marked resistance to ordinary sulphuric acid, may easily be converted into a trisulpho derivative by treatment with fuming sulphuric acid. The ordinary crystallised hydrochloride of magenta is used. It is introduced in a finely-powdered condition into fuming sulphuric acid; the mixture is then heated to a temperature not below 120° and not above 170° . Hydrogen chloride is given off, and the sulpho derivative is formed. When the operation is finished, it is diluted with water and worked up in the usual manner, by first preparing the lime-salt and then converting it into the sodium salt. The para derivative has the composition $C_{18}H_{12}N_2O_3S_3Na_3$, the higher homologue $C_{20}H_{14}N_2O_3S_3Na_3$; the ordinary acid magenta is a mixture of the two. The constitution of

the para derivative may be represented by the following formula:



from which it will be seen that the sulpho-groups occupy the *ortho* positions relative to the amino groups. It forms a metallic green powder, very soluble in water with magenta colour, which disappears completely on addition of caustic alkali, the sulpho derivative of the colourless triamino-triphenyl carbinol being formed.

Acid magenta may also be obtained by acting with chlorosulphonic acid upon dry magenta base (E. Jacobsen, D. R. P. 8764, 1879; Eng. Pat. 2828, 1879).

By using the various by-products of magenta instead of the pure dye-stuff, acid derivatives of these may be obtained which prove particularly valuable for dyeing mixed shades.

Magenta base (red base, rosein base). A large proportion of the fuchsin produced is transformed into the corresponding base, the composition of which has already been discussed. For the production of a good base, crystallised fuchsin only should be used. This is dissolved in a large volume of boiling water, and made alkaline either with milk of lime or with ammonia. In the latter case, the product obtained consists partly of the amino derivative already mentioned. No caustic alkali should be used. From the filtered solution the base settles out on cooling in crystals, which have the shape of a fern-leaf of pale-pink colour. In the air they generally become darker, because a certain amount of magenta carbonate is formed on their surface. The base thus prepared is sold for conversion into violets and blues (*q.v.*).

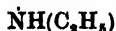
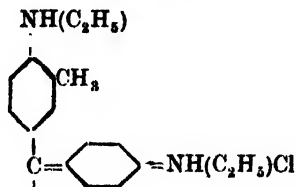
COLOURING MATTERS DERIVED FROM ROSANILINE.

The brilliant researches of A. W. Hofmann proved, at an early period, that rosaniline is capable of having the hydrogen atoms of its amino groups replaced by alkyl groups, and that the substances so formed are remarkable not only for the brilliancy, but also for the great variety, of their shades. Hofmann himself introduced the alkyl radicals of the fatty series into the molecule of rosaniline, and thus obtained the colouring matters which for a long time played an important part under the name of Hofmann's violets. Girard and De Laire discovered a method of introducing the phenyl and other aromatic groups into the molecule of rosaniline, and thus inaugurated the manufacture of aniline blues. It was then attempted, first by Lauth, to produce alkylated rosanilines by direct oxidation of alkylated aniline, and this method proved of great practical importance in the hands of Bardy, although the theory of this

process was only understood at a much later period. Finally, a synthetical method for the production of certain alkylated rosaniline derivatives which cannot be produced by direct alkylation of rosaniline itself, was discovered by Kern, whose processes are based on the theoretical researches of Michler.

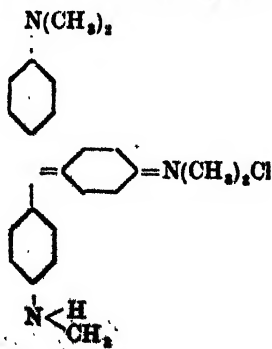
All these colouring matters will now be described, and the methods of their formation discussed.

1. Hofmann's violet $C_{26}H_{32}N_3Cl$, hydrochloride of triethyl-rosaniline



is obtained by heating magenta base with ethyl iodide, bromide, or chloride, and a sufficient quantity of alcoholic soda solution to neutralise the acid formed in the reaction. The magenta base is prepared by decomposing a very weak fuchsin solution with milk of lime or ammonia. From the filtered solution the base crystallises in small leaflets of a pink colour. The alkylation is effected in closed vessels of copper or cast-iron, which are heated to 80° – 100° by steam or in a water-bath. The trimethyl-rosaniline hydrochloride, which is slightly bluer in shade, was formerly also prepared. This is no longer employed. By using less of the alkyl haloids than is necessary for completing the reaction, redder shades were obtained, which were mixtures of the mono- and di-ethyl- or methyl-rosanilines. In commerce, the more or less reddish tinge of their shade is marked by the addition of the letter R, thus: Violet R, RR, up to 5 R.

2. Methyl violet B. C. Lauth, wishing to find a new method for the production of Hofmann's violets, tried to oxidise methylated aniline. He obtained a violet of much bluer shade. Bary worked out the method, which was patented by Poirrier and Chappat (Fr. Pat. 71970, dated June 16, 1866). The product obtained was proved to be the hydrochloride of pentamethyl para-rosaniline $C_{24}H_{28}N_3Cl$ —



This dye-stuff, which became of great importance, was for a long time known under the name of *Violet de Paris*. At present it is sold by the various colour works under the name Methyl Violet B to 3 B.

The mode of formation of this colouring matter is very interesting. Many researches have shown that it is best prepared from pure dimethyl-aniline, which should be as free as possible from every trace of monomethyl-aniline. If three molecules of dimethylaniline be oxidised into one molecule of the dye-stuff, one of the six methyl groups present serves to form the central carbon atom, whilst the other five remain combined with the amino groups of the dye-stuff formed.

The process of oxidation employed is totally different from those resorted to in the manufacture of magenta or fuchsin. Cupric chloride is used as an oxidiser at a temperature which is little above that of the atmosphere. The cuprous chloride formed is again transformed into cupric salt by the oxygen of the air. The air should, therefore, have ready access to the mixture. To fulfil this condition, a porous condition is given to the melt by the admixture of sand or other indifferent materials. Cakes are formed of the mass, and these are left on trays in a hot chamber. The following proportions have been recommended:

100 parts sand,	
10 „ dimethylaniline,	
3 „ cupric nitrate,	
2 „ sodium chloride,	
1 „ weak acetic acid.	

The cakes, which show a dull greenish colour at first, gradually assume a bronze lustre and become hard and brittle. They now contain the violet formed as an insoluble compound with cuprous chloride. To obtain the violet the cakes should be powdered, and all soluble substances extracted with water. The double salt of violet and cuprous chloride should then be decomposed. Various means have been adopted for this purpose.

The original process consists in treating the material with a weak solution of sodium sulphide. Insoluble copper sulphide is formed, and the free violet is dissolved. From the filtered solution it may be precipitated by the addition of salt. It comes out in the shape of a gold-coloured tar of metallic appearance, which is collected and dried in jacketed pans. When dry it forms a brittle mass of metallic aspect, showing no tendency whatever to crystallise. It is sold under the name of 'Methyl violet B' or 'direct violet.'

The use of sodium sulphide has this inconvenience, that any excess of the reagent acts as a reducing agent on the violet, transforming it into its leuco compound, which cannot be separated from the violet, and impairs its strength, besides producing other complications. To remedy this drawback, several factories used gaseous hydrogen sulphide instead of the 'sodium' compound. Hydrogen sulphide has no reducing action on the violet in neutral or slightly acid solutions. The use of this gas on a large scale is, however, extremely dangerous, and accidents, which happened

repeatedly, have led to the abandonment of its use.

The following methods admit of the extraction of the violet without the use of sulphides.

The first is based on the fact that, although the violet combines with cuprous chloride in the shape of its hydrochloride, this is not the case if the two be present as sulphates. If, therefore, the crude insoluble melt is boiled with dilute sulphuric acid, the violet goes into the solution together with the copper. The solution is then filtered off from the sand. If now salt were added in order to precipitate the violet, the insoluble compound would rise from chlori-

for precipitating the violet, which comes out as sulphate, whilst the copper remains in the solution. The violet sulphate is now carefully washed, re-dissolved, and re-precipitated in the shape of chloride by the addition of common salt.

Another process, which gives equally good results, is based upon the fact that the insoluble compound becomes soluble if the cuprous chloride contained in it be oxidised into cupric salt. For this purpose the crude cake is triturated with a solution of ferric chloride. It is then filtered off and washed. The violet, which has become soluble, may now be extracted with water, and precipitated by the addition of salt.

Great improvements have been effected in the melt itself. First of all, it was recognised that the cakes, if left to themselves, were apt to lose too much dimethylaniline by evaporation; they also remained insufficiently oxidised in their interior. To obviate this, the use of bread-kneading machines was resorted to, through which a current of air was blown. This current was made to pass through a vessel containing sulphuric acid, after leaving the machine. Complete oxidation was thus obtained, whilst the base which distilled over was recovered in the acid.

Later on, the quantities of the copper salt were reduced, and some potassium chlorate was added to the mixture. This yielded the necessary oxygen, the presence of a current of air became superfluous, and the evaporation of the base could be stopped by using closed vessels or kneading machines.

Another great inconvenience is the sand. It is necessary as a diluting agent, but in the after-operations it is very troublesome, being very heavy and producing great wear of the apparatus. It was, therefore, a great improvement to use clean salt instead of sand. The salt is quite as indifferent as the sand, but after having done its duty, it may be easily removed by solution, leaving the insoluble compound of the violet and cuprous chloride in the shape of a fine dark powder, which is admirably fitted for being worked up into soluble product.

By such improvements it was possible to raise the yield of colouring matter, which at first hardly reached 45 or 50 p.c. of the dimethylaniline used, to 90 p.c. and more. If we remember that 30 p.c. of pure colouring matter is a fair yield in the manufacture of magenta, we may well understand that methyl violet, although manufactured from a much more

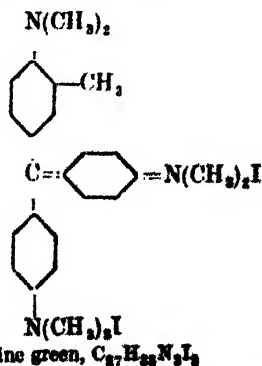
expensive raw material than fuchsin, soon became much cheaper than its parent substance.

The yields of violet have been further increased by a curious procedure. It consists in adding some phenol to the mixture. The action of the phenol, which may be recovered, is that of a solvent; by its use the yield of violet becomes very nearly theoretical.

In the manufacture of violet, especially by the older methods, there is always some tri- and tetra-methylrosaniline formed along with the penta-methyl derivative, because the methyl groups are attacked, and transform the violet is, therefore, slightly redder than it ought to be. To compensate for this loss, Bardsy treated his direct violet with benzyl chloride, and thus introduced benzyl groups wherever methyl was wanting. The violet of very blue shade thus obtained was brought into commerce under the name of *Methyl violet 5 B* or *Benzyl violet*. It has now lost its importance, having been to a great extent replaced by the very beautiful crystallised violets obtained by the synthetical method of Kern.

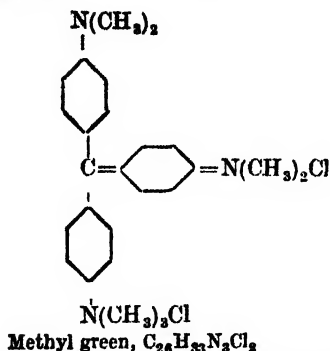
3. *Iodine green* and *Methyl green*. It has already been said that Hofmann's process of direct alkylation of rosaniline does not go beyond the tri-alkyl derivatives. If the action of alkyl halides be still continued, ammonium bases are formed. Thus by heating Hofmann's violet with methyl iodide in a methyl alcohol solution, Keisser obtained (1866) a green colouring matter, which was manufactured and sold for many years under the name of *iodine green*. A very similar dye-stuff was prepared from methyl-violet in a like manner by Bardsy, who used, however, methyl nitrate instead of the iodide. After several explosions, the use of the nitrate was abandoned, and methyl chloride or bromide, also ethyl bromide, were used instead. The dye-stuff thus obtained was sold under the name of *methyl green*. It did not contain any iodine, and was therefore much cheaper than the iodine green, which it quickly replaced.

Chemically, the two may be considered as homologues of similar constitution, viz. as methyl ammonium derivatives of hexamethyl-rosaniline and hexamethyl-pararosaniline. *Iodine green*, being a derivative of ordinary rosaniline, contains one tolyl group:



The methyl groups in this formula may also partly be replaced by ethyl groups if ordinary Hofmann's violet were used as a raw material.

Methyl green is the corresponding derivative of pararosaniline:

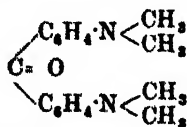


Both these dye-stuffs were brought into commerce in the shape of their zinc double chlorides. The iodine green formed a dark powder, whilst the methyl green formed pretty green needles or leaflets.

To prepare these dye-stuffs the violets were simply heated with the alkyl halides in closed enamelled iron vessels to 120° . Some wood spirit, or common alcohol, was added as a solvent. A pressure of 10–12 atmospheres was observed, which decreased when the reaction was finished. The crude product was dissolved in water. This solution was of dark-blue colour, because there was always some violet which remained unattacked. To separate this, the solution was shaken up with amyl alcohol, which dissolved out the violet. The green remained in the aqueous solution, from which it could be precipitated by the addition of zinc chloride and common salt. To obtain crystals, the crude green was re-crystallised from spirit.

These greens have now almost entirely been replaced by the diaminotriphenylmethane derivatives already described, which are not only more brilliant in shade, but also much more stable and at the same time very much cheaper. Iodine green and methyl green are decomposed and turn a dirty violet even by the action of a gentle heat, as produced in the process of cylindering fabrics, and on many other occasions.

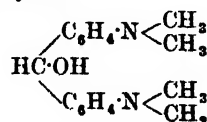
Pararosaniline derivatives prepared by Kern's method.—Another way of preparing alkylated pararosanilines was indicated by Kern, who started from the observations published by W. Michler (Ber. 1876, 9, 716). This chemist had shown that by acting with carbonyl chloride COCl_2 upon dimethylaniline, dimethylaminobenzoyl chloride is formed, which acts again on dimethylaniline, yielding tetramethyldiaminobenzophenone:



At the same time, as Michler observed, an intense blue colouring matter is formed. A. Kern (1883) followed up Michler's observations, and discovered not only the nature of the blue colouring matter, but also the conditions under which it may be obtained as the sole product of the reaction. The colouring matter proved to be pure hexamethylpararosaniline, the forma-

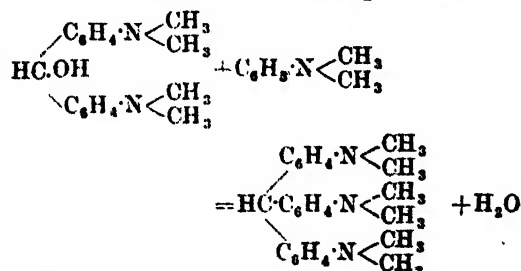
tion of which is due to the action of another molecule of dimethylaniline upon tetramethyldiaminobenzophenone. This action is, however, not very energetic, and must be intensified by the addition of certain substances, or by substituting for the ketone certain of its more active derivatives. A number of different processes have thus been worked out, the more important of which will now be described.

A. Kern's original modification of Michler's experiment is based upon the fact that tetramethyldiaminobenzhydrol, the secondary alcohol derived from the ketone tetramethyldiaminobenzophenone, acts readily upon aromatic bases, forming triphenylmethane derivatives. This process is described in Kern's Eng. Pat. 5450 (1883), and the corresponding D.R.P. 27032, Bad. Anilin- und Soda-Fabrik. Tetramethyldiaminobenzhydrol:



which had already been obtained by Michler by the action of sodium-amalgam upon the ketone may, according to this patent, be prepared industrially by boiling a solution of the ketone in amyl alcohol with caustic soda and zinc-dust. When the reduction is finished, the alcohol is blown off with steam, the residue dissolved in hydrochloric acid, and purified by fractional precipitation with caustic soda.

The product thus obtained may be condensed with primary, secondary, and tertiary aromatic bases, yielding in every case alkylated derivatives of paralucaniline; thus, for instance, with dimethylaniline the leuco base of hexamethylrosaniline is formed, if the two be brought together in a solution in weak sulphuric acid

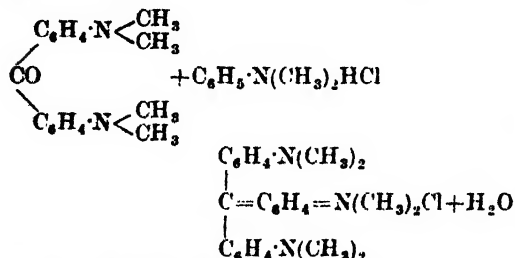


This leuco base may be oxidised into the corresponding dye-stuff by the method indicated for the production of benzaldehyde green—viz. by the action of lead peroxide upon the hydrochloride of the leuco base. The hexamethylrosaniline hydrochloride thus obtained is a beautifully crystalline substance, which forms green crystals if anhydrous, $\text{C}_{26}\text{H}_{30}\text{N}_3\text{Cl}$, or bronze-coloured prisms if containing water of crystallisation. In the latter case, its composition is $\text{C}_{26}\text{H}_{30}\text{N}_3\text{Cl} \cdot 8\text{H}_2\text{O}$. The power of crystallisation of this substance is very remarkable if we compare it with the ordinary violet obtained by direct oxidation of dimethylaniline; this, being a mixture of the tetra-, penta- and hexamethylrosanilines, shows no tendency whatever to crystallise.

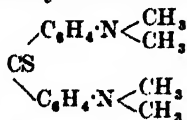
If in the process described diethyl-aniline be substituted for dimethyl-aniline, both for the

production of the hydrol base and its subsequent transformation, the result is, of course, hexaethylrosaniline, which cannot be prepared by any other process. This product is manufactured and sold under the name of '*Ethyl-purple, 6 B*' (ethyl violet). It is a very beautiful colouring matter, dyeing fine bluish-purple shades.

Very soon a simpler method than the one described was discovered by Kern and Caro (D. R. PP. 26016 and 29943; Eng. Pat. 4428, 1883). It was based upon the fact that the action of tetramethyldiaminobenzophenone upon dimethylaniline, which, in Michler's experiment, already had yielded a small amount of colouring matter, may be modified by the addition of certain substances, such as aluminium chloride, zinc chloride, and others. If these be present, the reaction of phosgene gas (carbonyl chloride COCl_2) upon dimethylaniline does not result in the formation of tetramethyldiaminobenzophenone; this is only formed as an intermediate product, which reacts at once upon another molecule of the base, forming hexamethyl-pararosaniline:

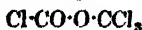


Many modifications of the processes here described have also been indicated and patented. Thus, instead of the carbonyl chloride, thio-carbonyl chloride (CSCl_2) may be used, which yields with dimethylaniline the thioketone



The latter may replace the oxygen compound in all its applications.

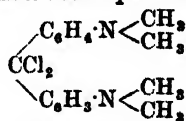
Again, trichloromethyl chloroformate



and similar substances have been proposed as substitutes for the carbonyl chloride.

The following is the method used at present for preparing *Crystal violet* and *Ethyl purple 6 B*: 100 kilos of dimethylaniline (or diethylaniline) are acted upon in a high-pressure pot at a temperature of 20° with 19–20 kilos of carbonyl chloride; after 24 hours' standing another 50 kilos of the base and 30 kilos powdered zinc chloride are added. The mixture is now heated to 40° – 50° , and 20 kilos more of the carbonyl chloride are introduced. After 6 hours' heating to 50° , the reaction is finished. The mixture is now introduced into a still, made alkaline with caustic soda, and the excess of dimethylaniline driven off with steam. The base of the colouring matter is then dissolved in weak sulphuric acid, and precipitated in the shape of its chloride by the addition of common salt. It is then recrystallised from water.

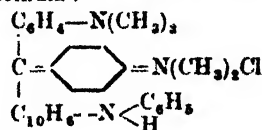
This process leads, of course, only to para-rosaniline derivatives in which the three amino-groups are substituted in the same manner. Besides the hexamethyl- and hexaethyl derivatives, the trimethyltriphenyl derivative has been obtained from methyldiphenylamine (Amer. Pat. 327953, Kern and C. Müller). It was, therefore, a great improvement when a method was found for effecting the condensation of tetramethyldiaminobenzophenone with all kinds of primary, secondary, and tertiary bases. This method, which was worked out by Kern and H. Caro, consists in the intermediate formation of the tetramethyldiaminobenzophenone chloride:



which, being more active than the ketone itself, reacts most easily upon bases of ever description. For the manufacture of colouring matters it is not necessary to isolate the chloride, an extremely unstable substance. It is sufficient to react with phosphorus trichloride upon a mixture of the ketone with the base which is to be introduced into the triphenylmethane derivative.

This process is described in the D. R. P. 277891, the Eng. Pats. 4850 and 5038, 1884, and a large number of corresponding American patents, which contain many examples of its application to the production of dye-stuffs. Of these, however, only few have obtained lasting importance. These are basic colouring matters of a beautiful blue shade, and interesting because they are the only members of the triphenylmethane group which contain the naphthyl radicle.

Victoria Blue B $\text{C}_{22}\text{H}_{22}\text{N}_3\text{Cl}$ has the constitutional formula:



It is prepared by mixing together

10 kilos tetramethyldiaminobenzophenone and

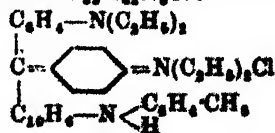
9 kilos α -naphthylphenylamine, and adding

7 kilos phosphorus trichloride to the mixture.

The reaction, which sets in at once, is finished by heating to 110° . The product is dissolved in water, and the solution precipitated with salt.

A similar dye-stuff, analogous in its constitution, but of a somewhat more reddish shade, is obtained if instead of α -naphthylphenylamine, monoethyl- α -naphthylamine be used. It is known under the name *New Victoria blue R*.

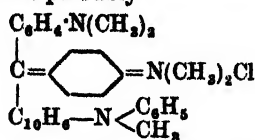
If α -naphthyl-*p*-tolylamine be taken instead of the naphthylphenylamine, and condensed with tetra-ethyl-diaminobenzophenone, a blue of a very greenish shade is obtained. It is sold under the name *Night blue (Nachtblau)* and has the composition $\text{C}_{22}\text{H}_{22}\text{N}_3\text{Cl}$:



Another blue of very red shade is the one sold under the name *Victoria blue 4 R*



It is prepared from tetramethyldiaminobenzophenone and α -naphthylmethylphenylamine. Its constitution is probably



In describing both the green dye-stuffs derived from diaminotriphenylmethane and the old and important magenta group, it has been mentioned how much the dyer values the possibility of dyeing the useful shades which these colouring matters supply from an acid bath and of thus being enabled to combine them with all the other wool dyes capable of such application, especially the azo colouring matters. The same necessity exists for the various shades of violet here described.

This want was at first supplied by the means which had proved successful in the case of magenta, viz. by the direct sulphonation with fuming sulphuric acid of the various violets, especially the redder shades obtained by the reaction of alkyl halides upon magenta base. The colouring matters thus produced were introduced at the end of the seventies under the name of *Acid violets* to which letters denoting the shade (R and B) were added. But they did not meet with the same ready reception that had been offered to acid magenta. It is now known that the sulphuric anhydride of the fuming acid is very apt to attack the alkyl groups and thus to tarnish the shade of the violets.

The new synthetical method which had produced *Crystal violet* and its many congeners and which is apparently analogous to the synthesis of *Victoria green* and its numerous homologues, could not fail also to indicate rational methods for the production of acid violets of every conceivable shade.

Some of these methods consisted—in strict analogy to what had been done in the group of the *greens*—in introducing the benzyl group into the molecule of the dye-stuff and utilising the capacity of this radicle for sulphonation. All the variations of this method given in the description of the acid greens are admissible in the violet group. In this way the following dye-stuffs have been obtained, the structural formulæ of which need not be given:—

Acid violet 4BN, 6B, 7B and N, prepared by the sulphonation of pentamethylbenzyl-pararosaniline or by the oxidation of the monosulpho derivative of pentamethylbenzyl-leucaniline.

Acid violet 6B or Guinea violet 4B. This is a disulpho derivative, obtained by oxidising the acid, which may be obtained by the condensation of dimethyl-*p*-aminobenzaldehyde with ethylbenzylaniline sulphonic acid. The corresponding derivative of diethyl-*p*-aminobenzaldehyde is also manufactured.

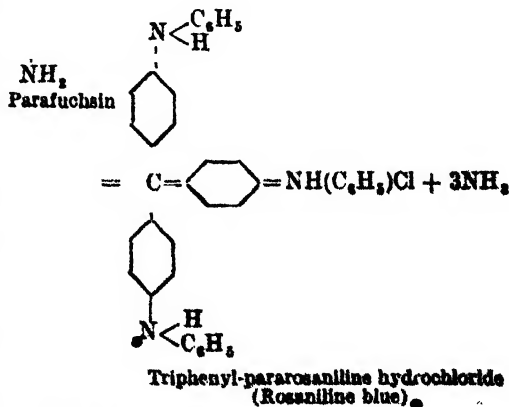
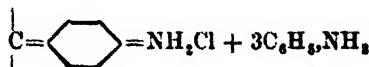
Another class of acid violets is derived from methyldiphenylamine, which may be introduced instead of dimethylaniline by all the synthetical processes described. The additional

phenyl group entering into the molecule of the leuco base of the dye-stuff derived from it by oxidation is capable of carrying a sulpho group which may be introduced into it by the usual means. Thus *Alkali violet 6B* and *Acid violet 7B* can be prepared, whilst in *Acid violet 7BN* ready formed methyldiphenylsulphonic acid is condensed with dimethyl-*p*-aminobenzoic acid.

The process of introducing elements capable of being sulphonated into the synthesis of rosaniline derivatives may be carried still farther. Thus a useful dye-stuff, called *Wool green*, is manufactured by several firms by condensing tetramethyldiaminobenzophenone (Michler's ketone) with β -naphthol and subsequently sulphonating the insoluble dye-stuff so obtained.

Rosaniline blues or phenylated rosanilines. These are of great importance, forming by far the majority of blue aniline dyes in the market. The chemistry of these compounds is, however, extremely complicated. The blues sent into commerce are not chemically pure substances, but mixtures of various isomerides; it is very difficult to classify them. Moreover, they are known under a great variety of fancy names, many of which are applied to products of different composition by different firms. The following is an attempt to classify the various blues.

The method of phenylation is very remarkable, and quite different from the methods of substituting fatty radicles for hydrogen in the amino groups of rosaniline. The general method in this case consisted in treating rosaniline base with the halogen derivatives of these radicles. Owing to the great stability of chlorobenzene C_6H_5Cl , the same process cannot be applied to the phenylation of rosaniline. This takes place, however, with great facility if we allow aniline to act upon rosaniline, ammonia being given off as a by-product:



It has already been shown that a consider-

able difference exists between pararosaniline hydrochloride or parafuchsin and the ordinary fuchsin of commerce. The former is a uniform compound $C_{15}H_{11}N_3Cl \cdot 4H_2O$, whilst the latter is a mixture of parafuchsin with at least two isomeric homologues. Both these substances may be phenylated; their phenyl derivatives are blue colouring matters of great intensity and beauty. But a greater difference is found to exist between the phenyl derivatives of pararosaniline and those of ordinary magenta than even between the two kinds of fuchsin themselves.

This method of phenylation, which has been indicated by Ch. Girard and G. de Laire, is invariably resorted to. It cannot, however, be applied on a practical scale to the hydrochloride, as assumed for simplicity's sake in our equation. Experience has shown that organic acids must be used in order to get good results. The majority of organic acids have been tried for the purpose; at present, however, only two are used, which give distinctly different results, viz. acetic and benzoic acids. The reason for this difference has not been definitely ascertained, but it is a fact known to every manufacturer that blues of a greenish shade can only be obtained with benzoic acid, whereas acetic acid yields more reddish compounds.

The phenylation of rosaniline cannot be pushed further than the formation of triphenylrosaniline. The tetra-, penta-, and hexaphenyl derivatives are not known. But even the formation of triphenylrosaniline, such as it is indicated by our equation, takes place in three successive stages, the phenyl groups entering the molecule one after another. It is, however, practically impossible to separate these stages. If, in the beginning of a blue melt, a certain amount of mono-phenylrosaniline be formed, the reaction proceeds simultaneously on this and on rosaniline, which has not yet been attacked; thus, in a second phase, monophenyl and diphenyl rosaniline, and rosaniline (which has not yet been attacked) will be present together. To these the triphenyl compound will presently be added, a very complex mixture being the result. By a more prolonged action it is possible to eliminate rosaniline itself and its monophenyl derivatives completely from the mixture. But some diphenylrosaniline will always remain present. Moreover, all these compounds seem to exist in various isomeric modifications. It is a mixture of these which forms the ordinary *crude* or *Opal blue*.

If, instead of pararosaniline, the ordinary rosaniline of commerce be used for the production of the blue (as is the case in most instances) the product becomes even more complicated by the presence of the homologous compounds. Some process of separation which splits up the crude product into fractions of different shades and reactions must be resorted to; and although some of these are crystallised, it cannot be said with certainty that they represent chemically pure individuals.

Mono- and di-phenylpararosaniline have hitherto not been prepared in a pure state. Nothing can, therefore, be said of their properties.

hydrochloride



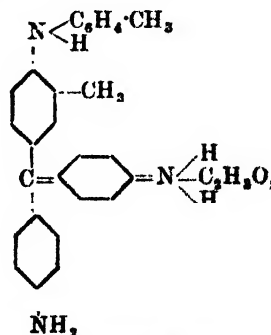
is the purest and brightest blue known. It is now invariably prepared by the phenylation of pararosaniline, but it may also be obtained by melting together diphenylamine and oxalic acid. The formic acid evolved in the decomposition of oxalic acid serves to link together three molecules of diphenylamine into one of triphenyl leuco aniline, which is then slowly oxidised into the rosaniline compound. It was this method which was formerly used for the production of this blue, which therefore is still frequently described as *Diphenylamine blue*; it is also sometimes called *Methyl blue*, because methyldiphenylamine was occasionally used for its production. Other names for the same product are:

Bleu direct, bleu lumière, bleu de Lyon, bleu de Mulhouse, bleu de nuit, bleu de Paris, light blue, night blue, Paris blue, Bavarian blue.

This product forms a microcrystalline powder of a bronzy appearance, completely insoluble in water, sparingly soluble, with a brilliant blue colour, in spirit. Its transformation into the soluble diphenylamine blues of commerce will be described hereafter.

When the same process of phenylation (the particulars of which will be given below) is applied to the ordinary rosaniline of commerce—which is, as will be remembered, a mixture—various products are obtained. Of these the following may be said to have been isolated:—

Monophenyl-rosanilines. These are the product of a very moderate phenylation. They are still soluble, in the shape of their acetates, in water, and dye fine purple shades. They have now, owing to the greater cheapness of methyl violets, almost completely disappeared from the market, in which they formerly played an important part under the name of *Regina purples* or *Regina violets*. It was customary to prepare them, not by the action of pure aniline on magenta acetate, but rather by that of the recovered oils or *échappés* from the magenta process, which contained a large proportion of *o*-toluidine. The action of the latter is slower than that of aniline; it is, therefore, easier to stop the reaction before a considerable proportion of the diphenyl or ditolyl rosaniline is formed. The regina purples consisted, therefore, to a great extent of the *o*-tolylrosaniline, the acetate of which is represented by the following formula:

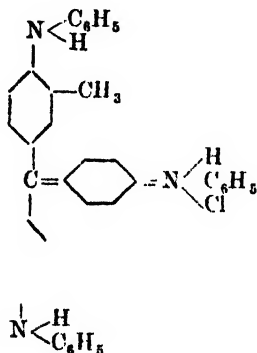


Regina purple.

Diphenylrosanilines. These were invariably obtained, together with the regina purples, from which they are distinguished by their complete

insolubility in water. They are, however, still of a purple shade; they are invariably present to some extent in crude tri-phenylrosaniline blue, if the latter be prepared with acetic instead of benzoic acid. This is the reason why such blue is always of a redder shade than the blue prepared with benzoic acid, in which the proportion of diphenyl derivatives is reduced to a minimum. A product which consists chiefly of diphenyl-rosanilines, is known under the name of *spirit purple*, *spirit violet*, or *opal violet*; it has also been sold as *regina spirit purple*. From it the *soluble violets* and *purples*, and *alkaline purples* of commerce are derived by sulphonation.

Triphenylrosanilines (see Supplement). The triphenyl derivatives of ordinary rosaniline may be subdivided into two classes: crystalline and uncrystallisable blues. The former may be extracted from every crude blue melt prepared with benzoic acid. They represent in a state of approximate purity the triphenyl derivative of the higher homologue of pararosaniline, and may therefore be represented by the following formula:



It is to this product, which forms the base of the high-class alkaline and water blues of commerce, that one should reserve the name of *Opal blue*, which has, however, been indiscriminately applied to a number of various products. This opal blue forms, in the shape of its pure hydrochloride, a mass of distinct, though very small, glistening crystals of a greenish brass-colour. It is completely insoluble in water and in spirit. If it be treated with alcoholic caustic soda, the free base is obtained in the shape of a tarry substance from which the acetate may be prepared by dissolving it in glacial acetic acid, and re-precipitating with water. This acetate is soluble in spirit, and, though sparingly, also in water. It was formerly sold and used under the name of *Opal blue 6 B for cotton*, *Gentian blue*, *Hessian blue*; also the names of *Bleu lumière*, *Bleu de nuit* (originally used for the para derivative), were occasionally applied to it. In Germany it was sold under the name of *Feinblau*, *Spirit-blau*. The latter expression is applied, however, to all blues soluble in spirit, not only to this acetate. Its use has been much restricted of late, owing to the unwillingness of the dyer to use spirit in the dye-bath.

The second class of triphenyl derivatives of ordinary rosaniline, comprises the uncrystallisable portions of crude blue melts. They contain a mixture of triphenyl and diphenyl-

rosanilines in various proportions, quite inseparable by the means which are at our disposal. They are (in the shape of hydrochlorides) insoluble in water, soluble in spirit. Caustic soda transforms them into a mixture of the corresponding bases, which are tarry masses. Their shade varies from a purplish-blue to a distinct clear blue of great strength and purity which, however, always shows a purplish hue if looked at by artificial light. This blue forms the starting-point for the production of innumerable brands and qualities of alkaline and water blues, varying in their shade and in the purity and strength of their colour. They are designated, according to the redness of shade, by the letters 3 R, 2 R, R, B, 2 B, and 3 B, whilst 4 B, 5 B, and 6 B may be said to be reserved for the derivatives of the true opal blue of varying purity. A large number of fancy names, such as *China blue*, *Marine blue*, *Serge blue*, &c., have been invented for this kind of blues.

Besides these blues a special kind of low-class blue should be mentioned which, under the name of *Blackley blue*, has enjoyed, and still enjoys, much favour, especially for dyeing paper-pulp, and also for the production of cheap woollen materials. This is the sulphonation product of a peculiar kind of phenyl rosaniline, prepared by acting with aniline upon crude magenta. It is consequently very impure, but also very cheap. It contains a mixture of the phenylation products of all the substances contained in crude magenta.

Tri-*p*-tolylrosaniline has been prepared by acting with *p*-toluidine in the presence of benzoic acid upon ordinary rosaniline base. It is a blue of remarkable beauty and brilliancy of shade, which offers, however, great resistance to the process of sulphonation. It has, therefore, only been manufactured and sold in the shape of its hydrochloride, which is soluble in spirit. It is sold for dyeing cotton under the name of *Grünlichblau* (Höchst) or *6 B extra opal blue* (English manufacturers). It has largely gone out of use of late years.

Manufacture of blues.—An immense number of prescriptions for blue melts has been published, and a larger number still circulates amongst manufacturers. It would be perfectly useless to reproduce any of them. The principles upon which they are based may be thus briefly stated:—

For the production of good blues a perfectly pure magenta base is the first requirement. For its preparation crystallised fuchsin only should be employed. If crude magenta or any of the magenta residues (*cerise*, *grenadine*, &c.) be used, the base obtained can only be employed for the production of *Blackley blues*. Pure pararosaniline, the base prepared from parafuchsin (*Neufuchsin*), should be used for the production of the so-called diphenylamine or methyl-blues (direct blues); whilst crystallised base from ordinary fuchsin forms the starting-point for all the ordinary blues from 4 R to 6 B, as well as for regina purples.

The second condition for the production of good blues is the use of very pure aniline, perfectly free from toluidine. It was in the manufacture of blues that the necessity of operating with pure aniline was first felt. The term *aniline*

for blue was, therefore, and is still occasionally, applied to perfectly pure aniline, boiling within one degree, and having a specific gravity of 1.0268-1.0270. Such aniline can only be prepared from pure crystallisable benzene.

If these two conditions—pure magenta base and pure aniline—be fulfilled, the shade of the blue obtained is still dependent upon :

1. The proportions of base and of aniline in the melt. It may be said that greenish blues will only be obtained if a very large excess of aniline be used, whilst reddish blues are produced in melts rich in magenta base.

2. The time and temperature of the melt. The formation of blue begins below 100°. It proceeds quickly at a higher temperature; 120°-140° may be assumed to be the most favourable temperature. From 140°-180° certain impurities (diphenylamine?) are formed, which impair the tendency of crystallisation of the blue. The temperature of high-class blue melts should therefore not be raised above 140°. The time required by a blue melt depends upon the proportion of base to aniline, and, to some extent, the quantities operated upon. The process proceeds quickly in highly-concentrated melts. Melts for high-class blues, which contain a large proportion of aniline, require prolonged heating—20 hours, and even more, before being finished. As a rule, the progress of the melt is tested by placing a drop of the melt on filter paper moistened with spirit. The gradual change of colour may thus be observed with great accuracy. When the melt is finished, there should be no reddish rim visible in the spot produced on the paper.

3. The nature and proportion of the acid used in the melt. It has already been said that organic acids only should be used, the action of hydrochloric acid being too slow. Acetic and benzoic acids are now used exclusively. The action of acetic acid is quicker than that of benzoic acid, but it seems impossible to transform all the rosaniline into its triphenyl derivative by the use of acetic acid. Benzoic acid acts more slowly, but it continues its action until all the rosaniline is transformed into the triphenyl derivative. At the same time, the whole of the melt is, even with benzoic acid, not entirely transformed into crystallisable opal. Moreover, acetic acid produces (by its simultaneous reaction on aniline) some acetanilide, which remains in the blue and is apt to prevent its subsequent crystallisation, whilst no benzanilide is formed by heating aniline with benzoic acid. For these reasons acetic acid is employed in the production of low-class reddish-blues (in concentrated melts), whilst benzoic acid is used only for the production of high-class opals. The greater part of the benzoic acid may be recovered from the melt, whilst the recovery of the acetic acid does not pay.

There is no advantage in using other acids instead of acetic and benzoic acid. As a rule, it may be said that the fatty acids (formic, butyric, valeric acids) act similarly to acetic acid, whilst the aromatic acids (toluic, phthalic, cinnamic acids) may take the place of the benzoic acid.

Upon these conditions all the prescriptions for blue melts are based. Taking the quantity of magenta base to be operated upon as unity,

the quantity of aniline added varies from four to twenty-five times its weight, the quantity of the organic acid from $\frac{1}{10}$ to $\frac{1}{2}$. The conditions of time and temperature have already been stated.

The apparatus necessary for blue-making is very simple so far as the melt is concerned, enamelled cast-iron pots with a lid and stirrer being always used. In the early times of the manufacture of aniline colours it was believed that blue melts could only be made in glass, and on a very small scale. In the 'Fuchsin' factory at Lyons the blue was therefore manufactured in large numbers of glass flasks heated in a sand-bath. At present it is believed that blue melts are best under control in large quantities; large melting-pots are therefore used as a rule. While the melt is in progress ammonia is given off, which carries a certain amount of aniline away. It is advisable to condense this aniline, and to absorb the ammonia by water or sulphuric acid.

When the melt is finished it must be worked up. This may be done by a variety of methods. Of these the simplest—which is, as a rule, resorted to in the manufacture of low-class and Blackley blues—consists in neutralising the melt with a quantity of caustic soda just sufficient to saturate the acid added to the melt. The excess of the aniline is then driven off with steam and recovered. The blue base remains in the still, and is run out whilst still hot, in a tarry state, together with the water. On cooling, it solidifies into a very brittle mass, which may be powdered, dried, and subjected to the process of sulphonation to be described hereafter.

For the production of high-class blues this simple process cannot be adopted. A separation of the crystallisable opal from the uncrystallisable blue, which invariably accompanies it, must take place, and for this separation the melt requires a special treatment. For this there are two distinct processes, of which one is very complete, although costly, because it requires large quantities of spirit. We may call it the *English process*, because it was worked and carried out chiefly in English factories. The other process, which is now used in most of the German works, is very rapid, and requires but little spirit. On the other hand, it does not give so pure a product; we may call it the *German process*.

The *English process* is the final outcome of the original French process for working up the blue melts, which consisted in boiling them out with dilute hydrochloric acid. The aniline was dissolved out together with the organic acid present, whilst the blue remained in the shape of its hydrochloride as a fine blue precipitate, which was filtered off and washed. It was then ready for sulphonation. When it was discovered that this blue was a mixture of different colouring matters it became customary to separate these by boiling the crude blue with spirit. This dissolved out the lower-class blues, leaving a better product as a residue. By repeating this process frequently, a residue was obtained at last which was quite insoluble in spirit. This represented the purest opal blue obtainable. It was by this tedious process that the once famous 'Bleu Mavi,' or 'Bleu MAVI' was obtained in

France and Switzerland. The improved English process much simplified things, and at the same time gave better yields and a purer colour by producing the opal blue in a crystallised condition, in which it is totally insoluble in spirit. This process consisted in adding to the melt (prepared with benzoic acid and a large excess of aniline), while still hot, a certain quantity of aniline hydrochloride; on cooling, the opal blue, being gradually converted into the hydrochloride, settled out in small glistening crystals, whilst the low-class blue remained dissolved in the aniline. The opal was then filtered off, and washed with spirit until quite pure. If necessary, it could be re-converted into base by treatment with alcoholic caustic soda. The base, re-dissolved in aniline, could again be converted into hydrochloride by again adding aniline hydrochloride. The opal then came out in very fine crystals, which represented the blue in a state of greatest purity. The aniline liquors obtained from these crystallisations had to be distilled in order to recover the spirit. They were then made alkaline in order to decompose the aniline hydrochloride present, the aniline was driven off by steam, and the remaining low-class blue obtained in the shape of base as described. Owing to the large quantities of spirit used for washing the crystallised opal, and the consequent loss of spirit by evaporation, this process (which may be recommended for laboratory experiments) was costly, and unable to compete with the rapid and cheap German process.

The German process is based upon the fact that the crystallisable blue opal is insoluble in a very hot solution of aniline hydrochloride, whilst the common non-crystallisable blues are soluble in this liquid. The solution of the aniline salt must, however, be so concentrated (in order to act properly) that it would solidify into a mass of crystals if cooled in the least degree. It is rather fused aniline hydrochloride that is required, and not an actual solution of the salt in water. In order to operate properly with such liquids, closed vessels must be used. The following is the principle upon which the plant in the majority of German works is constructed.

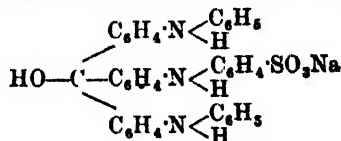
Near the melting-pot a battery of closed iron vessels, lined with lead, is erected. The first of these is filled with a quantity of hydrochloric acid, just sufficient to neutralise the aniline contained in the blue melt. The melt, when finished, is introduced into this vessel by means of air pressure. The vessel is fitted with a stirrer, which stirs up the mixture into a homogeneous mass. This is then pressed into a second vessel, which contains some filtering arrangement, upon which the blue crystals are deposited. The liquid which issues from this vessel is diluted with water, when the common blue hitherto dissolved in it is quickly deposited. The blue crystals remaining on the filter are washed with water, and may be purified by boiling them with spirit.

Blues soluble in water.—Very little of the blue that is manufactured is used in the opal state, viz. soluble in spirit. By far the largest proportion of it must be transformed into products soluble in water in order to become a marketable article. For this purpose sulphonation is resorted to.

The sulphonation of triphenylrosaniline takes place very easily, the phenyl radicles attached to the amino groups being readily substituted by the sulpho group SO_2H . As there are three of these phenyl radicles present, three sulpho groups may be introduced into the molecule of the blue. The pure, crystallisable, high-class opal blue is more easily sulphonated than the common blues. The sulphonation takes place in progressive stages, one sulpho group being introduced after the other. It is difficult to introduce more than two sulpho groups by the use of ordinary sulphuric acid. Fuming sulphuric acid must be resorted to in order to produce the trisulpho derivative. As this, however, is hardly ever required, being much too soluble for the purposes of the dyer, common sulphuric acid is invariably used, but the 'extra-strong' quality of 95–97 p.c. H_2SO_4 is, as a rule, preferred.

If this acid be allowed to act upon an aniline blue, the reaction begins at about 30° and results at first in the formation of the mono-sulpho derivative. The following are its properties:

In the free state triphenylrosaniline mono-sulphonic acid forms blue flakes, which are quite insoluble in water, in a solution of sodium bicarbonate, or even in weak ammonia. Sodium carbonate dissolves it on boiling; caustic soda in the cold. The solutions are perfectly colourless. They contain, in fact, the sodium salt of monosulphotriphenyltriaminotriphenylcarbinol:



The dry sodium salt is jet black.

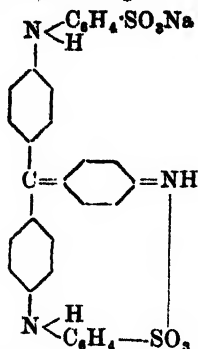
This compound has the curious property of combining with wool in an alkaline bath. The wool remains colourless, but after being washed with water it becomes brilliantly blue if immersed in weak sulphuric acid.

This curious property, discovered by Nicholson, has been made use of by wool dyers, who prefer the 'alkaline' or 'Nicholson' blues to all others for the production of bright and brilliant blues.

The alkaline blues originally manufactured by Nicholson and other makers were as nearly as possible the pure sodium salts of the mono-sulpho derivative. Owing to the difficulty of dissolving them even in boiling water, another kind of alkaline blues was produced later on; these new alkaline blues contain a proportion of the disulpho derivative. They form blue powders, easily soluble in water, giving a solution which is distinctly blue. The use of these new alkaline blues is exactly similar to that of the old quality.

If the sulphonation of the opal blue be carried farther by raising the temperature and allowing the reaction to continue for a longer period, the monosulpho acid gradually disappears and is replaced by the disulpho derivative. This is insoluble in weak sulphuric acid, but rather soluble in pure water, with an intensely blue colour. Its sodium salt forms bright coppery masses soluble in water with blue colour.

This salt contains probably the compound represented by the following formula :



The disulpho derivatives of the various classes of triphenyl-rosanilines are known under the names of *Cotton blue*, *Water blue*, *China blue*, *Navy blue*, *Guernsey blue*, and many others, which are again sub-divided by the use of the letters R and B. Thus a 6B cotton blue is the disulpho acid of a very high-class, crystallisable Opal blue, whilst a 4R Guernsey or Navy blue would be a reddish-tinted blue, manufactured from an opal prepared with acetic acid and a small excess of aniline in the melt.

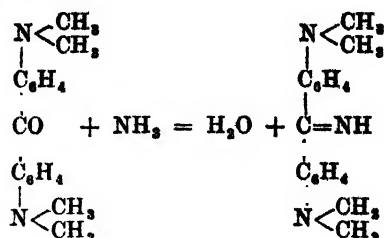
The process of sulphonation, though very simple in theory, requires great care and attention on the part of the manufacturer. The sulphonation is carried on in cast-iron pots into which the necessary quantity of sulphuric acid is introduced. The opal blue, which should be finely powdered and perfectly dry, is then stirred in, and the temperature raised gradually. Samples should be drawn from time to time, and the precipitate produced by the addition of water must be examined as to its solubility in water, weak ammonia, sodium carbonate, and caustic soda. When the desired degree of solubility is obtained, the liquid is poured into water, and the blues filtered off and carefully washed. When quite free from acid, they are dissolved in the necessary quantity of caustic soda; the solution is then filtered, and evaporated to dryness in jacketed pans. Cotton blues should be freed from the excess of sulphuric acid by the addition of slaked lime. The solution of the calcium salt is filtered and converted into the sodium salt by double decomposition with sodium carbonate. After another filtration, the solution of the blue is evaporated to dryness. Certain artifices are required to produce porous masses, such as the brand known as *China blue*, which is manufactured for export, and is required to possess a given bulk for a given weight.

Appendix to basic triphenylmethane colouring matters.

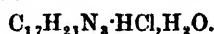
Auramine. This dye-stuff, although a derivative of diphenylmethane, is so closely connected with the manufacture of crystallisable violet that it cannot be omitted from this article.

It has been shown that crystal violet, as well as *Victoria blue* and other dye-stuffs, are manufactured from dimethyl and diethyl diamino-benzophenone. Now, if these ketones be heated with ammonium chloride in the presence of zinc chloride, an interesting reaction takes

place at the temperature of 150°–160°. The oxygen of the ketone is replaced by the imino group NH, thus :



The imides thus obtained are yellow colouring matters, and have received the name of *auramines*. The auramine of commerce is imino-tetramethyl-di-*p*-amino-diphenylmethane hydrochloride, containing one molecule of water of crystallisation :



It forms a yellow powder easily soluble in water. It is exclusively used for dyeing and printing on cotton.

Substituted auramines may be obtained by using the hydrochlorides of primary bases instead of sal-ammoniac. Thus a phenylated auramine of orange colour may be produced by acting with aniline hydrochloride upon tetramethyldiaminobenzophenone.

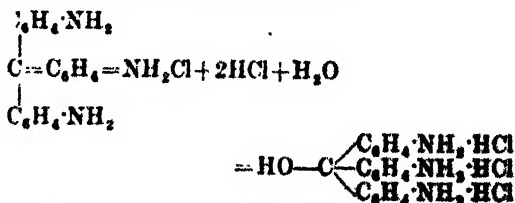
The auramines were discovered by Caro and Kern in 1884. They form the subject of the Eng. Pats. 5512, 1884, and 5741, 1884, and the D. R. PP. 29060 and 31936. (See art. AURAMINE, vol. i. 431.)

II. THE AURIN GROUP.

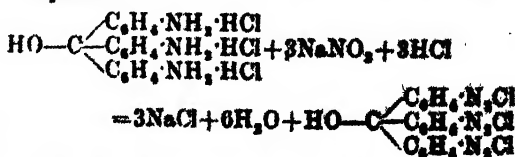
The members of this group contain oxygen in the place of the pentavalent nitrogen of the preceding one. If magenta and its congeners may be considered as quinone-imides, the aurins are the corresponding quinones.

The generic relation between the fuchsin and the aurin groups will be best seen by showing how the typical representative of the former, parafuchsin, may be transformed into the first representative of the aurin group, aurin itself.

We know that parafuchsin, if treated with an excess of acid, is transformed into the triacid salt of triaminotriphenylcarbinol :

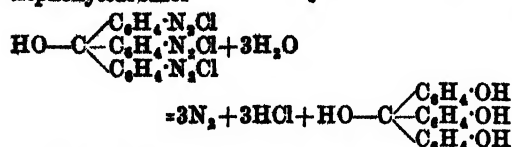


Now this salt, if treated with nitrous acid, is transformed into the corresponding diazonium compound.

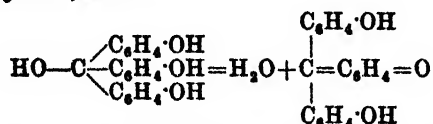


This, on being boiled with water, loses

nitrogen and is transformed into trihydroxy-triphenylcarbinol



The latter loses, in *statu nascendi*, one molecule of water, being transformed into its inner anhydride, aurin:



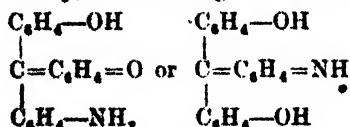
Thus aurin is parafuchsin in which all nitrogen has been replaced by oxygen.

This mode of formation has long been known, not for aurin itself, but for its higher homologue, rosolic acid, which was prepared from the ordinary fuchsin or magenta by the process described. The many co-ordinate points of aurin and rosolic acid were recognised at an early period. On the other hand, chemists were aware of the distinct difference between aurin and rosolic acid, which is just as considerable as that existing between parafuchsin and its higher homologue.

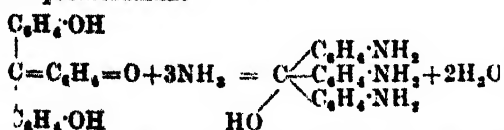
When an insight into the nature of the fuchsin group had been obtained, the knowledge of the constitution of the aurin group followed as a natural consequence.

But even before this was the case, another connection was discovered between aurin and fuchsin.

It had long been known that aurin (the mode of formation of which will be given later on) may be modified by heating it with alcoholic ammonia. F. Persoz produced a red dye-stuff, which he called *Pæonine*, by this process. This had, in all probability, the following constitution:



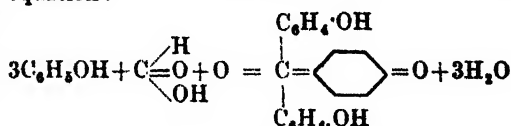
In 1878, Dale and Schorlemmer, whose researches on aurin are of great importance, showed that aurin, by very prolonged heating with alcoholic ammonia, may be transformed into pararosaniline



Thus the connection of the two typical dye-stuffs was definitely established. At present we know that the aurin group contains the acid counterparts of the basic members of the fuchsin group. A considerable number of them are known and described in chemical literature. As, however, almost all of them are of no practical value it would be useless to enumerate them in this article. We will therefore describe only those substances of the aurin group which are of some practical interest. There are very few of them.

1. Aurin $\text{C}_{18}\text{H}_{14}\text{O}_3$. The discovery of this substance, or one very nearly related to it, dates as far back as 1834, when F. Runge, the pioneer of the chemistry of coal-tar, observed that crude carbolic acid (containing cresol) was transformed into an acid red dye-stuff by oxidation. Later on (1859), Kolbe and Schmitt and F. Persoz simultaneously observed that pure phenol, when treated with oxalic acid, or with oxalic acid and sulphuric acid, was transformed into a similar red substance. The manufacture of the new dye-stuff was first taken up in Lyons by the firm of Guinon and Marnas. Later on, it was carried out on a large scale by C. Calvert and by C. Lowe; also by Roberts, Dale & Co., in Manchester. The crude aurin thus obtained is a non-crystallisable, brittle, pitchy mass, of a brilliant green metallic aspect, insoluble in water, but soluble in caustic soda solution, with a magnificent red coloration. It dyes silk and wool from an acid bath, producing an orange shade on these fibres. It was much used on silk in former days, but its use has been abandoned since the introduction of the azo-colouring matters, which produce brighter and faster shades.

The researches of Dale and Schorlemmer, Zulkowski, and others have shown that common aurin consists of a mixture of a number of substances which, in a pure state, are well crystallised. Of these, aurin itself $\text{C}_{18}\text{H}_{14}\text{O}_3$, oxyaurin $\text{C}_{18}\text{H}_{12}\text{O}_4$, methylaurin $\text{C}_{20}\text{H}_{16}\text{O}_3$, and pseudorosolic acid $\text{C}_{20}\text{H}_{16}\text{O}_4$, may here be mentioned. All these substances are produced by the action of nascent formic acid (generated from the oxalic acid) upon phenol. This mode of formation of aurin itself may be represented by the following equation:

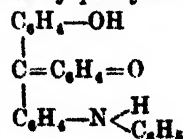


A large number of other reactions have been observed in which aurin is formed to a greater or lesser extent. Thus, for instance, it is obtained by acting with formaldehyde, with iodoform, with chloroform and caustic potash on phenol. These reactions have never attracted the attention of manufacturers, aurin having lost its practical interest.

The sodium salt of crude aurin is known in commerce under the name of *Yellow Corallin*.

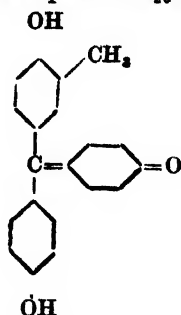
2. *Pæonin*, *corallin red*, *aurin red* is the sodium salt of the reaction product of alcoholic ammonia upon aurin, which has already been mentioned and the constitution of which is given above.

3. *Azullin* is a similar product, of a dirty violet shade, obtained by heating aurin with aniline. It is probably phenylated pæonin:



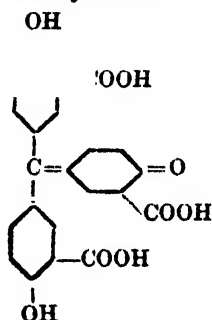
4. *Rosolic acid* is the name which was originally given by Runge to the oxidation product of crude carbolic acid. For a long time it was considered to be identical with aurin. At

present this name is reserved for the product obtained from the ordinary fuchsin of commerce by the diazotising process. It forms magnificent blue needles, which, being homologous to true aurin, have the composition $C_{20}H_{16}O_2$:



It dyes silk and wool orange shades, similar to those obtained with aurin. It is of no practical interest.

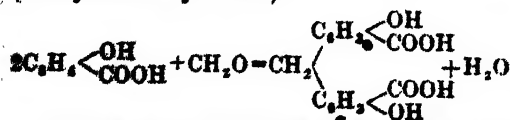
5. **Chrome violet** $C_{22}H_{12}O_6Na_3$ is the only member of the aurin group which is of considerable practical value. It is the sodium salt of aurin tricarboxylic acid:



It was discovered in 1889 by Sandmeyer, and patented (D. R. P. 49970, J. R. Geigy). It is prepared by acting with formaldehyde, or with a mixture of methyl alcohol and sodium nitrite, upon a solution of salicylic acid in sulphuric acid. The carboxyl groups are in the *ortho*-position to the hydroxyl groups. The result of this arrangement is that the dye-stuff combines readily with metallic mordants of the iron group, and especially with chrome mordant, producing violet shades of considerable fastness on cotton. It is chiefly used for printing on cotton.

The process patented for the production of chrome violet is interesting, because it forms a general and excellent synthetical method for the production of the aurins. It is strictly analogous to the synthetical method adopted for the production of 'Neu-fuchsin' by the 'Farbwerke' of Höchst. Two stages may be distinguished in the process:

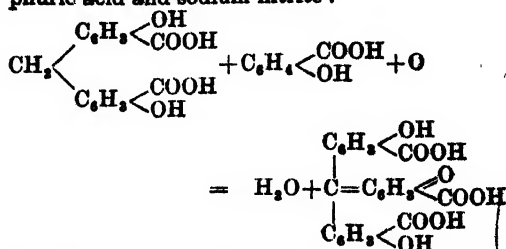
(a) In the first stage, formaldehyde (or methylal) acts upon two molecules of the phenol—in the case of chrome violet, salicylic acid—forming the diphenylmethane derivative (methylene salicylic acid):



This reaction may be facilitated by the addi-

tion of condensing agents, such as hydrochloric acid and others.

(b) In the second stage, the diphenylmethane derivative is simultaneously condensed and oxidised with another molecule of the phenol into the corresponding aurin by the mixture of sulphuric acid and sodium nitrite:

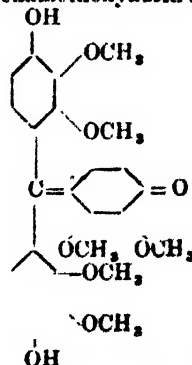


Any phenol, or substitution product of a phenol, may be substituted for the salicylic acid in the process.

Later on, N. Caro (Ber. 25, 940) prepared a large number of carboxylated aurins by this process, substituting resorcylic, gallic, and cresotinic acid for the salicylic acid in the patented process. The compounds obtained proved to be very similar to chrome violet.

6. Of the large number of aurins prepared, only one more need be mentioned here: **pittacal**, a curious substance discovered in 1835 by Reichenbach in certain portions of beechwood tar. Liebermann more closely investigated this substance, and gave to it the name of *eupittonic acid* (Ber. 1876, 9, 334; 1878, 11, 1104). Hofmann determined its constitution (*ibid.* 1878, 11, 1455; 1879, 12, 1371, 2261).

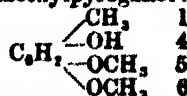
Pittacal is hexamethoxyaurin:



formed by the simultaneous oxidation of dimethylpyrogallol:



and dimethyl methylpyrogallol:



which are both contained in wood tar. The methyl group of the second compound yields the central carbon atom in the same way as occurred with cresol in the formation of the rosolic acid observed by Runge.

Pittacal is an orange substance, crystallising in beautiful crystals when pure. Its solution in caustic alkalis is of a beautiful blue colour.

By heating pittacal with ammonia, Grätzel

TRIPHENYLMETHANE COLOURING MATTERS.

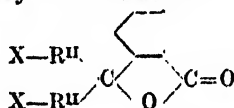
obtained a violet colouring matter, which proved of no practical value (*v. EUPITTONIC ACID*, vol. ii. 689).

III. THE PHTHALEIN GROUP.

The phthaleins were discovered by Baeyer in his memorable researches on the condensation of phthalic acid with aromatic hydrocarbons and phenols. Their constitution was, however, at first misunderstood. In 1880, when the curious properties of phthalic anhydride became more definitely known, the error was corrected and the phthaleins were recognised as congeners of the triphenylmethane group.

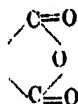
It is a well-known fact that every *o*-dicarboxylic acid is capable of forming, by losing the elements of water, an inner anhydride. These anhydrides act very easily on phenols, in some cases without the addition of condensing agents. Water is again eliminated, and a dye-stuff formed in every instance. Of the many colouring matters thus obtained, only those prepared from phthalic anhydride have, with one exception, become of general and practical interest, and these will here be described.

The central carbon in these dye-stuffs is afforded by one of the carbonyl groups of the anhydride of an *o*-dicarboxylic acid. If we restrict our consideration to phthalic anhydride, the formula may be thus modified :

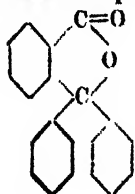


phthalic acid being benzene *o*-dicarboxylic acid.

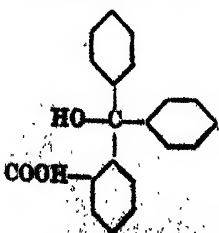
Phthalic anhydride, although perfectly symmetrical in its constitution



acts, in condensations, like an asymmetrical compound, only one of the carbonyl groups being attacked and losing its oxygen. Thus, by being condensed with two molecules of benzene it yields diphenyl-phthalide or phthalophenone :



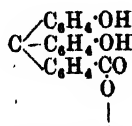
which is the parent substance of all the phthaleins, just as triphenylmethane is the parent substance of the fuchsin and aurin groups. Diphenyl-phthalide, however, is but the inner anhydride of triphenylcarbinol *o*-carboxylic acid



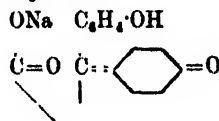
hence the near relation between the phthalein, fuchsin, and aurin groups.

Formerly it was considered as probable that the anhydride structure of phthalophenone was preserved in the dye-stuffs derived from it. At present, almost all chemists are of the opinion that such is not the case, that the carboxyl group becomes free after the condensation has taken place and that it simply serves as a salt-forming group of minor importance. The quinonoid structure is shifted to the pyrone ring which is always present in all the really useful members of this group. Phenolphthalein and diaminophthalophenone, which do not contain the pyrone ring, are of no value as dye-stuffs. The constitution of the more important members of this group will be seen from the structural formulae given for each of them.

1. Phenolphthalein $\text{C}_{20}\text{H}_{14}\text{O}_4$ was discovered by Baeyer in 1871 (*Ber.* 1871, 4, 658). Its constitution is



it may be considered as a substituted phthalophenone, but as in the free state it has no quinonoid structure, it is also colourless. It is easily prepared by heating phthalic anhydride with phenol in presence of sulphuric acid or stannic chloride. It forms pale-yellow crystals, which dissolve with a fine red colour in caustic alkalis. In the salt so formed the quinonoid structure is established and the substance thereby becomes a dye-stuff :



The practical importance of phenolphthalein is very small. Its only use is that of an indicator for alkalimetric purposes.

For observations on the colourless salts of phenolphthalein and on its value as a colorimetric standard, see Kober and Marshall, *J. Amer. Chem. Soc.* 1911, 33, 59. For the behaviour of phenolphthalein derivatives as indicators, see Rupp, *Arch. Pharm.* 1911, 249, 56.

2. *Tetranitrophenolphthalein* $\text{C}_{20}\text{H}_6\text{N}_4\text{O}_{12}$ has been proposed as an orange colouring matter for wool. Its sodium salt $\text{C}_{20}\text{H}_6\text{N}_4\text{O}_{12}\cdot\text{Na}_4$ is sold as an orange powder under the name of *Aurotine*. It was discovered by C. Dreyfus, H. Bull, and T. Hall, and patented in England under 3441 (1889), in Germany under 52211. In a pure state free tetranitrophenolphthalein forms orange crystals, melting at 344° .

It has long been known that phenolphthalein is not a good dye. The same applies to all the ordinary typical phthaleins. Phthalophenone (diphenylphthalide) is but a poor chromogen, but its properties are at once improved (as has already been shown above) if the two phenyl-radicles in its molecule be linked together by another group, preferably oxygen. We thus come to chromogens containing the pyrone ring

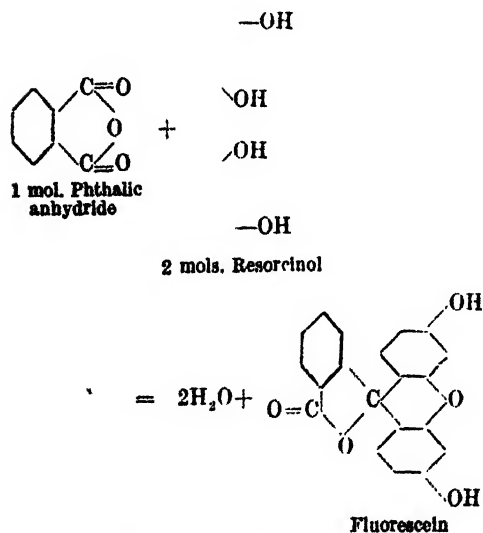
combined with the structure of triphenylmethane derivatives, which, by the introduction of auxochromic groups, give rise to some of the most beautiful dye-stuffs yet discovered. As in all cases, the auxochromic groups introduced may be either the hydroxyl or the amino group; and in the latter hydrogen may be replaced by organic radicles. We thus get phthalein colouring matters of either phenolic (acid) or aminic (basic) character. For a long time the former alone were known; we will therefore, consider them first.

A. Acid phthalein dye-stuffs.

The prototype of these is—

1. **Fluorescein** $C_{20}H_{12}O_6$. This beautiful substance is formed most easily if phthalic anhydride and resorcinol be mixed in molecular proportions and heated to 190° . In the factories this operation is carried out in enamelled cast-iron pots, heated in an oil bath. The ingredients melt, and large quantities of steam are given off. When the reaction is finished the mass solidifies into a cake of dark-brown colour, which consists of almost pure fluorescein.

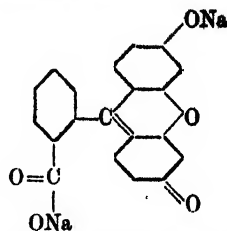
In this reaction two molecules of resorcinol combine with one of phthalic anhydride. At the same time they interact upon one another, losing one molecule of water, and forming the pyrone ring:



Fluorescein in a free state has thus a constitution quite analogous to that of phenolphthalein, although the presence of the pyrone ring is indicated by the intense brick-red colour of the substance. It is quite insoluble in water, sparingly so in the majority of other solvents. It, however, we dissolve it in alkaline liquids, it assumes, like phenolphthalein, its quinonoid nature and this change is marked by the intensity of its colour. In caustic alkalis and in ammonia it dissolves with a brown colour. The solutions have, especially when dilute, a most brilliant and beautiful green fluorescence. Hence the name of the substance.

Concerning the nature of the changes which take place when fluorescein is treated with

alkali, see Baeyer, Annalen, 1910, 372, 80, part iii.



Sodium salt of Fluorescein, showing quinonoid structure combined with pyrone ring

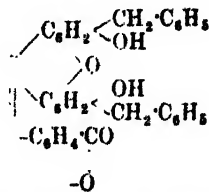
The crude fluorescein obtained in the manufacture, as above described, seems to contain two modifications of the substance (which may be isomerides). By treating the crude cake with boiling spirit, a certain amount of a soluble, non-crystallisable fluorescein is extracted, whilst the greater proportion of it remains undissolved, and is obtained as a crystalline residue on filtering. This process of purification is invariably used in the manufacture of the dye-stuff. Both the soluble and the insoluble part are worked up in the manner to be described hereafter, the insoluble fluorescein giving the better and purer qualities of the dye-stuffs, whilst the low-class qualities are made from the soluble fluorescein obtained by evaporating the alcoholic extract.

A small quantity of the fluorescein manu-
factured is transformed into its sodium salt



which is sold, under the name *Uranin*, in the shape of a yellow powder, very soluble in water. It is used for dyeing pale yellows on silk.

If benzyl chloride and some sulphuric acid be added to the fluorescein melt a substance is obtained which is supposed to be benzyl-fluorescein :



Its sodium salt is sold as a yellow dye-stuff under the name *Chrysolin*. This substance, discovered by Reverdin in 1877, is not of much practical importance.

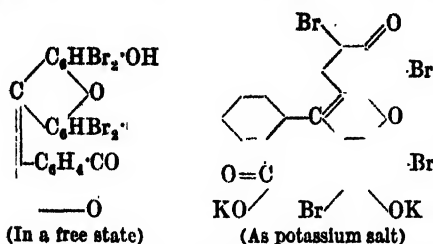
By far the greater part of the fluorescein produced is transformed into very beautiful red colouring matters by the introduction of halogen atoms into its molecule. The dye-stuffs so prepared are known by the generic name of *Eosins*.

If fluorescein be treated by substituting reagents, it is generally observed that four atoms of hydrogen are replaced by other groups. Further investigations have shown that this substitution takes place in the phenyl radicals, which entered the fluorescein in the shape of resorcinol, whilst the phenyl radicals derived from the phthalic anhydride is never attacked by these reagents.

The most important of the dye-stuffs so prepared is

2. Eosin $C_{20}H_{12}O_{10}Br_2K_2$, the potassium salt

of tetrabromofluorescein. The sodium salt is also occasionally met with, but it does not crystallise so well. The constitutional formula of eosin is :



Eosin is prepared by acting with four molecules of bromine upon one molecule of fluorescein. The crystallisable, modification of the latter is used for the manufacture of a good product. On the small scale a solution of the fluorescein in glacial acetic acid is prepared, and the bromine introduced gradually.

For manufacturing purposes glacial acetic acid is too expensive. The following process, which admits of operating in aqueous solutions, may be used instead.

The bromine is dissolved in exactly the necessary quantity of caustic soda, and the solution is evaporated to dryness. The resulting salt consists of a mixture of sodium bromide and sodium bromate. It is dissolved in water and mixed with a solution of the theoretical quantity of fluorescein in caustic soda. The mixture is then acidified with hydrochloric acid. The bromine generated acts at once upon the fluorescein, and the precipitate obtained is eosin, which need only be dissolved in a solution of potassium carbonate and evaporated to crystallisation.

The quantity of bromine used may be reduced to half (two molecules or four atoms) by using a mixture of potassium bromide and potassium or sodium chlorate, instead of the salt obtained by evaporating the solution of bromine in caustic soda.

This process, although cheap and simple, is not generally used, because the bromine is found to act too energetically. A certain amount of the eosin is destroyed, and the remainder is not so brilliant in colour as it might be.

The bromination proceeds much better in an alcoholic solution; alcohol is, therefore, frequently used for the purpose in the manufacture of eosin. The fluorescein is finely ground, and suspended in strong spirit. The necessary quantity of bromine is added. The bromination takes place slowly and gradually, and an excellent product is obtained. The spirit is recovered by distillation.

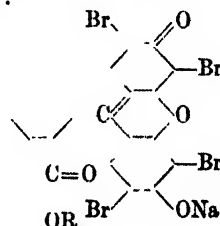
In order to reduce the bromine in this as in the aqueous process to two instead of four molecules, the addition of a chlorate is necessary. But a chlorate must be used which is soluble in spirit. Cupric chlorate is preferred to any other. It is prepared by mixing concentrated aqueous solutions of sodium chlorate and cupric chloride or sulphate. The solution obtained is added to the operation in progress.

Eosin forms either a dark-brown powder, or dark-brown crystals with a green metallic lustre. The potassium salt may also be obtained in flesh-coloured crystals by re-crystallisation from spirit. These crystals contain alcohol of crys-

tallisation. According to strength and purity of shade, the commercial eosins are distinguished by certain letters and additions, such as 'eosin B,' 'A,' 'GGF,' 'DH,' 'extra,' 'extra-fine,' 'soluble,' and others. All these brands dissolve easily in water, with a scarlet coloration. Dilute solutions show a marked greenish fluorescence.

Eosin is used for dyeing silk and other fibres, also for staining paper, and for preparing red inks of a very fine scarlet colour. Large quantities are used for the last-named purpose. Eosin is not a fast colour, but its brilliancy of shade secures a ready sale for the large quantities produced.

3. Eosin soluble in spirit (*Primrose, methyl eosin*). These names are applied to certain products, which are produced by boiling eosin, dissolved in spirit, with caustic soda and methyl iodide, or ethyl bromide. The carboxyl group is thus alkylated, whilst the hydroxyl group remains combined with alkali. The sodium salts thus obtained form glistening crystals, insoluble in water but soluble in spirit. They have the constitution :



in which R stands for either methyl or ethyl. Small quantities of these substances are prepared and employed as an addition to the vermilion used in cotton printing, in order to increase the brilliancy of its shade. Spirit eosin was formerly also used for silk dyeing, but for this purpose it has been replaced by the bluish eosins soluble in water, to be described later on.

If the hydroxyl group of eosin is also to be alkylated, this can only be effected by acting with alkyl iodide or bromide upon the silver salt of eosin. The dialkyl-ethers thus obtained are colourless.

4. Eosin scarlet (*Eosin B, BN, BW, scarlet, J, JJ, V, &c.*). Sodium salt of dinitrodibromofluorescein $C_{20}H_6N_2O_5Br_2Na$.

If fluorescein be treated with nitric acid, dinitrofluorescein is obtained, which has found no application as a colouring matter. But by subsequent bromination it yields a brilliant scarlet. The same product (or an isomeric very similar to it) may be prepared by first brominating the fluorescein and then treating it with nitric acid.

This dye-stuff was hailed with enthusiasm when it made its appearance in 1875, but its use was soon much restricted by the introduction of the scarlet azo-dyes which are quite as brilliant, and at the same time faster, cheaper, and more easy in their application.

5. Erythrosin (*Bluish Eosin, Dianthin, Primrose soluble, Pyrosin B, and other names*).

This is the sodium salt of tetraiodofluorescein $C_{20}H_4O_5I_4Na$. The potassium salt is also met with occasionally. It is prepared by iodinating fluorescein with iodine and oxidising agents, such as mercuric oxide, iodic acid, cupric chlorate,

&c. It may also be prepared by introducing iodine monochloride into an alcoholic suspension of fluorescein.

Erythrosin dissolves in water, with a fine red colour, and very slight fluorescence. It dyes silk in shades which are much more bluish than those obtained with eosin.

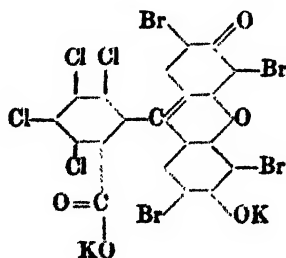
Erythrosin was introduced into the market in 1876 by Bindschedler and Busch. It was well received by the silk dyers. Owing to the high price of iodine, a mixture of eosin and Bengal red is now used for producing the same shades.

There is one application, however, for which pure erythrosin is still required—for producing orthochromatic dry plates for photographic purposes. As a sensitiser of silver bromide, erythrosin holds a prominent place amongst all the colouring matters hitherto tried.

Di-iodofluorescein was sold and used for a very short time as an orange dye-stuff, under the name '*Pyrosine J.*'

6. **Phloxin** (*Potassium salt of dichloro- or tetrachloro- tetrabromofluorescein*).

This colouring matter, discovered in 1876 by Nölting, together with the following ones, formed a new departure in the manufacture of the eosin dyes. The characteristic feature of these substances is the fact that they contain halogen atoms substituted for hydrogen, not only in the resorcinol groups, but also in the phenyl group derived from the phthalic anhydride. Now, it has already been said that a substitution of this kind cannot be effected in ready-made fluorescein. To prepare phloxin, therefore, or any of its congeners, a special fluorescein must be used, prepared not with ordinary phthalic anhydride, but with the anhydrides of dichloro- or tetrachloro- phthalic acid. Dichlorophthalic acid is best prepared by oxidising dichloronaphthalene, whilst tetrachlorophthalic acid may be obtained by chlorinating phthalic anhydride in the presence of finely divided iron. Both acids give colouring matters of very similar shades, the tetrachloro derivatives being but very little bluer than the dichloro derivatives. The process of manufacture of the dye-stuffs is identical with that described for eosin. The constitutional formula of phloxin is

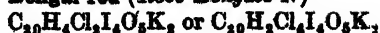


if derived from tetrachlorophthalic acid. The phloxin derived from dichlorophthalic acid contains, of course, two atoms of chlorine less.

Commercial phloxin is a red powder, soluble in water, with a red colour and no fluorescence. It dyes beautiful bluish-red shades on silk, which resemble those obtained with erythrosin.

7. **Cyanosin** is the monomethyl ether of phloxin. It is soluble in spirit, and dyes shades still bluer than phloxin.

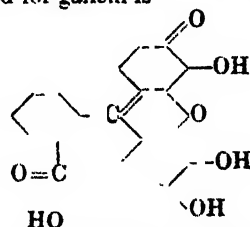
8. Bengal red (*Rose Bengale N*)



is the iodo derivative of this series. It is the bluest eosin dye-stuff obtained. It is very expensive, and was formerly used in large quantities to produce the most brilliant bluish-reds on silk. It has now, to a great extent, been replaced by the rhodamines. Its methyl ether, soluble in spirit, received the name of *Cyanosin B*. Its application never became important.

The phthalein derivatives of resorcinol are all very brilliant dyes. There are, however, some other acid phthaleins which, although important as colouring matters, are of much milder hues. They are derivatives of pyrogallol.

9. **Gallein** $\text{C}_{20}\text{H}_{12}\text{O}_7$. If phthalic anhydride be condensed with pyrogallol, the reaction takes place quite as easily as with resorcinol. The product obtained is, as might be expected, dihydroxyfluorescein. The constitutional formula now adopted for gallein is



For the manufacture of gallein it is not necessary to prepare pure pyrogallol. Gallic acid may be used instead, which, losing carbon dioxide, is at once transformed into gallein by the action of the phthalic anhydride.

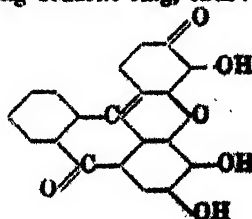
Gallein is generally sold in the shape of a violet paste. It is sparingly soluble in water, easily soluble in caustic alkalis, with a bright-blue coloration. It dyes mordanted wool and cotton. Chrome mordants are used preferably, and dark-violet shades are obtained.

On account of the similarity of the application of gallein to that of alizarin, gallein is also sold under the name of *Alizarin violet* or *Anthracene purple*.

10. **Cerulein** (*Alizarin green, Anthracene green*) $\text{C}_{20}\text{H}_8\text{O}_6$. This is one of the most important dye-stuffs for wool and cotton, dyeing a beautiful and very fast olive green on chrome mordants. The cotton printer uses it constantly, both pure and mixed, with other dye-stuffs of the alizarin family.

It was discovered in 1871 by A. Baeyer, who obtained it by heating gallein with concentrated sulphuric acid to 200°. By the same process it is now prepared in immense quantities on the large scale.

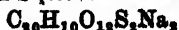
In this process the substance loses one molecule of water and the carboxyl group forms a new hexagon ring by condensing with the neighbouring benzene ring, thus:



TRIPHENYLMETHANE COLOURING MATTERS.

Cœrulein forms a black paste, insoluble in water. It is soluble in caustic alkalis, with a greenish-blue coloration.

11. Cœrulein S (soluble cœrulein)

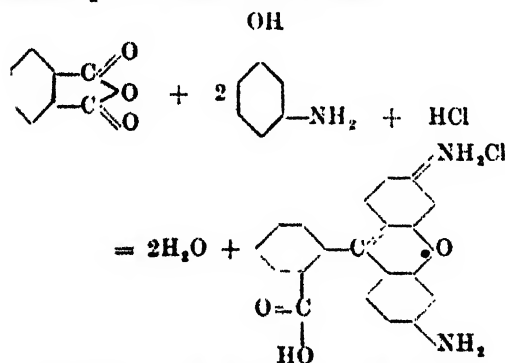


This is the product of the reaction of sodium bisulphite upon cœrulein; its manufacture is carried on by the Badische Anilin and Soda works at Ludwigshafen. It forms a black powder, soluble in water, with a brown coloration. It is easily decomposed by the addition of acids or by heat. It is used for the same purposes as cœrulein, and is very convenient, on account of its easy solubility. In dyeing with it, it is, of course, decomposed, the ordinary cœrulein being deposited on the fibre.

B. Basic phthalein dye-stuffs.

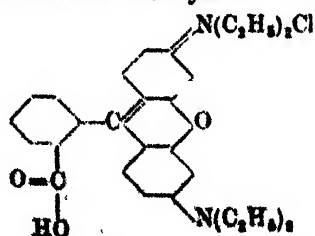
For a long time these were not known. The manner in which they might be obtained had, of course, suggested itself to the consideration of chemists, but the substances required for their synthesis seemed to be quite out of the reach of the manufacturer. In 1887, however, M. Ceresole, of the Badische Anilin- und Soda-Fabrik, successfully effected the synthesis of the first basic phthalein, which proved to be of such value that a thorough search for a good means of preparing the necessary ingredients was made, which led to complete success.

To obtain the basic substance analogous to fluorescein, it is merely necessary to replace one of the hydroxyl groups of resorcinol by an amino-group; or, in other words, to employ *m*-aminophenol instead of resorcinol:



Experience has shown that the compound thus obtained has no practical value. If, however, diethyl *m*-aminophenol is used instead of the *m*-aminophenol, a most beautiful colouring matter is obtained, known under the name of

1. Rhodamin B $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3\text{Cl}$. The commercial product is the monohydrochloride:

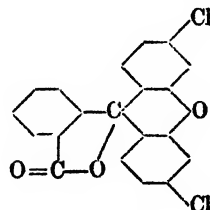


It forms beautiful needles of a metallic green appearance, easily soluble in both water and spirit. Weak solutions show a most mag-

nificent orange fluorescence, which disappears on heating, and reappears in the cold. This is the most beautiful red colouring matter ever prepared, dyeing silk, wool, and cotton a most brilliant pink of a bluish shade.

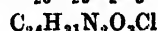
The process described for the production of rhodamin is patented by the Badische Anilin- und Soda-Fabrik, Eng. Pat. 15374, 1887; D. R. P. 44002. The diethyl-*m*-aminophenol is prepared from diethylaniline by heating it with fuming sulphuric acid to 60°, diethylaniline *m*-sulphonic acid is formed, which yields the phenol by fusion with caustic soda.

There is, however, another process for the manufacture of rhodamin, discovered by the Farbwerke of Höchst (D. R. P. 48367, 1888). It consists in treating free fluorescein with phosphorus pentachloride, when the fluorescein chloride

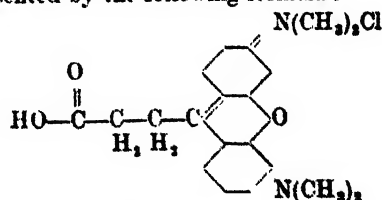


is formed. This is transformed into rhodamin if heated with diethylamine under pressure.

2. Rhodamin S $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3\text{Cl}$, and



These two colouring matters, which are identical in their practical properties and applications, are not, strictly speaking, triphenylmethane derivatives; nor are they derived from phthalic acid. They must, however, be mentioned here, because they are near congeners of rhodamin B. They are obtained by treating dimethyl- or diethyl-*m*-aminophenol, not with phthalic, but with succinic, anhydride. Succinic acid is the typical *o*-dicarboxylic acid of the fatty series. Like phthalic acid, it forms an anhydride, which condenses with resorcinol into fluorescein-like dye-stuffs; these, however, offer no practical interest. The succineins of dimethyl- and diethyl-*m*-aminophenol, however, show a sufficient difference from rhodamin to be manufactured and sold as a special brand. The constitution of the dimethyl compound may be represented by the following formula:



It is, therefore, not a triphenylmethane derivative. It is sold in the shape of its zinc double chloride.

Rhodamin S shows great affinity to unmordanted cotton. It is one of the few members of this group which may be considered to be what is now called a substantive colouring matter.

The properties of rhodamin S are very similar to those of rhodamin B. It forms crystals with a green metallic lustre, easily soluble in water, with a red coloration, and a marked

yellow fluorescence. The shades obtained with it are yellower than those produced with rhodamin B.

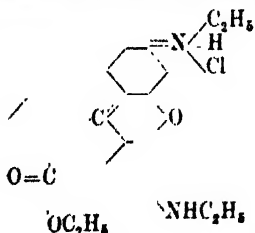
Rhodamin B and S remained for some time the only important members of this magnificent group of dye-stuffs. After a while, however, some new representatives of it made their appearance, of which the more important may be here shortly described.

Rhodamin G $C_{26}H_{27}N_3O_3Cl$ is obtained by heating rhodamin B with aniline hydrochloride. One of the ethyl groups is split off in the shape of ethyl chloride and the recovered dye-stuff is a tri-ethyl-rhodamin which dyes wool and silk in red shades of a much more yellowish tinge than the original rhodamin B.

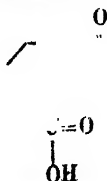
The process of alkylation, which produced such remarkable results in the eosin group, proved equally applicable to the rhodamins. It was carried out at first by using alkyl chlorides, but later on it was discovered that a much cheaper and simpler way to the same end consists in saturating alcoholic solutions of rhodamins with hydrogen chloride. As this is a method which is exclusively applicable to the alkylation of organic acids, the possibility of using it for the rhodamins formed a proof of the presence of a free carboxyl group in the dye-stuffs and went a long way in establishing the modern views about their constitution.

Rhodamin 3B, *Aniline*, was the first of the alkylated rhodamins. It dyes a more bluish shade of red than rhodamin B, and is, if possible, even more brilliant and pure in its tinge, which strongly resembles that of certain flowers such as the 'Crimson Rambler' rose.

Rhodamin 6G was obtained by the same process from *sym*-diethylrhodamin (produced by the condensation of phthalic acid with two molecules of mono-ethyl-*m*-aminophenol), and has consequently the following constitution:

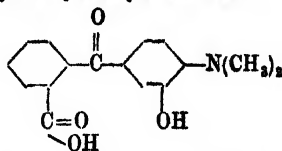


When once the constitution of the rhodamins was recognised, it was clearly seen that they may also be considered as derivatives of *o*-benzoyl-benzoic acid:

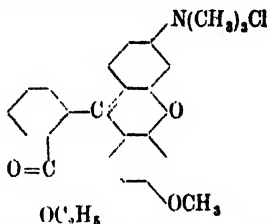


Suitable substitution products of this acid may therefore be used for the synthesis of rhodamins. This is important because it enables us to produce asymmetrical rhodamins, whilst the original process was applicable only to the production of symmetrical members of this important class of dye-stuffs. As an example of this method, *Rhodamin 12 GM* may be quoted,

which is prepared by acting with dimethyl-amino-hydroxybenzoylbenzoic acid:

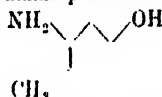


upon monomethylresorcinol and subsequent esterification of the product obtained. This dye-stuff is consequently quite asymmetrical and has the constitution:



It dyes silk, wool, and cotton a beautiful yellowish red.

If in the process given for the production of rhodamin 12 GM the monomethylresorcinol be replaced by *m*-amino-*p*-cresol:



a new and exceedingly beautiful dye-stuff is obtained, which is sold under the name *Irisamin* or *Rhodin 3G*. It dyes silk, wool, and mordanted cotton a flaming, beautiful red.

Several other members of this group have been prepared by various methods, amongst which the reaction of formaldehyde upon ready formed rhodamins may be mentioned. All the rhodamins have also been found applicable not only to the regular dyeing of textile fabrics, but also to the staining processes so largely used for paper, wood and confectionery. Very large quantities of these dyes are used for such purposes.

Few groups of synthetical dye-stuffs have proved so prolific as that of which a short description has here been given. The triphenyl-methane group contains some of the oldest artificial colouring matters known, but for more than half a century it has continued to yield new additions to the vast number of such compounds which chemical science has placed at the disposal of our textile industries. O. N. W.

SUPPLEMENT.

Recent progress in this group of colours, which already contains dyes of almost every shade, and suitable for nearly all kinds of dyeing processes, has been mainly towards the production of colours having greater fastness than is possessed by many of the earlier members of the group. It is interesting to note that whilst work has been undertaken in very numerous directions, the most important practical results have thus far been obtained upon a few fairly well defined lines.

In addition to the extension of the group in new directions, some interesting conclusions in connection with the constitution of phenylated

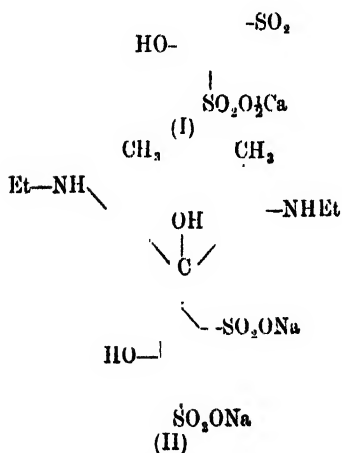
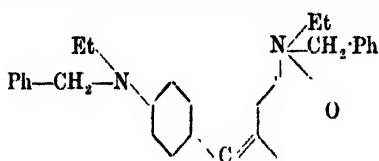
fuchsin need to be noted, whilst the connection between colour and chemical constitution and other problems of a theoretical nature concerning the triphenylmethane compounds have not ceased to claim attention.

The application of Brilliant Green as an antiseptic and in connection with the detection of typhoid carriers, is of considerable interest, and our knowledge in this field has been greatly added to by the work of Fairbrother and Renshaw (J. Soc. Chem. Ind. 1922, 41, 134 T), whilst Casella (Eng. Pat. 14742, 1912) claims that compounds of the rosaniline group which have halogens in the 'ortho' position to the amino group are of value in medicine on account of their action on tripanosomes.

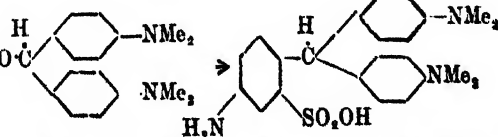
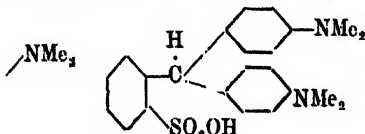
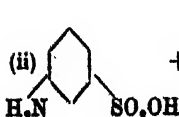
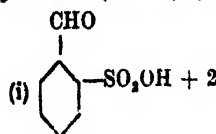
I. THE FUCHSIN GROUP.

(A) Diamino-triphenyl-methane derivatives.

In this group the extension of the 'Patent Blue' class calls for most notice. Substitution



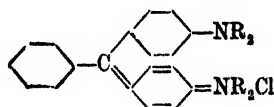
derivatives such as *Patent Blue A*, (I), and *Cyanol FF* (Casella), (II), have been produced



By the use of such groups as NO_2 , COOMe , CN , or the halogens Cl and Br , in place of the sulphonic acid group in the ortho position, it has been possible to produce other products having similar properties. In this connection a further

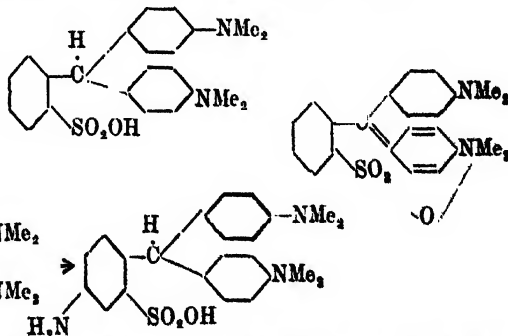
by the use of ethyl-benzyl-aniline and mono-ethyl-*o*-toluidine respectively in place of dimethyl- or diethyl-aniline in the processes for the manufacture of 'Patent Blue.' When patent blue itself is oxidised (D. R. PP. 60961, 61478; Friedl. 3, 152, 153) a new dye, *Cyanin B* (M. L. B.), is produced, which is faster to light and washing than patent blue, and dyes similar shades. Concerning the structure of cyanin B, little is definitely known, but it is considered probable that during the oxidation an ethyl group is removed.

Very interesting and useful results have been obtained from investigations of the effect produced upon the tinctorial properties of compounds of the malachite green type



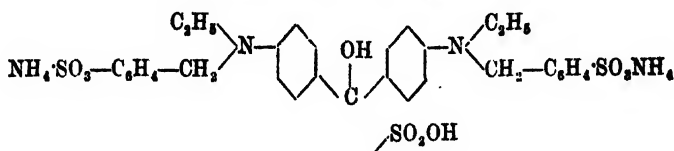
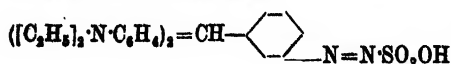
by substitution in the third phenyl group. Not a little of the work of this nature has resulted from the desire to explain the very bluish shade of patent blue and its fastness to alkalis in comparison with other closely related colours.

In the first instance it was considered that the hydroxy group present in the 'meta' position was responsible for these differences. Sandmeyer (J. Soc. Dyers and Cols. 1895, 154) and Suais (Bull. Soc. chim. 1897, 517) independently succeeded in showing that this was not the case, but that the effects mentioned were due to the sulphonic acid group in the 'ortho' position to the methane carbon atom. This conclusion was arrived at in two ways: (i) by condensation of benzaldehyde *o*-sulphonic acid (see Vol. I. p. 569) with dimethylaniline followed by oxidation of the leuco compound thus produced, and (ii) by condensation of tetramethyl-diamino-diphenyl-carbinol with metanilic acid, elimination of the amino group from the resulting leuco compound, then oxidation of the product. In either case the final product is the ortho-sulphonic acid of malachite green, and this resembles patent blue in that it gives dyeings fast to alkali and more blue to tone than malachite green. The two series of reactions may be represented thus:



observation of Suais (Bull. Soc. Ind. Mulhouse, 1912, 82, 703) is of interest. He concludes that the property of fastness to alkalis is not confined to the dyes containing an acid group in the 'ortho' position to the central carbon atom.

but is shared by the 'meta' diazo-sulphonates of this series. As instance of this class of compounds he mentions a green dye obtained by oxidation of the leuco base:



This latter is produced from the corresponding amine by treating its diazo compound with sulphite.

The following are some representative commercial products in which ortho substitution of the type mentioned above occurs:

Erioglaucine A

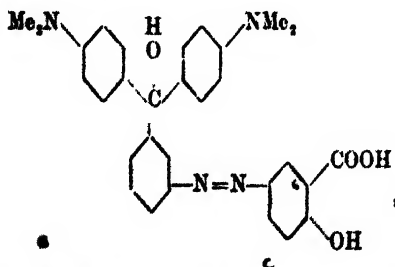
is obtained by condensation of benzaldehyde *o*-sulphonic acid with ethyl-benzyl-aniline sulphonic acid, oxidation of the leuco compound produced and conversion of the product into the acid ammonium salt (D. R. P. 89397; Frdl. 4, 184). It gives bright shades fast to alkali. *Eriochlorine* is said to be the above mixed with yellow and violet.

Benzyl Green B is a product in which the sulphonic acid group in the ortho position to the methane carbon atom of erioglaucine A is replaced by a chlorine atom.

Setoglaucine, obtained by condensation of *o*-chloro-benzaldehyde with dimethylaniline and oxidation of the leuco compound formed (D. R. P. 94126), is *o*-chloro-malachite green. When the same aldehyde is taken but condensed with ethyl-benzyl-aniline, or mono-ethyl-*o*-toluidine, the dyes produced are *Night Green 2B* and *Setocyanine* respectively. The introduction of further substituents in the benzaldehyde used is exemplified in *Glacier Blue*, which is made from 2:5-dichloro-benzaldehyde and mono-methyl-*o*-toluidine (D. R. P. 71370), and *Night Blue B*, made from 2-chloro-5-nitro-benzaldehyde and ethyl-benzyl-aniline sulphonic acid. An interesting extension of this series is found in the dye produced by the condensation of benzaldehyde 2:4-disulphonic acid with one molecule of diethyl-*m*-amino-phenol and one molecule of mono-ethyl-*m*-amino-*p*-cresol, closing the pyrone ring then oxidising the leuco compound thus formed. The dye gives red shades on silk, but does not colour cotton (U.S. Pat. 1006738).

The development of malachite green derivatives has not been entirely along these lines, and a number of 'para' compounds have been described (cf. Fr. Pat. 422843; Eng. Pat. 1913, 7757; and J. pr. Chem. 1915, 91, 341).

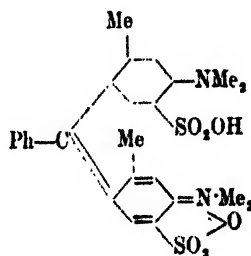
Azo Green



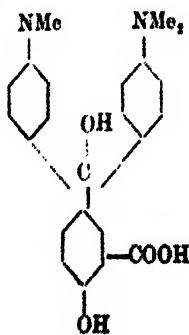
a 'meta' derivative, is an interesting colour

which is a member both of the triphenyl-met and of the azo group of dyes. It is formed by diazotisation of *m*-amino-malachite green and coupling with salicylic acid, and is a mordant colour giving yellowish-green shades on chrome mordanted wool. It is also used for calico printing (cf. also Eng. Pat. 234950).

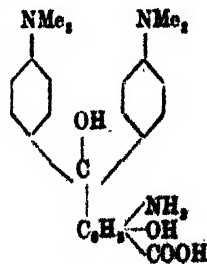
Green dyes of considerable fastness are also produced by condensation of benzaldehyde (or homologues not containing an amino group in the para position) with alkyl, or aryl, derivatives of *m*-toluidine sulphonic acid and oxidation of the leuco compound formed. Alternately, the condensation product of benzaldehyde and *m*-toluidine may be sulphonated then oxidised (Bayer, Fr. Pat. 461810). The dyes are of the type:



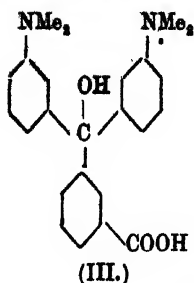
A number of mordant colours derived from malachite green, chiefly by the introduction of hydroxyl and carboxylic acid groups into the third phenyl residue, are included in the series of chrome colours of the Bayer company, e.g. *Chrome violet* (I.) (D. R. P. 58483; Frdl. 3, 120). *Chrome bordeaux* (II.), and *Chrome green* (III.) (D. R. P. 60606; Friedl. 3, 25).



(I.)



(II.)

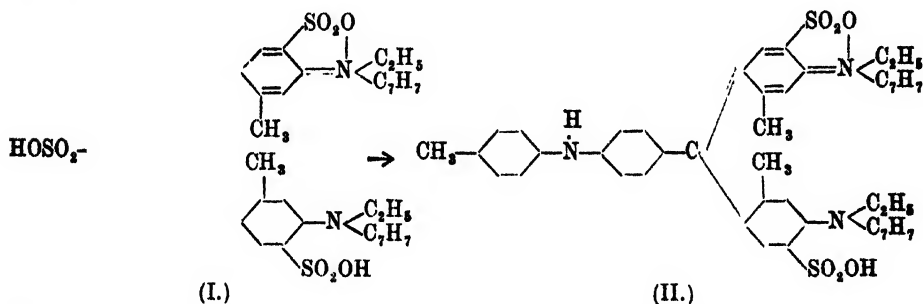


An interesting comparison of the properties of Malachite Green, with those of an analogous *furane* dye, has been made by Renshaw and Naylor (J. Amer. Chem. Soc. 1922, 44, 862), whilst Bogert and Nisson (Proc. Nat. Acad. Sci., 1924, 10, 421) have similarly compared a bis-triphenylmethane dye.

(B) *Triamino-triphenyl-methane derivatives.*

In this group considerable interest is attached to the work dealing with the phenylation products of rosaniline and *p*-rosaniline. Baeyer and Villiger (Ber. 1904, 37, 2870), Lambrecht (Ber. 1907, 40, 145), and Knecht (J. Soc. Dyers and Col., 1907, 119), have succeeded in showing that the phenylation of rosaniline proceeds rather differently from what has been generally assumed in the past. As the result of this work

it is concluded that whilst *p*-rosaniline may be converted into triphenyl-*p*-rosaniline by phenylation in the usual manner, in the case of rosaniline the reaction cannot be made to proceed beyond the formation of diphenyl-rosaniline. It is considered that this difference is due to steric hindrance, the methyl group in the ortho position to one of the amino groups in ordinary rosaniline preventing the entrance of the phenyl nucleus into the amino group of that aromatic residue, whereas in *p*-rosaniline this effect is not observed, as no methyl group is present in the ortho position to any of the amino groups. Baeyer and Villiger concluded from the examination of a sample of commercial aniline blue that it consisted of almost pure diphenyl-rosaniline. The production of *ppp*-triamino-triphenyl-methane colours from derivatives of *pp*-diamino-triphenyl-methane is of interest and forms a link between the products of this and of the preceding group of dyes. The Bayer company describes the preparation of triamino-triphenyl-methane colours, which give bluish shades, by treating *pp*-diamino-triphenyl-methane compounds containing a halogen or alkoxy group in the para position to the methane carbon, with amines or their salts (Fr. Pat. 474260), or by similar treatment of the corresponding para sulphonic acid derivatives (D. R. P. 287003). The latter process is exemplified by the formulæ:

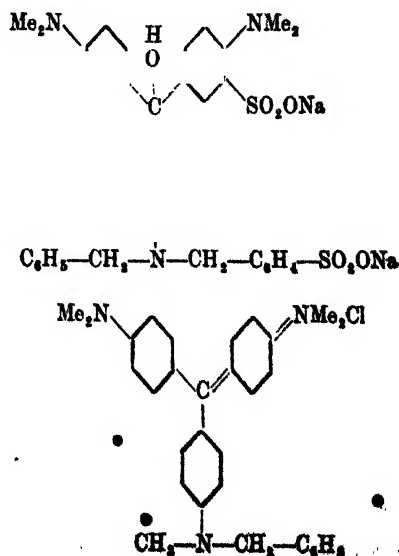


and it is stated that this should prove to be a cheap technical method for the production of dyes of this type. In passing from (I.) to (II.), the shade of the dye changes from green to blue. For this type of process, see also D. R. PP. 292998, 293322 (M. L. B.).

Suiss (Bull. Soc. Ind. Mulhouse, 1912, 82, 691) describes the treatment of crystal violet (magenta, Paris violet, malachite green, and brilliant green react similarly) with *m*-toluylene-diamine at 160°–180°C., whereby a yellow fluorescent basic dye is produced and dimethylaniline liberated. It is probable that the products produced in this way are identical with the compounds obtained from the condensation of Michler's ketone with *m*-diamines (Eng. Pat. 1352, 1895).

In connection with the development of this group of dyes, the relationship that exists between *Eriocyanin A* (which may be prepared by condensation of tetra-methyl-diaminobenzhydrol monosulphonic acid with dibenzylaniline mono- or di-sulphonic acid and oxidation of the leuco compound produced (D. R. P. 88085; Frdl. 4, 219), and the much older colour *Benzyl Violet 7B* (1866), is perhaps worthy of

mention. This is clearly seen by comparison of their respective formulæ:



The important colour *Azo Green* (see above), is directly derived from *mpp*-tri-amino-triphenylmethane, and green azo-triphenylmethane dyes closely related to it are mentioned in D. R. PP. 175825, 175826 (M. L. B.).

According to Copisarow (Chem. Soc. Trans. 1920, 117, 1542) *Carbazol Blue* is a tricarbazyl-methane compound represented by $(C_6H_4NH)_3C = C_6H_4NHCOOH$. It is produced by fusing together carbazol and oxalic acid, and the linkage to the central carbon atom is presumed to be in the *para* position to the nitrogen atom in each carbazol nucleus.

Auramine.

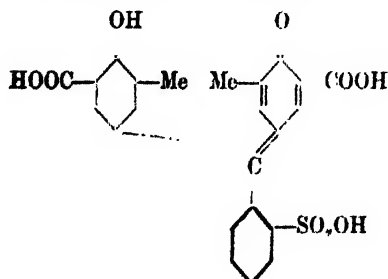
In D. R. P. 287994, the Badische company indicate that very good yields of N substituted 4:4'-diamino-diaryl-thio-benzophenones are readily obtained from the corresponding hydrocarbons by treatment with polysulphides. The products are useful for the production of auramine derivatives (see article on AURAMINE, vol. i. p. 431).

II. AURIN GROUP.

In this group a considerable number of colours have been described which are related to the members of the diamino-triphenylmethane group in the same way as aurin is related to para-rosaniline.

Most of the colours of this sub-group contain carboxyl groups in the ortho position to the hydroxyls, and are of value as chrome colours. As in the case of the compounds of the Patent Blue group, increased fastness to alkalis is obtained by the introduction in the third benzene nucleus of a substituent (halogen, sulphonic acid, &c.) in the ortho position to the methane carbon atom. The following are typical commercial products of this class:

Eriochrome cyanin R is obtained by condensing benzaldehyde-*o*-sulphonic acid with *o*-cresotinic acid and oxidising the leuco compound produced (D. R. P. 189938; Frdl. 9, 200). This colour gives red dyeings on wool which change to violet-blue when after-chromed.



If *o*-cresotinic acid is condensed with an *o*-chloro-benzaldehyde, and the product oxidised, the resulting dye is *Eriochrome azurol B* (D. R. PP. 198909, 199943; Frdl. 9, 201, 204). For the preparation of *Chrome azurol S*, an *o*-chloro-benzaldehyde sulphonic acid is used in the condensation (D. R. P. 199943; Frdl. 9, 204). Members of the Chromoxan series of dyes (Bayer) are said to be produced in a similar manner from naphthalene aldehydes.

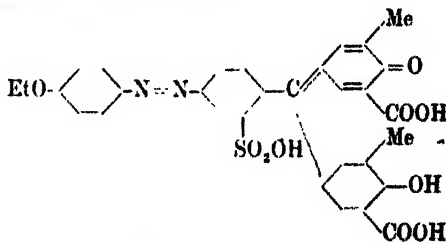
The use of penta- and tetra-chloro-benzalde-

hydes for the production of colours of this group has been described in D. R. P. 234519 (Bayer) and Eng. Pat. 13970, 1915 (Casella) respectively. The use of chlorination products of xylene—which are first converted to chloro-aldehyde-benzoic acid derivatives—for the production of dyes of this group has also been described by Casella (Eng. Pat. 16317, 1914).

When di-ortho-substitution products of benzaldehyde are used it is stated that colours of great depth and fastness result (D. R. PP. 199943, 213502).

In patent literature various chrome colours, belonging to this group, are also described, in which the non-hydroxylated benzene nucleus contains an amino, or substituted amino group (Eng. Pat. 12130, 1910; Fr. Pat. 417490; D. R. P. 252287 (M. L. B.); Fr. Pats. 424723, 425676 (Bayer); and Eng. Pat. 10335, 1911 (Geigy)), and these products give fast shades when chromed.

Azo colours which are members of this group have also been investigated, and the Bayer company (Fr. Pat. 413383; U.S. Pats. 1021364, 1021365, 1021366) describe the production of dyes which give yellow to red shades on wool from an acid bath, the colours passing to blue or black when after-chromed. These products are obtained by condensing amino-benzaldehyde (or its nuclear substitution products, e.g. *o*-chloro-*m*-amino-benzaldehyde) with 2 mols. of an aromatic hydroxy-carboxylic acid, diazotising and coupling the leuco compound produced, then oxidising the product. Green and Sen (Chem. Soc. Proc. 1912, 28, 137) have also examined azo dyes of somewhat similar type, but obtained by condensing azo-aldehydes with hydroxy-toluic or salicylic acids. The following formula represents a typical member of the series obtained by them:



The dyes are polygenetic, dyeing wool directly in red shades, and producing various shades with different metallic mordants. The final oxidation may, in the production of the chrome lakes (which are black), be carried out on the fibre by dyeing with the azo-methane derivative then treating with an acid solution of bichromate. A similar dyeing with a leuco compound, followed by simultaneous oxidation and formation of chrome lake on the fibre, is referred to in respect of other dyes of this sub-group in Eng. Pat. 25007, 1910; Fr. Pat. 421564 (A. G. F. A.).

In the true aurin group—that containing dyes derived from *ppp*-tri-hydroxy-triphenyl-carbinol—considerable attention has been paid to the production of chrome colours. A number of such products, belonging to the triphenylmethane or diphenyl-naphthyl-methane groups, have been described (cf. D. R. PP. 216924, 217571, 216686; Eng. Pat. 11083, 1911, &c.), most of them being prepared by condensation of hydroxy-

aldehydes (or their derivatives) with hydroxy-carboxylic acids (or derivatives), though use has also been made of the methylene-disalicyclic acid process. This work has resulted in the range of colour obtainable with this type of dye being considerably extended. In a large number of cases the after-chroming of material dyed with these products gives rise to a very marked change in shade.

Products have also been investigated in which the hydroxyl group in the third benzene nucleus is in the meta position to the methane carbon atom (Fr. Pat. 404800). In such cases the meta hydroxyl group may be introduced either by use of hydroxy- or amino-aldehydes; in the latter case the amino group is converted to hydroxyl by use of the diazo compounds either before or after the oxidation of the leuco triphenyl-methane derivative (D. R. P. 234805).

III. THE PHTHALEIN GROUP.

Here questions of structure and constitution have been responsible for a considerable amount of work. On the other hand, evidence is not lacking of attempts to extend the list of commercially useful products belonging to this group. The structure of the salts of the phthaleins has been discussed at length by Green (J. Soc. Chem. Ind. 1909, 638), whilst the production of isomeric forms of fluorescein and their salts has been described by H. v. Leibig and their probable constitution considered (J. pr. Chem. 1912, 86, 472). The effect of the introduction of additional auxochromes into compounds of the phthalein and benzein series of dyes has been studied by Watson (Chem. Soc. Trans. 1915, 107, 1579).

Various attempts have been made to obtain new dyes of this series, and the following are typical examples of these. By introduction of nitro groups, either by use of nitro derivatives of phthalic acid, or nitro-resorcinol and its derivatives (D. R. P. 245231), products have been obtained which give good dyeings on chrome mordanted wool. D. R. P. 290508 describes the condensation of pyrogallol (or other derivatives of resorcin having a para position to one of the OH groups free) with α -hydroxy-naphthoyl- α -benzoic acid, whereby chrome mordant dyes of the phthalein series are produced. Wool dyes have been prepared by treatment of eosin, or phloxin, with aniline, whereby the halogen is wholly or partially replaced by the amine residue, followed by sulphonation of the product (Chem. Zentr. 1913, 2, 2126). Colours of this group have been described by Lucius and Brüning (D. R. PP. 290540, 291883), in which selenium has been introduced into the molecule by treatment of phthalins—obtained by reduction of phthaleins—either with selenium halides or selenium oxy-chloride.

In the rhodamine group it is interesting to note the description by Block (Bull. Soc. Ind. Mulhouse, 1913, 83, 81) of the use of tetrachlorophthalic anhydride in the production of derivatives of rhodamine, as in the acid group it may be used for the preparation of phloxin. When condensed with dimethyl-*m*-amino-phenol it is stated that it yields a dye giving shades which are very fast to light and alkali.

Intermediates.

In conclusion, it should be noted that the extension of the triphenyl-methane group of dyes has given rise to a considerable amount of investigation of the derivatives of benzaldehyde and to the manufacture of quite a number of these, which were previously but rarely met with. For further details the article on BENZ-ALDEHYDE, vol. i. 565, should be consulted.

A. E. E.

TRIGEMININE. Pyramidone butyl chloral hydrate.

TRILITE. Syn. for trinitrotoluene, used as an explosive.

TRINOL. Syn. for trinitrotoluene.

TRIPHYLITE. A manganese lithium phosphate LiMnPO_4 , occurring naturally as large, rough (orthorhombic) crystals and coarsely cleavable masses. By the isomorphous replacement of manganous oxide by ferrous oxide it passes into the closely allied mineral lithiophyllite (LiFePO_4). The colour is grey or bluish, but, the mineral being readily weathered, the masses are usually dark brown on the surface. Triphylite occurs in pegmatite-veins, often in association with spodumene and other lithium-bearing minerals, and sometimes with tin ore. It is found at Bodenmais in Bavaria, Huréaux and Chanteloube in Haute-Vienne, Branchville in Connecticut, Pala in California, the Black Hills in South Dakota, and King's Mountain in North Carolina. Containing 8.1–9.4 p.c. of lithia, it has occasionally been collected when mining for other minerals, and used as a source of lithium salts.

L. J. S.

TRIPLASTITE. An explosive consisting of a mixture of di- and trinitrotoluene (70 pts.), gun-cotton (1.2 pts.), and lead nitrate (28.8 pts.).

TRIPLITE. Fluorophosphate of manganese and iron ($\text{Mn,Fe}[(\text{Mn,Fe})\text{F}]\text{PO}_4$, crystallised in the monoclinic system. Calcium and magnesium are also often present in small amount. The rough crystals and compact masses are dark-brown to black with a resinous lustre; the powder is yellowish-grey. Sp.gr. 3.6–3.8; H. 5–5½. The mineral is soluble in hydrochloric acid, and with sulphuric acid evolves hydrofluoric acid. It occurs in pegmatite-veins and in quartz-veins in the vicinity of granite masses; and is found at Limoges in France, Rabenstein in Bavaria, &c. In the Singar mica mines, in the Gaya district of Bengal, it occurs in considerable quantity as large masses with pitchblende. A variety containing very little iron and of a pale salmon-pink colour is found with wolframite and bismuth minerals in White Pine Co., Nevada.

L. J. S.

TRIPOLITE or **TRIPOLI** v. **DIATOMITE**.

TRITICUM. Couch grass or *Agropyrum* of the B.P. The dried rhizome of *Agropyron repens* (Beauv.).

TRITOL, TRITOLO. Syn. for trinitrotoluene.

TRITOPINE v. **OPPIUM**.

TRIXIDIN. Trade name for an emulsion of antimony trioxide.

TROCHOL. A neutral unsaponifiable crystalline substance obtained by the saponification of red Japanese bird-lime made from the bark of *Trochodendron aralioides*. After purification by precipitation from chloroform solution by light petroleum and recrystallisation from chloroform.

alcohol, trochol forms colourless needles or prisms $C_{22}H_{44}O_8$, $\frac{1}{2}(C_2H_5O + H_2O)$, m.p. 252° [$\alpha_D^{15} + 20^\circ$ (in chloroform alcohol)]. Yields a *diacetate*, colourless prisms, m.p. 217° ; *dibenzate*, colourless needles, m.p. 172° (sintering at 145°). Trochol occurs as the palmitic ester in the bird-lime; by heating the components together at 200° in a vacuum the ester is obtained as a colourless viscous substance (Hidekichi Yanagisawa, J. Pharm. Soc. Japan, 1921, No. 471, 405; 1922, 179). *Trochic acid* $C_{21}H_{40}O_8$, white powder, m.p. 225° , exists in the bird-lime in the free state (cf. Yushichi Nishizawa, J. Chem. Soc. Japan, 1922, 43, 154). Trochol yields a *diphenylcarbamate* $C_{28}H_{42}O_8(CO \cdot NPh)_2$, colourless prisms, m.p. 167° ; *formate*, nacreous scales, m.p. 306° , and *phthalate*, a white crystalline powder, m.p. 224° – 228° . On oxidation with hydrogen peroxide in glacial acetic acid the alcohol gave a dihydroxymonoketone, *trocholone* $C_{20}H_{40}O_8$, an amorphous powder, m.p. about 100° ; *trochol peroxide* $(C_{21}H_{42}O_8)_2$, colourless scales, m.p. 215° ; (*semicarbazone*, fine white needles, m.p. 290° ; *acetyl derivative*, fine white needles, m.p. 205° ; *oxime*, small white needles, m.p. 217°); and *trocholic acid* $C_{22}H_{42}O_8$, white granules, m.p. 282° (diacetate, white crystalline powder, m.p. 145°). The authors conclude that trochol is a secondary-tertiary, but not a primary alcohol. When a mixture of trochol and chromic anhydride is treated with water an odour of butyric acid is produced, and acetic acid can be isolated by the distillation of the mixture with steam (Hidekichi Yanagisawa and Norikazu Takashima, J. Pharm. Soc. Japan, 1923, No. 494, 251–258; Chem. Soc. Abstr. 1923, 124, i. 1008).

TROGERITE v. URANIUM.

TROILITE. A name applied by Haidinger to ferrous sulphide FeS , occurring in meteorites. V. PYRRHOTITE.

TRONA, URAO, or NATURAL SODA. The sodium carbonates occurring as minerals are: *thermonatrite* $Na_2CO_3 \cdot H_2O$ (orthorhombic); *natron* (q.v.) $Na_2CO_3 \cdot 10H_2O$ (monoclinic); *trona* $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (monoclinic); and possibly the anhydrous salt. Of these, trona is by far the most important and constitutes the larger part of the deposits of natural soda. It forms beds of white, cavernous material with acicular or bladed crystals lining the cavities; and is usually intermixed with more or less earthy matter and sodium chloride and sulphate. It is deposited from the water of soda-lakes and forms an efflorescence on the surface in desert regions. The Natron Lakes of Lower Egypt are well known, and similar lakes and surface efflorescences of soda are met with in many parts of the Sahara and Sudan. Extensive deposits are found in the neighbourhood of Lake Chad, and a large deposit has been opened up at Lake Magadi in Kenya Colony, East Africa. The latter has an area of 324 sq. miles, and the reserves of over a hundred million tons of soda are being constantly increased by springs in the lake. The material contains 98.5 p.c. of soda crystals, with sodium chloride 0.2% and sodium sulphate 0.1 p.c. Soda-lakes also occur in the western states of North America, viz. in Arizona, California, and Nevada.

The name 'trona' is said to be of Arabic

origin; and 'urao' is a native name for the soda deposited at the bottom of a lake at Lagunilla in Venezuela.

References.—F. W. Clarke, *Data of Geochemistry*, 3rd ed., Bull. U.S. Geol. Survey, No. 616, 1916; A. Lacroix, *Minéralogie de la France et de ses Colonies*, 1909, vol. iii. R. Wegscheider in C. Doelter's *Handbuch der Mineralchemie*, 1911, vol. i. 141–193. L. J. S.

TROOSTITE. A constituent of steel intermediate in characteristics between sorbite and martensite (q.v.). It is obtained by quenching highly heated steel in oil or by quenching from the transformation temperature in cold water, and is plentiful in tempered steels.

It acquires a deep brown or black tint when etched with picric acid, and can thus be distinguished under the microscope. Benedick regards it as a colloidal solution of carbon iron (J. Iron and Steel Inst. 1905, ii. 352; 18 ii. 217). The name troostite is also given to a variety of *Willemite* (q.v.).

TROPACOCAINE v. COCAINE AND SYNTHETIC DRUGS, TROPEINES.

TROPAEOLINE v. AZO-COLOURING MATTERS.

TROPEINES. The Solanaceous Alkaloids.

This group comprises the following members, and possibly others not yet fully examined:—

Atropine and hyoscyamine $C_{17}H_{23}O_3N$;
Noratropine and norhyoscyamine

$C_{16}H_{21}O_3N$

Apoatropine and belladonnine $C_{17}H_{21}O_3N$;

Tropacocaine $C_{18}H_{19}O_3N$ (see p. 221);

Hyosine (scopolamine) $C_{17}H_{21}O_4N$;

Meteloidine $C_{18}H_{21}O_4N$.

These are all tertiary bases except *nor-atropine* and *nor-hyoscyamine*, and on hydrolysis furnish an acid and an amino alcohol. Of the eight naturally occurring alkaloids only three are of importance in medicine, viz. atropine, hyoscyamine, and hyosine. Homatropine, a synthetically prepared tropeine, is also of importance in medicine. The best known sources of the three alkaloids are belladonna (*Atropa Belladonna* (Linn.)), henbane (*Hyoscyamus niger* (Linn.)), stramonium (*Datura Stramonium* (Linn.)), all of which are used in medicine. Other plants which contain them in important quantities, and either are or may be used commercially as sources of the alkaloids, are *Hyoscyamus muticus* (Linn.), *H. albus* (Linn.), and *H. reticulatus* (Linn.), *Datura Metel* (Linn.), *D. arborea* (Linn.), *D. quercifolia* (H. B. and K.), *Duboisia myoporoides* (R.Br.), *Duboisia Leichhardtii*, *Scopolia carniolica* (Jacq.), and *S. japonica* (Maxim.), *Mandragora officinarum* (Linn.), and *Solandra longifolia*. As a rule, at least two of the alkaloids are found together in each plant, but *H. muticus* is remarkable in containing only hyoscyamine. It is probable that atropine rarely, if ever, occurs preformed in plants, and the traces generally found in the extracted alkaloids are due to racemisation of hyoscyamine either during the drying of the plant or by the action of chemical agents used for extraction. In general, the alkaloids are present in the stem, leaves, root, and seed, and the amount of total alkaloid present in each of these parts shows great variation.

Preparation.—The method used for the extraction of these alkaloids varies to some extent with the material employed, but the

following general process gives good results as a rule. The finely-ground, air-dry drug is exhausted by percolation with cold 90-95 p.c. alcohol and the greater part of the solvent removed by distillation. The semi-solid extract is then treated with dilute (0.5 p.c.) hydrochloric or sulphuric acid, until no more alkaloid is removed. This acid liquid is filtered, shaken with small quantities of chloroform, if necessary, to remove traces of chlorophyll, oil, or other soluble non-basic matters, then made slightly alkaline with dilute ammonia, and the alkaloid extracted by means of chloroform. The latter is distilled off, leaving, as a rule, a clean gum-like residue. From this, by solution in chloroform and careful addition of light petroleum, hyoscyamine may be caused to separate in crystalline form. If hyosine be present it remains dissolved in the chloroform, and may be caused to separate by further addition of light petroleum. The salts of these alkaloids being more stable than the free alkaloids they are best purified by recrystallising their salts from water. Hyoscyamine may be finally purified by re-crystallisation from alcohol by addition of water. The best source of hyoscyamine is the Egyptian plant, *Hyoscyamus muticus*.

ESTIMATION OF TOTAL ALKALOIDS. Dunstan and Ransom have devised the following methods:

For the root.—Exhaust by hot percolation 20 grms. of the finely-powdered root with a mixture of equal parts of chloroform and absolute alcohol. Agitate the solution with two successive quantities of 25 c.c. of distilled water, adding a small quantity of dilute sulphuric acid. The salts pass into the aqueous layer, and the colouring matter remains dissolved in the chloroform. Wash the aqueous extract with a little pure chloroform to remove adhering impurity, then add ammonia in slight excess, and dissolve out the liberated alkaloids by agitation with chloroform in the usual way. The residue of alkaloid left on the evaporation of the chloroform is dried at 100° and weighed and finally titrated (Pharm. J. 1883-4, [iii.] 14, 623).

For the leaves.—20 grms. of the finely-powdered dry leaves are exhausted with absolute alcohol. The liquid is largely diluted with water, acidified with hydrochloric acid, and repeatedly extracted by agitation with chloroform until the whole of the chlorophyll, fat, &c., has been removed. The liquid is then made alkaline with ammonia, and extracted with chloroform, which, on evaporation, leaves a residue of alkaloid. This must be dried at 100° before being weighed. This process answers equally well for stems or fruit capsules, and for seeds, if the latter are first extracted with light petroleum to remove oil (Pharm. J. 1885-6, [iii.] 16, 237).

Extract of the leaves.—From 1 to 2 grms. of the extract are dissolved, as far as possible, in warm dilute hydrochloric acid, any residue being extracted with the dilute acid until all the alkaloid has been dissolved. The acid liquid is then extracted with chloroform until nothing further is removed, and, after this treatment, is made alkaline with ammonia, and the free alkaloid removed by agitating again with chloroform, which on evaporation leaves a residue of alkaloid that is dried at 100°C. and

weighed and finally titrated (*ibid.* 1885-6, [iii.] 16, 238).

Alcoholic extract of the root.—2 grms. of this extract are dissolved as far as possible in dilute hydrochloric acid. This solution is then treated as described under the leaf extract (*ibid.* 1885-6, [iii.] 16, 777).

No method is yet available for the quantitative separation and estimation in mixtures of the individual mydriatic alkaloids, but the approximate amounts of each present may sometimes be determined by careful fractionation with gold chloride.

Atropine $C_{17}H_{23}O_3N$ is the racemic form of hyoscyamine, from which it is readily formed by the action of alkalis. It was first obtained by Mein (Annalen, 1833, 6, 67) from the root of *Datura Stramonium* (Linn.), and called by him *daturine*. Geiger and Hesse obtained it independently (*ibid.* 1833, 5, 43; 6, 44; 7, 269) from belladonna root, and their material was analysed by Liebig, who assigned to it the empirical formula now in use. Atropine is stated to occur with hyoscyamine and a little hyosine in belladonna and stramonium and with more hyosine in *Scopolia japonica* (Maxim), but there is reason to believe that the alkaloid does not exist pre-formed in plants, although it may be produced in the course of preparation by the action of alkalis on hyoscyamine. In any case, the commercial alkaloid is now obtained invariably by conversion of hyoscyamine by the action of very dilute alcoholic alkali hydroxide (Will and Bredig, Ber. 1888, 21, 2797; cf. Gadamer, Arch. Pharm. 1901, 239, 294).

Properties.—Prismatic crystals, m.p. 118°. Readily soluble in alcohol or chloroform, less soluble in ether or hot water, sparingly soluble in cold water. The aqueous solution is alkaline to litmus, hæmatoxylin, and phenolphthalein. The fact that atropine is alkaline to phenolphthalein serves to distinguish it and its isomer from most other alkaloids. Atropine is optically inactive. One of the most remarkable properties of atropine is that of causing sustained dilatation of the pupil of the eye, a property which is often made use of in detecting it and other alkaloids of this group, several of which exert this mydriatic action. A drop or two of an aqueous solution, containing 1 part of atropine in 130,000 parts of water, when introduced into the eye of a cat is sufficient to produce this effect. When taken internally atropine is highly poisonous. It diminishes glandular secretions, causes paralysis of the vagus terminations, and acts as a sedative to involuntary muscles. Some of the alkaloid is apparently excreted unchanged in the urine.

The ordinary salts of atropine are crystalline and soluble in water. The sulphate



is commonly used in medicine; it forms colourless needles, m.p. 187°-188°, 194° (dry). The aurichloride $B \cdot HAuCl_4$ appears as an oily precipitate when produced in the ordinary manner. This soon solidifies to a crystalline mass, which may be re-crystallised from water acidified with hydrochloric acid. The crystals melt at 137°-139°. This salt and the picrate, m.p. 175°-176°, are useful for the identification of the alkaloid,

since the corresponding salts of the other alkaloids of this group melt at different temperatures.

Reactions and constitution.—Among the characteristic qualitative reactions of atropine may be mentioned one which has been modified by Labat (Bull. Soc. Pharm. Bord. April, 1914, 148), and consists in treating a particle of the alkaloid with 2 c.c. of a 10 p.c. solution of sulphuric acid and adding one drop of a saturated aqueous solution of potassium chromate, on warming, the characteristic hawthorn odour develops and changes to that of benzaldehyde. The latter odour is also produced when the alkaloid is boiled with a dilute solution of sodium hypobromite. This well-known test introduced by D. Vitali (Zeitsch. anal. Chem. 1881, 20, 563; Pharm. J. 1881, [iii.] 12, 459) has been modified by Arnold (Arch. Pharm. 1882, 20, 564), also by Flückiger (Pharm. J. 1886, [iii.] 16, 601), whilst E. Beckmann (Arch. Pharm. 1886, [iii.] 24, 481) points out that veratrine gives a somewhat similar reaction unless certain modifications are employed; and Droop Richmond (Analyst, 1918, xliii. 506) demonstrates other points which should be noted. Other characteristic colour reactions are described by Richard (Chem. Zeit. 1904, 28, 1048).

The reactions of atropine and other alkaloids with mercuric chloride were described by A. W. Gerrard (Pharm. J. 1884, [iii.] 14, 718), who in a later paper (Pharm. J. 1891, [iii.] 21, 898) modifies and more precisely defines the method of making the test, and gives details of the distinctive reactions observed with atropine, hyoscyamine, homatropine, and hyoscyne, under these conditions. The value of Gerrard's test has also been confirmed by Flückiger (Pharm. J. 1886, [iii.] 16, 601), who found cocaine gave a pure white precipitate which very soon turned red.

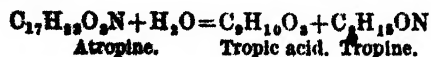
Amongst the more modern researches which may be mentioned are those of Eder in the Schweiz. Wchschr. f. Chem. u. Pharm. 1913, 51, 228; and Schweiz. Apoth. Zeit. 1917, 54; the latter of which contains a series of papers on the detection of atropine, whilst Wasicky (Zeitsch. anal. Chem. 1915, 54, 393) describes a colorimetric method of identifying atropine and allied alkaloids by means of *p*-dimethylamino-benzaldehyde.

In 1917, Rasmussen (Ber. Deut. pharm. Ges. 1917, 27, 193) described a method based on the precipitation of the sparingly soluble silicotungstate



as foreshadowed by O. Javillier (Bull. Sci. Pharm. 1910, 315); this salt is soluble in less than 1 part in 40,000 water.

Atropine readily undergoes hydrolysis with either acids or alkalis; in the latter case it yields tropic acid and tropine in accordance with the equation



When the hydrolysis is effected by an acid, especially concentrated hydrochloric acid, the tropic acid loses the elements of water, and

atropic acid $\text{C}_8\text{H}_7\text{O}_2$ results, whilst at a high temperature this latter compound is more or less changed into its polymers α and β -isatropic acid $\text{C}_{15}\text{H}_{19}\text{O}_2$.

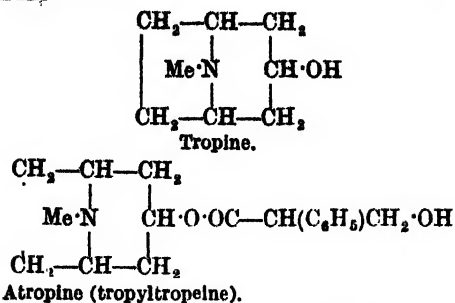
The hydrolysis of atropine is preferably effected by heating the alkaloid with saturated barium hydroxide solution to 60° or 80° for a few hours. Dilute sulphuric acid is added until a drop ceases to give a pink coloration with phenolphthalein. The liquid is filtered, and the filtrate acidified with hydrochloric acid and twice shaken with ether, the ether is separated, and on evaporation yields the acid constituents of the hydrolysis; to obtain the basic product, the aqueous layer is shaken with an excess of alkali hydroxide and extracted with chloroform.

Atropine yields an anhydride (*apotropine*) (see below) when heated with dilute nitric acid (Pesci, Gazz. chim. ital. 1881, 11, 438; 1882, 12, 60), which Hesse subsequently isolated from belladonna root and named atropamine (Annalen, 1892, 271, 124; cf. Merck, Zeitsch. anal. Chem. 1892, 31, 229; and Hesse, Annalen, 1893, 277, 290). Apotropine is not mydriatic.

TROPINE $\text{C}_8\text{H}_{15}\text{ON}$ forms large, colourless tablets, m.p. 63° ; b.p. 229° ; sp.gr. 1.0392 at $76^\circ/4^\circ$, soluble in water, alcohol, or ether. It is a strong base, which forms crystalline salts. It is poisonous, but does not dilate the pupil of the eye. Tropine and tropic acid unite to form tropine tropate $\text{C}_8\text{H}_{15}\text{NO} \cdot \text{C}_8\text{H}_7\text{O}_2$, and this salt, when heated with dilute hydrochloric acid, loses water and furnishes atropine, identical with the natural alkaloid (Ladenburg, Annalen, 1883, 217, 74). Similarly, by heating other organic salts of tropine with dilute hydrochloric acid, dehydration occurs, with production of the acyl derivative of tropine. The bases thus formed have been called by Ladenburg *tropines*. In this way *l*-atropine (*l*-tropyltropine), *d*-atropine (*d*-tropyltropine), *pseudo*atropine (*atro*-*lactyltropine*), and atropamine (*apotropine*, *atropyltropine*) have been prepared (cf. Wolfenstein and Mamlock, Ber. 1908, 41, 723; and Wolfenstein and Rolle, *ibid.* 1908, 41, 733). Several of the tropines exert a mydriatic action. *Phenylglycolyltropine* or *mandelyltropine* $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}$ is used in medicine under the name *homatropine*. Its mydriatic effect is less persistent than that of atropine. As a result of Ladenburg's work it has been generally assumed that only those tropines produce a mydriatic effect which contain an alcoholic (not phenolic) hydroxyl in the aromatic acid residue, thus acetyl-, benzoyl-, and salicyltropines are not mydriatic, whilst mandelyltropine is mydriatic. Jowett and Pyman find that this is not strictly true, mydriasis being produced by terebyltropine (Chem. Soc. Trans. 1906, 89, 360), and only slightly by *o*-carboxyphenylglyceryltropine (*ibid.* 1906, 91, 93; 1909, 95, 1020; and Proc. Int. Cong. Appl. Chem. 1909) which should be very active. Certain tropines containing a lactone group become less active when the lactonic grouping is opened by the action of alkali.

Tropine has been the subject of numerous investigations especially by Ladenburg, Merling and Willstätter culminating in its synthesis by the last-named from suberone as a starting-point (Ber. 1901, 34, 3163; Annalen, 1903, 326, 23). On the basis of these results tropine and atropine

are now generally represented by the following formulae—

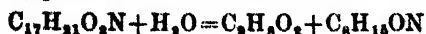


Tropine undergoes a series of interesting decompositions under the action of various reagents. The most interesting of these are as follows: When heated with dehydrating agents it furnishes *tropidine* $\text{C}_8\text{H}_{12}\text{N}$ (Ladenburg, Annalen, 1883, 217, 177), a strongly alkaline oil, b.p. $162^\circ\text{--}163^\circ$, sp.gr. 0.9467 at $19^\circ/4^\circ$, which has an odour recalling that of coniine. On oxidation with chromic acid tropine yields in turn *tropinone* $\text{C}_8\text{H}_{12}\text{ON}$ (Willstätter, Ber. 1896, 29, 396), m.p. $41^\circ\text{--}42^\circ$, b.p. $224^\circ\text{--}225^\circ$, *tropinic acid* $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$ (Merling, Annalen, 1883, 216, 348; Willstätter, l.c.), and finally *ecgoninic acid* $\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ (see under *Cocaine*), which was shown by Willstätter and Bode to be N-methylpyrrolidine-2-acetic acid (Ber. 1901, 34, 519), thus proving the presence of a pyrrolidine ring in tropine. For a detailed account of the important researches in the tropine series, Schmidt's Über die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide, i. 1900; ii. 1904 (Enke, Stuttgart), should be consulted.

Atropamine (*Apo-atropine*) $\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$ is the anhydro derivative of atropine (Pesci, Gazz. chim. ital. 1881, 11, 538; 1882, 12, 60). It is reputed to occur naturally associated with atropine and hyoscyamine in the solanaceous plants (Hesse, Annalen, 1892, 271, 124; Merck, Zeitsch. anal. Chem. 1892, 31, 229; and Hesse, Annalen, 1893, 277, 290); but is best prepared from either of the two latter alkaloids by adding the substances gradually to strong nitric or sulphuric acid, or by heating them with acetic or phosphoric anhydrides.

Atropamine crystallises from ether in prisms, m.p. $60^\circ\text{--}62^\circ$, which are very slightly soluble in water and petroleum ether, readily in alcohol, chloroform, benzene, and carbon bisulphide. It forms salts which crystallise well from water. The sparing solubility of the hydrochloride and hydrobromide affords a ready means of separating atropamine from the other alkaloids of this group. The aurichloride crystallises from water in fine yellow needles, m.p. $110^\circ\text{--}112^\circ$.

On hydrolysis atropamine yields atropic acid and tropine

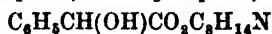


Atropamine is optically inactive, does not redden phenolphthalein (being thus unlike atropine and hyoscyamine), but colours red litmus blue. It has a bitter taste, does not possess mydriatic properties, but produces a burning sensation when dropped into the eye. The hydrochloride $\text{B}\cdot\text{HCl}$, m.p. $237^\circ\text{--}239^\circ$, forms leaflets, and the aurichloride $\text{B}\cdot\text{H}\cdot\text{AnCl}_2$, needles, m.p. $110^\circ\text{--}112^\circ$.

Belladonnine $\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$. This alkaloid is stated to occur in the leaves and root of *Atropa Belladonna* (Linn.) (Hübschmann, J. 1858, 376; Kraut, Ber. 1880, 13, 165; Dürkopff, *ibid.* 1889, 22, 3183; Hesse, Annalen, 1891, 282, 100); and is generally found in the mother-liquors of hyoscyamine and atropine. According to Merling (Ber. 1884, 17, 381) it has the formula $\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}$, and is isomeric with anhydro-atropine (apoatropine), and this was confirmed by Hesse (l.c. 1892, 271, 123; 1893, 277, 295), who stated that it can be prepared by the action of (1) sulphuric acid on atropine or hyoscyamine, or (2) hydrochloric acid on atropamine (apoatropine). Belladonnine is a resinous, uncrystallisable base, which is hydrolysed with much greater difficulty than the other solanaceous alkaloids, yielding tropine $\text{C}_8\text{H}_{13}\text{ON}$ and atropic acid (Merling). It appears to be devoid of mydriatic power.

The salts are amorphous $\text{B}\cdot\text{H}_2\text{PtCl}_4$ and BHAuCl_4 , are yellow pulverulent precipitates quite insoluble in cold water.

Homatropine (*Mandelyltropine*)



is the chief artificial tropine used in medicine. It is a lower homologue of atropine, in which the CH_2OH group is replaced by OH, and is prepared by passing hydrogen chloride gas through a mixture of 7 parts of tropine, 10 parts of mandelic acid, and 2 parts of water; it crystallises from dry ether in prisms, m.p. $99^\circ\text{--}100^\circ$, it is also soluble in castor and olive oils, and such solutions are employed in ophthalmic surgery for instilling into the eye. Homatropine resembles atropine and hyoscyamine in its general physiological effects, but it is much less toxic and in small doses is a true hypnotic. It has a powerful mydriatic effect which is produced and passes off more rapidly than is the case with the natural tropeines. Homatropine hydrobromide crystallises in flat rhombic prisms or plates, m.p. $212^\circ\text{--}214^\circ$; the hydrochloride has m.p. $219^\circ\text{--}227^\circ$; the sulphate, m.p. $222^\circ\text{--}226^\circ$; the aurichloride forms yellow prisms slightly soluble in water, it is precipitated first as an oil, but subsequently becomes crystalline; homatropine methobromide has m.p. $192^\circ\text{--}196^\circ$.

Hyoscyamine $\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}$. An isomeride of atropine. It is the most common of the solanaceous alkaloids, being the principal alkaloid in *Atropa Belladonna* (Linn.) (Schmidt, Arch. Pharm. 1905, 243, 303), and *Hyoscyamus niger* (Linn.), and *H. albus* (Linn.), the sole mydriatic alkaloid in *H. muticus* (Linn.) (Dunstan and Brown, Chem. Soc. Trans. 1899, 75, 74; 1901, 79, 72), and the chief alkaloid in *Datura Stramonium* (Linn.), *Duboisia myoporoides* (R. Br.), *Scopolia carniolica* (Jacq.) (Dunstan and Chaston, Pharm. J. 1889-1890, [iii.] 20, 461), and *S. japonica* (Maxim.) (Schmidt, Arch. Pharm. 1888, [iii.] 26, 185, 214), and in other similar plants; it exists in minute quantities in lettuce, *Lactuca viroea* (Linn.) and *L. Scariola* (Linn.) (Dymond, Chem. Soc. Trans. 1892, 61, 90).

Preparation.—Hyoscyamine may be extracted from the various plants containing it by means of the process described in the introduction to this section. The best source of the alkaloid is the stem and leaves of *Hyoscyamus*.

been partly racemised during its isolation, there being no method of purifying the amorphous base.

Hyoscyne hydrobromide $B \cdot HBr \cdot 3H_2O$ has m.p. 193° – 194° , $[\alpha]_D$ (in water) -25.9° ; it forms large rhombic tablets; the commercial salt generally contains 11–12 p.c. of water and is variable in its optical rotation, owing to the presence of *d*-*l*-hyoscyne. The picrate forms slender matted needles, m.p. 187° – 188° , the aurichloride, yellow prisms, m.p. 198° – 200° , and the auribromide, brown prisms, m.p. 210° . The aurichloride forms needles with serrated edges, m.p. 204° – 206° ; the auribromide forms red leaflets, m.p. 187° – 188° .

By the action of alkalis or by direct heat hyoscyne is racemised to *i*-scopolamine. Hyoscyne resembles atropine and hyoscyamine in its physiological action, producing more powerful but less lasting paralysing effect upon the peripheral nerve endings and depression of the motor area. It does not, however, stimulate the brain initially, and is consequently employed by preference for cerebral affections. It is of great use in acute mania.

When warmed with dilute alkalis or barium hydroxide *l*-hyoscyne is hydrolysed, yielding tropic acid and a new base, which has been variously called oscine, scopoline, or oxytropine. If hydrolysis be effected with dilute hydrochloric acid *l*-tropic acid and *d*-*l*-oscine result.

***d*-*l*-Hyoscyne** (*i*-Scopolamine, *Atroscine*) $C_{17}H_{21}O_4H$ is the optically inactive isomeride of hyoscyne. It forms 2 crystalline hydrates; with $2H_2O$, m.p. 37° – 38° , with $1H_2O$, m.p. 56° – 57° , the anhydrous base melts at 82° – 83° . It furnishes crystalline salts, the hydrobromide crystallises in rhombic tables, containing $3H_2O$, and has m.p. 181° , other salts are the hydriodide, m.p. 192° , the picrate, m.p. 173° – 174° , the aurichloride which forms needles with one edge serrated, m.p. 214° – 215° , and the methobromide, m.p. 216° – 217° .

Oscine (*Scopolone*) $C_8H_{13}O_2N$ results from the hydrolysis of hyoscyne (Hesse, Annalen, 1892, 271, 114; 1893, 276, 84; Luboldt, Arch. Pharm. 1898, 236, 11). It crystallises in prisms from light petroleum or chloroform, m.p. 109° – 110° , b.p. 241° – 243° . It is readily soluble in water and alcohol, and less readily in ether. Oscine is optically inactive, but unlike tropine it can be resolved into its *d*- and *l*-constituents (Tutin, Trans. Chem. Soc. 1910, 97, 1793).

Like tropine, oscine contains a hydroxy group and is readily esterified, forming a series of esters, the scopoleines. None of the scopoleines have been used in medicine.

i-Oscine yields a crystalline monoacetyl derivative, m.p. 53° , a benzoyl derivative, m.p. 68° – 70° , together with other crystalline salts. The hydrochloride forms (hydrated) tablets and (anhydrous) prisms, m.p. 273° – 274° , the picrate crystallises in flattened rhombs, m.p. 237° – 238° , the *d*-*l*-isomerides have the same melting-points.

Mandragorine $C_{15}H_{19}O_2N$ was obtained by Ahrens (Ber. 1889, 22, 2159) from *Mandragora officinarum* (Linn.), and from the same source by Hesse (J. pr. Chem. 1901, [iii.] 64, 274), along with hyoscyamine, hyoscyne, and norhyoscyamine. According to Thoms and Wentzel (Ber.

901, 34, 1023), Ahrens' mandragorine was merely a mixture of hyoscyamine with hyoscyne and possibly a third alkaloid (*v.* MANDRAGORA ROOT, vol. iv. p. 210).

Meteloidine $C_{15}H_{21}O_2N$ was obtained by Pyman and Reynolds (Chem. Soc. Trans. 1908, 93, 2077) from *Datura meteloides* (DC.) along with atropine, and hyoscyne (scopolamine) to the extent of 0.07 p.c. It crystallises in abular needles, m.p. 141° – 142° , and furnishes a crystalline, optically inactive hydrobromide $B \cdot HBr \cdot 2H_2O$, m.p. 250° (anhydrous), and an aurichloride, m.p. 149° – 150° . On hydrolysis by baryta water meteloidine furnishes tiglic acid $CHMe : CMe \cdot COOH$ and a new base *teloidine* $C_8H_{13}O_2N$, which crystallises with $1H_2O$ and has m.p. 168° – 169° (anhydrous); the aurichloride $B \cdot HAuCl_4 \cdot \frac{1}{2}H_2O$ has m.p. 225° , and crystallises in hexagonal plates.

Norhyoscyamine $C_{15}H_{21}O_2N$ occurs in *Scopolia japonica* (Maxim), *Datura Metel* (Linn.), *Datura meteloides*, *Duboisia Myoporoides*, *Duboisia Leichhardtii*, *Salandra longifolia*, and *Mandragora officinarum*. It is a white crystalline base, m.p. 140.5° , strongly basic in character (being alkaline to phenolphthalein). It forms beautifully crystalline salts, of which the following have been characterised: the hydrochloride, m.p. 207° , the sulphate, m.p. 249° , oxalate, m.p. 245° – 246° , aurichloride, m.p. 178° – 179° , platinichloride, m.p. 141° , picrate, m.p. 220° . A solution of the base in 50 p.c. ethyl alcohol gives $[\alpha]_D -23.0^\circ$. On treatment with methyl iodide it yields hyoscyamine (its nitrogen methyl derivative), and by the action of dilute alkalis gives rise to noratropine (Carr and Reynolds, Trans. Chem. Soc. 1912, 101, 946; Petrie, Proc. Linn. Soc. N.S.W. 1917, 815).

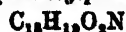
Noratropine $C_{16}H_{21}O_2N$ is a white crystalline base, m.p. 113° – 114° , which readily combines with water forming a monohydrate, m.p. 73° ; it is optically inactive, being the racemic modification of norhyoscyamine, it forms well-crystallised salts of which the following have been characterised: the hydrochloride, m.p. 193° , the sulphate, m.p. 257° , and the aurichloride ($B \cdot HAuCl_4$), which forms rosettes of leaflets which melt under hot water and crystallise on cooling, m.p. 157° .

Both norhyoscyamine and noratropine possess mydriatic properties, but are less active than hyoscyamine or atropine.

Pseudohyoscyamine was the name given to a compound isolated by Merck (Arch. Pharm. 231, 117) from the plant *Duboisia myoporoides*. The formula $C_{17}H_{23}O_2N$ was wrongly assigned to it; subsequent investigations, however, of the alkaloids of this plant (Carr and Reynolds, Trans. Chem. Soc. 1912, 101, 946) have shown that the so-called pseudohyoscyamine of Merck was impure nor-hyoscyamine contaminated with a little hyoscyamine.

Solandrone. Solandrone was the name given by Petrie to the alkaloid isolated from solandra leaves in 1908. When later it was characterised it was found to be identical with norhyoscyamine (*l.c.*).

Tropacocaine (*Benzoylpseudotropine*)



was first isolated by Giesel (Ber. 1891, 24, 2336), from Java coca leaves and subsequently by

TROPEINES.

Heese (J. pr. Chem. 1902, [ii.] 66, 401) from Peruvian coca. Hara and Sakamoto have described the preparation of trapacocaine from the petroleum extract of coca leaves produced in Java (J. Pharm. Soc. Japan, 1924, 503, 33; Chem. Soc. Abstr., 1924, 126, i. 870). It crystallises in needles, m.p. 49°, and its solubility in dilute ammonia affords a means by which it can be separated from the accompanying alkaloids. Its alcoholic solution is strongly alkaline and optically inactive. The hydrochloride has m.p. 283° (decomp.), and the aurichloride, m.p. 208°.

On warming with either mineral acids, or alkalis, the base undergoes hydrolysis and furnishes benzoic acid and pseudotropine (Liebermann, Ber. 1891, 24, 2338).

Pseudotropine $C_8H_{13}ON$ is isomeric with tropine, it forms colourless tablets or prisms, is optically inactive, and has m.p. 108°, and b.p. 240°; it readily esterifies with organic acids, furnishing a series of derivatives which from their analogy with the tropeines have been called pseudotropeines, but, unlike the former, exert no mydriatic action. F. H. C.

TROPILENE v. KETONES.

TROTYL. Syn. for trinitrotoluene, used as an explosive.

TRUFFLES, subterranean fungi, highly prized as food. Many species are known. König divides the edible truffles into two chief classes—

(1) **White truffles**, the best of which is the African truffle, *Tuber niveum* (Desf.) or *Terfezia Leonis* (Tul.), but also including the Italian truffle, *Tuber magnatum* (Pico.) or *Tuber album* (Balb.), with a garlic-like odour, and the German white truffle, *Tuber album* (Bull.) or *Chæromyces meandriiformis* (Vitt.), of much less value.

(2) **Black truffles**, which include the highly prized French truffle *Tuber melanospermum* (Vitt.), which is usually in size between a walnut and an apple, of dark brown or black colour, and covered with polygonal warts. It possesses a strong aromatic odour, resembling that of the strawberry; the winter truffle, *T. brumale* (Vitt.) occurs in France and Italy, resembles the French truffle, but has not such an aromatic smell and taste. The summer truffle, *T. aestivum* (Vitt.) is the one most usually found in England, generally in beech, oak, or birch woods, and in marly soils. It is gathered from July to September.

König gives, as the mean composition of truffles—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
77.1	7.6	0.5	6.6	6.4	1.9

Chatin (Compt. rend. 1890, 110, 376, and 435) found the dry matter in French truffles to vary from 20.8 to 25.0 p.c. of the original fresh material, and to contain from 4 to 9 p.c. of its weight of nitrogen, and from 5.6–11.2 p.c. of ash. The ash, in different samples, contained: silica 10–35 p.c., potash 17–28, soda 0.6–2.1, lime 6.0–9.4, magnesia 0.2–3.1, ferric oxide and traces of alumina 3.2–8.4, manganese oxide, traces to 0.05, phosphorus pentoxide 18.4–30.2, sulphur trioxide 2.1–4.6, chlorine with traces of iodine 0.2–0.4 p.c. Much larger proportions of potash and phosphorus pentoxide were found in the ash of truffles by Kohlrausch and Loewcke,

quoted by König. The amount of alumina is also apparently very variable, since Pizzi (quoted by König) found, in the ash of black truffles, 5.77 p.c. of alumina, in that of white truffles, 7.17 p.c.

As to the nature of the nitrogenous constituents of truffles, little appears to be known; probably a considerable proportion of it is in the non-proteid form.

In the non-nitrogenous extract, mannitol, trehalose and malic and citric acids have been found.

For an examination of the *tubulane* or Caucasian truffles, and of various species of *Terfezia*, known as 'terfas' and 'kames' in the north of Africa and in Western Asia v. Chatin (Compt. rend. 1893, 114, 46; and Revue intern. des falsific. 1893, 14).

Truffles are sold, either in the fresh condition, imbedded in lard, dried, or cooked and preserved in olive oil, or in hermetically sealed cases.

König gives, as the mean of 9 analyses of the air-dried product—

Water	Protein	Fat	N free extract	Crude fibre	Ash
4.4	33.9	2.0	24.9	27.1	7.7

H. I.

TRUXILLINES v. COCAINE AND THE COCA ALKALOIDS.

TRYEN, *p*-iodo-*o*-sulphooxy-cyclo-hexatriene pyridine.

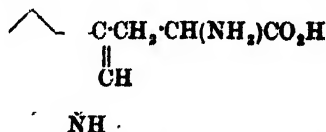
TRYGASE v. SYNTHETIC DRUGS.

TRYPAFLAVIN (*Diaminomethylacridinium chloride*), a yellow dyestuff employed therapeutically in the form of a 0.1 p.c. solution as a bactericide. The solution is sensitive to sunlight and turns brown on exposure even to diffused daylight. Kept in the dark, or in dark-coloured bottles, especially in strong solutions, it may be preserved unchanged.

TRYPAN BLUE AND TRYPAN RED. Azodyes derived from benzidine having a strong trypanocidal action.

TRYPSIN v. FERMENTATION.

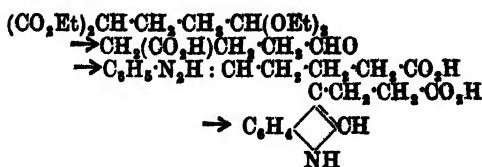
TRYPTOPHAN, β -indole- α -aminopropionic acid



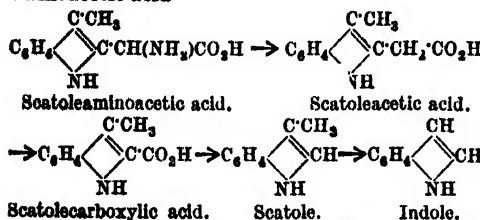
It has been known since the researches of Gmelin, Barnard, and others of the earlier physiologists that on tryptic digestion a substance is formed from proteids that gives a reddish-violet coloration with chlorine or bromine. Other methods of decomposing proteids, such as putrefaction or alkali or acid hydrolysis, give rise to the same substance, for which the name *tryptophan* was suggested by Neumeister (Zeitach. Biol. 1890, 26, 234), and *proteinchromogen* by Stadelmann (*ibid.* 491). The compound itself was not known until 1901 when Hopkins and Cole (J. Physiol. 1901, 27, 418) isolated it from the products formed by the tryptic digestion of casein; they showed that it possessed the formula $C_{11}H_{13}O_2N_2$, yielded scatole and indole when heated, and adopting Neumeister's suggestion named it *tryptophan*.

Tryptophan occurs among the products of

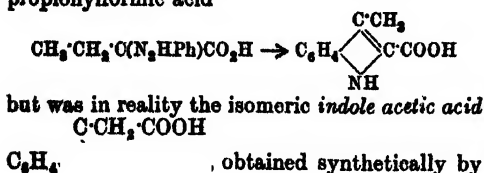
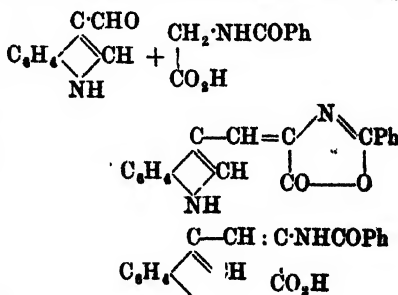
Ellinger (Ber. 1905, 38, 2884) further showed that Nencki's scatoleacetic acid was identical with indole propionic acid obtained by a similar synthetic process from ethyl propionacetal-malonate



Constitution and synthesis.—The formation of indole (Kühne, Ber. 1875, 8, 206; Nencki, *ibid.* 336), of scatole (Brieger, *ibid.* 1877, 10, 1027), of scatole carboxylic acid (E. and H. Salkowski, *ibid.* 1880, 13, 2217) and of scatole-acetic acid (Nencki, Monath. 1889, 10, 506) on putrefaction of proteins was attributed by Nencki to the presence of a scatoleaminoacetic acid in the protein molecule; and when Hopkins and Cole found tryptophan to have the empirical formula $C_{11}H_{12}O_2N_2$, and to yield indole, scatole, scatole carboxylic acid and scatoleacetic acid on putrefactive decomposition, they regarded their substance as Nencki's hypothetical scatole-aminoacetic acid.



by oxidising tryptophan with ferric chloride (Hopkins and Cole, J. Physiol. 1903, 29, 451; Ellinger, Ber. 1906, 39, 2515), and can also be prepared by the action of chloroform and potassium hydroxide on indole; it condenses with hippuric acid to form an *azlactone*, or its 1-*acetyl* derivative (Ellinger and Matsuoka, Zeitsch. physiol. Chem. 1920, 109, 259), which on hydrolysis yields *α -benzoylaminoindolyl-acrylic acid*. This compound on reduction and subsequent hydrolysis yields *α -amino- β -indole-propionic acid*, identical with *dl*-tryptophan

[illegible]

Properties.—The tryptophan obtained from proteids is laevorotatory in aqueous solution. Hopkins and Cole (J. Physiol. 1901, 27, 418) found $[\alpha]_D -33^\circ$, H. Fischer (Zeitsch. physiol. Chem. 1908, 55, 74) found $[\alpha]_D -34.5^\circ$ for one specimen, whilst others gave values varying from -29.75° to -40.3° ; Abderhalden and Baumann (ibid. 412) found $[\alpha]_D^{20} -30.33^\circ$. In alkaline or acid solution, *L*-tryptophan is dextro-rotatory, having $[\alpha]_D^{20} +5.7$ to $+6.3^\circ$ in a 2-3 per cent. solution in *N*/2NaOH solution, or $+4.6^\circ$ in

+6.12° in 10-12 p.c. N/1NaOH solution (Abderhalden and Kempe, *ibid.* 1907, 52, 207; Abderhalden and Baumann, *l.c.*); lower values were found by Fischer (*l.c.*), $[\alpha]_D^{20} +5.56^\circ$ to 5.69° in a 2-3 p.c. solution of a N/1NaOH solution. This is probably due to partial racemisation as Abderhalden and Baumann (*l.c.*) found $[\alpha]_D^{20} +5.27^\circ$ for a specimen that had been repeatedly recrystallised; a 6 p.c. solution in N/1 hydrochloric acid gave $[\alpha]_D^{20} +1.31^\circ$ (Abderhalden and Kempe, *l.c.*). *l*-Tryptophan crystallises in six-sided and rhombic plates, is sparingly soluble in cold, readily so in hot water and has a slightly bitter taste; it darkens when heated at 240° and melts at 252° (Hopkins and Cole, *l.c.*), at 273° (Neuberg and Popowsky *l.c.*), at 289° (corr.) (Abderhalden and Kempe, *l.c.*). The brown pigment found in its solutions on standing is probably a condensation product (Abderhalden, *Zeitsch. physiol. Chem.* 1912, 78, 159).

dl-Tryptophan is prepared synthetically and also readily formed from *l*-tryptophan which racemises on crystallisation from pyridine, or by the action of ammonia or by heating at 170° with hydrochloric acid (Abderhalden and Baumann, *l.c.*; Allers, *Biochem. Zeitsch.* 1907, 6, 272; Neuberg, *ibid.* 276); the racemic compound differs from the natural compound only in being optically inactive and in having a sweet taste. For the dissociation constants, see Aristides Kanitz (*Biochem. Zeitsch.* 1910, 29, 126).

Reactions.—The Adamkiewicz or Liebermann reaction given by certain proteins—namely, the formation of a blue-violet ring at the junction of the two liquids when concentrated sulphuric acid is added to a mixture of the protein with acetic acid or ether—is due to the presence of tryptophan in the protein and of glyoxylic acid in the acetic acid or ether (Adamkiewicz, *Ber.* 1875, 8, 161; v. Liebermann, *Zentr. Med. Wissensch.* 1887, 321, 450; Hopkins and Cole, *Proc. Roy. Soc.* 1901, 68, 21; *J. Physiol.* 1901, 27, 418; Cole, *J. Physiol.* 1903, 30, 311; Osborne and Harris, *J. Amer. Chem. Soc.* 1903, 25, 855; Bardachzi, *Zeitsch. physiol. Chem.* 1906, 48, 145; Dakin, *J. Biol. Chem.* 1907, 2, 289). According to Homer (*Proc. Camb. Phil. Soc.* 1912, 16, 405), who has studied the behaviour of tryptophan towards certain aldehydes, it is formaldehyde rather than glyoxylic acid that is the substance essential to the formation of the characteristic violet colour in the Adamkiewicz reaction (see also Fearon, *Biochem. J.* 1920, 14, 548).

For other colour reactions of proteins due to the presence of tryptophan, see Cole (*l.c.*); Dakin (*l.c.*); Fleig (*Proc. Soc. Biol. med.* 1908, 65, 193); Rosenheim (*Biochem. J.* 1, 233); Granström (*Beitr. Chem. Physiol. Path.* 1908, 11, 132); Heimrod and Levene (*Biochem. Zeitsch.* 1910, 25, 18); Mörrner (*Zeitsch. physiol. Chem.* 1919, 107, 203).

The red-violet colour produced by chlorine or bromine water on tryptophan is only given by free tryptophan, not by its polypeptides. The coloration attains a maximum when the amount of halogen is equivalent to four atoms per gram-molecule of tryptophan, and when concentrated solutions are used red amorphous

precipitates of the monohalogen derivatives are obtained $C_{11}H_{11}O_2N_2Cl$ and $C_{11}H_{11}O_2N_2Br$. These compounds are soluble in amyl alcohol, ether, or ethyl acetate, and the use of these solvents has been suggested to render the reaction more intense. The addition of excess of halogen converts the red compounds into yellow perhaloids $C_{11}H_{11}O_2N_2Cl_2$ and $C_{11}H_{11}O_2N_2Br_2$, (Neuberg and Popowski, *Biochem. Zeitsch.* 1907, 2, 357; Neuberg, *ibid.* 1910, 24, 423; Abderhalden and Kempe, *l.c.*).

Detection and estimation.—According to Herzfeld (*Biochem. Zeitsch.* 1913, 56, 258) a distinct blue colour may be detected if there is 1 part of tryptophan in 1,000,000 by means of *p*-dimethylaminobenzaldehyde; 20 grms. of *p*-dimethylaminobenzaldehyde are dissolved in 500 c.c. concentrated hydrochloric acid a 500 c.c. water. To 50 c.c. of the solution to tested 10 c.c. of the reagent are added and mixture diluted to 100 c.c. with concentrated hydrochloric acid. The colour can be estimated against an ammoniacal copper sulphate solution; see also Fasal (*Biochem. Zeitsch.* 1912, 44, 392); Thomas (*Ann. Inst. Pasteur.* 1920, 34, 701); for a colorimetric method for the estimation of tryptophan, Levene and Rouiller (*J. Biol. Chem.* 1907, 2, 481); Fürth and Nobel (*Biochem. Zeitsch.* 1920, 109, 103, 124); Fürth and Lieben (*ibid.* 1921, 116, 224; 1921, 122, 58); Ide (*Z. expt. Med.* 1921, 24, 166); Lüscher (*Biochem. J.* 1922, 16, 556).

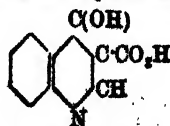
For the estimation of tryptophan in proteids, Homer (*J. Physiol.* 48, iv-v) recommends hydrolysing the proteid with baryta and estimating the tryptophan by means of bromine which has been standardised against a known solution of pure tryptophan. See also Folin and Looney (*J. Biol. Chem.* 1922, 51, 421).

For the microchemical detection of tryptophan in plants, see Kretz (*Biochem. Z.* 1922, 130, 86).

Tryptophan is decomposed on heating into carbon dioxide, indole and scatole; when fused with potassium hydroxide, scatole, to the extent of 65 p.c. of the calculated amount, is the chief product (Hopkins and Cole, *l.c.*).

Tryptophan is coloured yellow to orange by *Bacillus proteus vulgaris* only at P_H 8.9-9.4. The practical bearing of this is concerned with the manufacture of Stilton cheese (Mattick and Williams, *Biochem. J.* 1921, 15, 213). *l*-Tryptophan is converted by *B. proteus* into *l*-indole lactic acid (Sasaki and Otsuka, *Biochem. Z.* 1921, 121, 167).

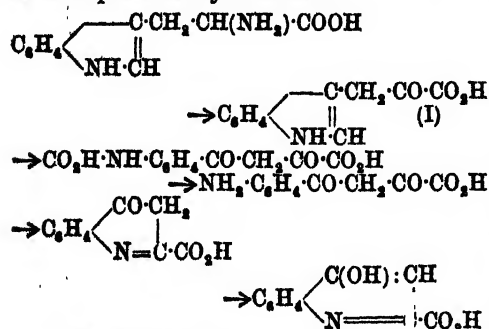
In the animal economy, tryptophan undergoes bacterial decomposition with the formation chiefly of indole; in the case of dogs it is partially converted into *kynurenic acid* (4-hydroxyquinoline 3-carboxylic acid)



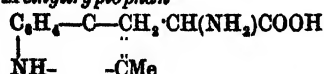
(*v.* QUINOLINE) and excreted as such. The administration of tryptophan causes an increased excretion of kynurenic acid (Kretschy, *Ber.* 1879, 12, 1873; Weiss, *Abd. Ber.* 1881, 33, 181, 171; Monastch, 1883, 4, 156; 5, 16; Solomon, *Zeitsch. physiol. Chem.* 1907, 33, 497; Capaldi,

1842, 1897, 23, 32; Mendel and Jackson, Amer. J. Physiol. 1898, 2, 1; Camps, Ber. 1901, 34, 2703; Mendel and Schneider, Proc. Amer. Physiol. Soc. 1900, ix-x; Amer. J. Physiol. 1901, 5, 427; Gies, *ibid.* 1901, 5, 191; Glaessner and Langstein, Beitr. chem. Physiol. Path. 1901, 1, 28; Ellinger, Ber. 1904, 37, 1801; Abderhalden, Löffler and Pinoussohn, Zeitsch. physiol. Chem. 1909, 62, 139; Homer, J. Biol. Chem. 1915, 22, 391; Matsuoka, J. Biol. Chem. 1918, 35, 333; Späth, Monatsh. 1921, 42, 89).

Ellinger and Matsuoka (Zeitsch. physiol. Chem. 1920, 109, 259) find that when indolepyruvic acid (I) is administered subcutaneously to a dog, it is possible to isolate from the urine kynurenic acid in amount rather less than one-half of that obtained when tryptophan is injected; and the conclusion is drawn that the conversion of tryptophan into kynurenic acid is best represented by the scheme



1-2-Methyltryptophan



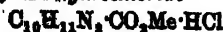
crystallises with 1MeOH in colourless prisms, m.p. 263°-273°, according to the rate of heating; the picrate, $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{C}_6\text{H}_5\text{O}_2\text{N}_3$, crystallises in orange plates, m.p. 173° (Barger and Ewins, Bio-Chem. J. 1917, 11, 58).

Salts of 1-tryptophan.—1-Tryptophan has an acid reaction towards litmus, and forms salts both with acids and bases; the *copper salt* ($\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3$)₂Cu, sparingly soluble grey-blue precipitate (Abderhalden and Kempe, Zeitsch. physiol. Chem. 1907, 52, 207); the *silver salt* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\text{Ag}$; the *sodium salt* has $[\alpha]_D + 2.50^\circ$ in 2 p.c. solution (H. Fischer, l.c.). The *hydrochloride* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{HCl}$ has m.p. 251° and $[\alpha]_D - 13.44^\circ$ in 2 p.c. aqueous solution (H. Fischer); the *picrate* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{C}_6\text{H}_5\text{O}_2\text{N}_3$, forms bright red lustrous needles or plates, m.p. 195°-196° (decomp.); the *picrolonate*



forms orange red needles, m.p. 203°-204° (Mayeda, Zeitsch. physiol. Chem. 1907, 51, 261).

Esters and acyl derivatives.—The *methyl ester* $\text{C}_{11}\text{H}_{11}\text{N}_3\cdot\text{COOMe}$ forms crystalline plates, m.p. 89.5° (corr.); the *hydrochloride*



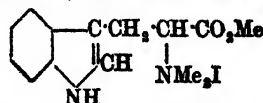
crystallises in microscopic needles, melts with decomposition at 214° (corr.); the *hydrochloride of 1-tryptophan* $\text{C}_{11}\text{H}_{11}\text{N}_3\cdot\text{COCl}\cdot\text{HCl}$ melts and decomposes at 238° (corr.) (Abderhalden and Kempe, l.c.). The *phenylcarbamide derivative* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3$ crystallises in

needles, m.p. 166°; the *carbamide* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{CONH}\cdot\text{C}_6\text{H}_5$, m.p. 159°-160°; the *benzenesulphonic derivative* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{SO}_3\text{Ph}$ melts and decomposes at 185° and forms a sparingly soluble sodium salt; the *β-naphthalenesulphonic derivative* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_7$ melts at 180°, the *sodium salt* at 304° (corr.) (Abderhalden and Kempe, l.c.; Ellinger and Flamand, Ber. 1907, 40, 3029).

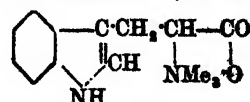
d-Tryptophan-anhydride, m.p. 230°-245° (decomp.), has $[\alpha]_D + 20.59^\circ$ in water (Fränkel and Feldsberg, Biochem. Zeitsch. 1921, 120, 218).

Other derivatives of tryptophan are *monochlorotryptophan* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\text{Cl}$, an amorphous red precipitate, m.p. 280°, converted by excess of chlorine into the *perchloride* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\text{Cl}_4$, a yellow precipitate decomposing at about 100°; *monobromotryptophan* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\text{Br}$, an amorphous red precipitate with a black reflex, m.p. 270°-280°; the *perbromide* $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_3\text{Br}_3$ is yellow and decomposes at 75° (Neuberg and Popowsky, Biochem. Zeitsch. 1906, 2, 357).

The *betaine* of tryptophan is identical with the alkaloid *hypaphorine*, discovered by Greshoff (Mededeelingen uit's Lands Plantentuin, 1890, 7, 29) in the seeds of *Erythrina hypaphorus* (Boerl.), and is of considerable biochemical interest as it is the only naturally occurring simple derivative of tryptophan. The alkaloid can be synthesised from tryptophan by the action of methyl iodide, sodium hydroxide and methyl alcohol, which yields the *iodide of methyl α-trimethylamino-β-indolepropionate*



m.p. 197°, and this on hydrolysis gives *hypaphorine* or *α-trimethylamino-β-indolepropionbetaine*



of which the *nitrate* has m.p. 215°-220° and $[\alpha]_D + 94.7^\circ$. Greshoff found $[\alpha]_D 91^\circ-93^\circ$ for the natural base (van Romburgh and Barger, Chem. Soc. Trans. 1911, 2068).

M. A. W.

TSCHIEFFKINITE.* A titano-silicate of cerium earths (Ce_2O_3 , &c., 23-47 p.c.) of doubtful composition, and probably only an alteration product lacking in homogeneity. Two analyses (R. Hermann, 1866) show ThO_2 20.9 and 14.4 p.c. The mineral is black, opaque, and pitted, with a brown weathered crust on the exterior. Sp.gr. 4.2-4.5. It is found in pegmatite in the Ilmen Mtns., Urals; Kanjamalai Hill, near Salem in Madras; Nelson and Bedford counties in Virginia, here as masses up to 20 lb.; and in Madagascar.

L. J. S.

TSCHEN or CHEN. Chinese coins of a brass or bronze-yellow colour, containing 55-64 p.c. copper, 26-35 p.c. zinc, and from 1-2 p.c. tin, 2-4 p.c. iron and 1-6 p.c. lead; and occasion-

* This is the usually-accepted spelling, but the transliteration from the Russian (тешкины) is partly German and partly French. The original is Tschewkins (G. Rose, 1869); and equivalent would be Chevkinite.

ally small quantities of antimony, arsenic, and nickel (Pöpplein, Chem. Zentr. 1859, 494).

TSCHERMIGITE. The mineralogical name for ammonium-alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. In nature it is found as crystalline crusts on lignite containing streaks of pyrites at Tschermig, Brüx, and Dux in Bohemia. The white, fibrous, platy masses somewhat resemble fibrous gypsum; but distinct cubo-octahedral crystals are also found. In some quantity it has been found in bituminous shale near Wamsutter in Wyoming (E. T. Erickson, J. Wash. Acad. Sci. 1922, 12, 49). It is also recorded as a volcanic product from the solfatara of Pozzuoli near Naples.

L. J. S.

TSCHEWKINITE v. TSCHEFFKINITE.

TSE-HONG. A mixture of white lead, alumina, ferric oxide, and silica, used by the Chinese for painting on porcelain.

TSING-LIEN. A red pigment used in porcelain painting. Consists of a mixture of stannic and lead silicates with copper oxide or cobalt and gold.

TUBA. The Malay name for *Derris elliptica* (Benth.), used in Java to kill fish. Contains tubatocin $\text{C}_{12}\text{H}_{11}\text{O}_8$, white crystals from alcohol, m.p. $163^\circ\text{--}165^\circ$, soluble in most organic solvents, insoluble in water, acids, and alkalis. Reduces ammoniacal silver and alkaline copper solutions. Produces in fish, frogs, and mammals general motor paralysis. Lethal dose for rabbit (intravenous) 0.009 grm. per kilo (Ishikawa, Jap. Med. Lit. 1917, 1, 7; Chem. Abstr. 1917, 11, 2371; cf. Greshoff, Ber. 23, 3537; van Sillevoldt, Arch. Pharm. 1899, 237, 595; Power, Arch. Pharm. 1903, 6, 1).

TUFA v. TRAVERTINE.

TUFF or VOLCANIC TUFF (from Ital. *Tufo*).

A pyroclastic rock consisting of more or less compacted dust and fragmentary material ('ashes,' *lapilli*, *scoriae*), produced by volcanic explosions. The composition varies between wide limits, depending on the kind of lava or rock from which the material has been derived; logists distinguish rhyolite-tuff, trachyte-tuff, andesite-tuff, basalt-tuff, palagonite-tuff, and ultrabasic-tuff. Further, there may be an intermixture of fragments of sedimentary rocks and other foreign material; and if deposited in water they are stratified, and may shade off into shale, limestone, sandstone, &c. They also vary much in texture and physical characters, from loose and earthy to hard and compact. Those interbedded with the older sedimentary strata may have their characters so obliterated that they are difficult to recognise as tuffs. For instance, the green roofing slates of the English Lake District were deposited as tuffs in Ordovician times; and other silicified tuffs are now used for road-stones.

The *pozzolana** of the Phlegrean Fields, the island of Ischia, and elsewhere near Naples, is an incoherent trachyte-tuff which has been extensively used, mixed with lime, for making hydraulic mortar, cement (pozzolanic cement), concrete, and artificial stone. The colour varies from yellow to grey (*tufo giallo* and *tufo bigio*). A similar sandy tuff which has been used for the same purpose (Roman cement) since the time of the Romans also occurs in the extinct

* Also spell *pozzolana*, *pozzuolana*, *puzzolana*; from *pozzuoli* near Naples.

volcanic district around Rome. Here also there is a more compact, though soft and easily worked, granular tuff, in which the ostacombs are excavated; and a harder stony tuff (*tufo liscio*) employed as a building stone. Another compact tuff, which has been much used as a building stone in ancient and modern Rome, is the *peperino*† (*lapis Albanus*) of the Alban Hills. This is a leucite-basalt-tuff, showing black grains suggestive of peppercorns embedded in a grey ground. Sandy volcanic tuffs similar in character to pozzolana occur at many other localities, from some of which it is exported for the manufacture of cement, e.g. Santerin, Auvergne, Hungary, Canary Islands (here known as 'tosca'), Crimea, Eifel. In the Eifel it is known locally as *trass* (or *duckstein*), and is extensively quarried in the Brohl and Nette valleys, between Andernach on the Rhine the Laacher See. This also is a trachyte-tuff, composed largely of glassy fragments of pumice with fragments of *grauwacke* and clay-slate. It is dull and earthy with a yellowish, grey, brown colour; 40–70 p.c. is soluble in hydrochloric acid. The looser material is used for manufacture of hydraulic cement, whilst some of the more compact is employed as a building stone, and as a fire-stone in ovens. The latter is very porous (weight per cubic foot, 85½ lbs.; porosity, 29–45 p.c.), is easily worked, and it hardens on exposure; on account of its lightness it is especially adapted for vaults and arches.

Analysis I is of yellow pozzolana (poasil tuff) from Cape Posilipo, Naples (also CO_2 3.16; Mn_2O_3 0.54; 90 p.c. of the material is soluble in hydrochloric acid; sp.gr. 2.46); II pozzolana from near Naples (ignited material; also NaCl 2.56); III red pozzolana from near Rome; IV, trass from Brohl valley, Rhine; V, trass from Andernach; VI, blue trass (*duckstein*) from Plaidt, Nette valley, Rhine (also MnO 0.58).

	I.	II.	III.	IV.	V.	VI.
SiO_2	53.27	59.14	40.15	58.32	57.5	53.07
Al_2O_3	15.53	21.28	23.19	20.88	10.1	18.28
Fe_2O_3	4.37	4.76	6.42	4.15	3.9	3.43
CaO	3.10	1.90	8.52	2.19	7.7	1.24
MgO	0.68	—	2.25	1.10	1.1	1.31
K_2O	8.22	4.37	3.01	3.91	6.4	4.17
Na_2O	trace	6.23	trace	4.11	—	3.78
H_2O	9.84	—	10.40	5.87	12.6	12.78

98.71 100.24 99.94 100.53 99.3 98.69

L. I. S.

TULA METAL. An alloy of silver, copper, and lead made at Tula in Russia.

TUNG OIL is obtained from the seeds of *Aleurites cordata* (Muell. Arg.) *Elaeagnus cordata* [Bl.]; *Elaeagnus vernicea* [Juss.]; *E. sinensis* (*Dryandra vernicea* [Cox.]), and *A. fordii*, trees indigenous to China and Japan. Trees belonging to the same species also grow abundantly in Indo-China, Tonkin, Annam, and Cambodia.

The fruits form a nut, in which three seeds, having a hard shell and an oleaginous kernel, are enclosed; in China the oil is frequently termed 'nut oil,' and in America is known as China wood oil.

Three kinds of seeds are distinguished—

† Not to be confused with 'tung' (= *Trachypithecus*).

yellow, drab, and white. The seed of the Japanese tung tree is smaller than that of the Chinese variety (*Alseurites fordii*), and yields an oil which gelatinises less readily on heating. A Japanese oil had the following characters: iodine value, (Wij's) 150.2, (Häbl.) 154.4; saponif. value, 193.2; acid value, 0.9; sp.gr. at 15°/15°, 0.9342; $n_D^{25} = 1.4982$. Two samples had n_D^{40} , 1.5078 and 1.5116 respectively, and showed a decrease in refractive index of 0.000395 for each 1°C. rise in temperature (H. E. Goldsmith, Ind. Eng. Chem. 1923, 15, 786; J. Soc. Chem. Ind. 1923, 938 A).

The viscosity is intermediate between that of Chinese tung oil and raw linseed oil (Gardner and Ratliff, Chm. 138, U.S. Paint Manufacturers Assoc. Nov. 1921). There are four species of tung oil trees in Japan, viz. (a) Japanese tung oil tree, *Alseurites cordata*, (b) Chinese tung oil tree, *A. fordii*, (c) Kangtung tung oil tree, *A. montana*, and (d) Bakoly (or tropical) tung oil tree, *A. moluccana* (better known as candlenut oil). Of these (a) is grown all over the interior of the country and the others in Formosa.

Other analyses are as follows:—

Oil contents.	(a)	(b)	(c)	(d)
In seeds, p.c.	37.77	44.11	37.43	23.61
In endosperm, p.c.	59.15	66.29	59.78	70.66
Time for drying at 95°C. (min.)	65	55	60	270
Sp.gr. (15°C.)	0.9340	0.9488	0.9372	0.9267
Acid value	0.47	1.52	0.59	0.80
Saponif. value	194.79	196.76	194.31	195.13
Iodine value (Wij's)	151.37	157.17	154.85	146.31
Refract. index (25°C.)	1.5065	1.5210	1.5147	1.4785
Reichert-Meißl value	0.39	1.10	0.35	0.71
Unsaponif. matter, p.c.	0.41	0.59	0.99	0.97

(I. Miura, Kōgyō-Kwagaku Zasshi, J. Chem. Ind. Japan, 1923, 26, 316-321; J. Soc. Chem. Ind. 1923, 42, 786 A.)

Analyses of the oil from *A. montana* and

Japanese *A. fordii*, and a comparison with the proposed American standard, based on the examination of oils from the Chinese *A. fordii*, are as follows:—

	<i>A. montana</i> .	<i>A. fordii</i> (Japanese).	American specification, for China wood oil.
Specific gravity at 15°/15°C.	0.9467	0.9439	0.938-0.943
Refractive index n_D^{15}	1.494	1.4917	$n_D^{25} 1.515-1.520$
Acid value	3.4	Nil	7.0 max.
Saponification value	203	204	190-195
Unsaponifiable matter, p.c.	0.6	—	0.75
Iodine value	141.4	157.7	163
Heat test	16"	19.5"	12"
Iodine jelly test	45"	35"	—
"Titre test"	54-54.5	—	—

The heat test is considered the most satisfactory criterion (Rau, Robertson, and Simonsen, Indian Forest Rec. 1924, 10, 1; Analyst. 1924, 49, 399).

In China the seeds are roasted, crushed between stones, and expressed in wooden presses. The kernels contain about 53 p.c. of oil, but yield only 40-41 p.c. The cold-drawn oil is pale yellow (*white tung oil*), and is the variety chiefly imported into Europe as China wood oil. The oil obtained by hot pressing is dark brown (*black tung oil*), and is consumed at home; it has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. This odour, attributed to damaged kernels, precludes its use for many purposes. Tung oil is also expressed in Madagascar, where the oil is known under the name 'Bakoly oil,' probably a corruption of 'bancoulier' (*Alseurites moluccana*; candlenut oil). The Chinese and Japanese oils differ in specific gravity, iodine value, and gelatinising power (see *Characteristics* under *Oils, Fats, and Waxes*). The chief shipments of oil are made from Hankow and Wuchow in

China; comparatively smaller quantities are exported from Japan (Hokkaido).

Tung (China wood) oil contains little, if any, saturated fatty acid and relatively little oleic acid, elaeostearic acid, $C_{11}H_{21}O_2$, being the characteristic acid. Both the glyceride and the fatty acid (α -acid) derived from it change to isomeric forms (β) of higher melting-point by exposure to light or under the influence of catalysis (Bauer and Herberts, Chem. Umschau, 1922, 29, 220; cf. Morrell, J. Soc. Chem. Ind. 1918, 181 T). It does not yield any ether-insoluble bromide. In the 'elaidin test' an oily layer is obtained resting on the lower, nearly solid product; when stirred up, the whole mass flows.

Tung oil contains from 75 to 85 p.c. of glyceryl α -elaostearate, which changes under the influence of light into the solid geometrical isomeric, glyceryl β -elaostearate. Both the α - and the β -triglycerides increase in weight at about the same rate when exposed to the air in thin films. After standing for 10 months in a closed brown glass bottle, β -elaostearin became insoluble in acetone and no longer melted, but charred at about 265°. Both α - and β -elaostearic acids

m.p. 46° and 72° respectively, were prepared from tung oil which had stood for some time, by extracting it with ethyl alcohol and fractionally crystallising the extract from this solvent at about 0°. Another acid (m.p. 106.5°), presumably a cleavage product, was obtained from the residue insoluble in cold alcohol. After 8-10 days a thin layer of the α -acid was transformed into a clear yellow syrup, whilst the β -acid was only transformed into a clear yellow, viscous syrup after 4 weeks' exposure. Only two of the three possible geometrical isomerides of elaeostearic acid have been obtained. It is considered that the α -acid is probably the *cis-cis* form and the β -acid the *cis-trans* form. Bromination of both α - and β -acids yields the same tetrabromide (m.p. 114°). The transformation of the α - into the β -geometrical isomeride, on treatment with bromine, is considered to be a peculiarity confined to compounds containing two double linkings separated by two methylene groups, a constitution which explains the high reactivity of elaeostearic acid. Evidence is adduced in favour of the view that the conversion of the α - into the β -acid plays very little part in the mechanism of the drying of tung oil, which appears to be a colloidal phenomenon involving transformation from the sol to the gel form rather than a case of molecular polymerisation (A. Eibner, O. Merz, and H. Munzert, Chem. Umschau. 1924, 31, 69; Chem. Soc. Abstr. 1924, 126, i. 609). Boeseken and Ravensway (Rec. trav. Chim. 1925, 44, 241) conclude from refractometric determinations that elaeostearic acid has three double bonds and belongs to the linolenic series. This is confirmed by Kaufmann (Ber. 1926, 59, 1390), who finds that thiocyanogen is absorbed at only two of the double bonds, but that the third double bond can be saturated with bromine when the oil is exposed to the rays of a mercury vapour lamp. Kaufmann thus found two specimens of tung oil to have the following composition: I. elaeostearin, 78.5; olein, 22.8 p.c.; II. elaeostearin, 87.1; olein, 13 p.c.

Thomas and Yu (J. Amer. Chem. Soc. 1923, 45, 120) have devised a qualitative test for elaeomargaric acid, which consists in treating the insoluble magnesium salts from tung oil with 90 p.c. alcohol, and then liberating the fatty acid in the absence of air. A yield of about 20 p.c. (m.p. about 44°) is obtained.

The oil may be identified by its strong characteristic smell, and also by the manner in which it dries. Although it forms a skin more rapidly than does linseed oil, the skin it yields, e.g. on a glass plate, when dry, is opaque, wax-like, and has no elasticity. Therefore, tung oil cannot replace linseed oil, but is nevertheless largely used as a substitute for it. A number of patents have been taken out for the manufacture of boiled oils, varnishes, rubber substitutes, and linoleums, in which larger or smaller quantities of tung oil are used in place of linseed oil. V. VARNISH.

Drying of Tung Oil.—Tung oil appears to dry in about two days in moist air, but the resulting film is always wrinkled or cracked and uneven. In dry air a smooth coherent film is obtained, but the time required is about 14-21 days. In either case, however, the full gain in (129-133 p.c.) requires about

21-30 days, and it is concluded that tung oil is really a slow-drying oil, and that the rapid apparent rate of drying in moist air is not 'drying' in the usual sense (i.e. oxidation and polymerisation), but is a colloidal coagulation in which moisture acts as the coagulant (W. Schmidt, Farben-Zeit. 1924, 29, 1261; J. Soc. Chem. Ind. 1924, 43 B, 604).

A characteristic property of tung oil is that it forms a jelly on being heated to 250° for a short time, or even when kept at 180° for an hour or two. Tung oil gelatinised by heating to 200°-250°C. and extracted with ether yields an extract which can be divided into two fractions by treatment with acetone, viz. 12 p.c. of a thick insoluble oil, a bimolecular triglyceride of elaeostearic acid, and 88 p.c. of oil soluble in acetone. The former fraction (thick oil) is soluble in benzene, ether, and chloroform, and is converted by heating or exposure to air into a solid insoluble mass having about the same iodine value as the acids from the thick oil and as the acids isolated from the solid product insoluble in ether obtained by heating tung oil. Coagulated tung oil contains, in addition to unchanged oil, oily and solid polymerisation products both in the sol and gel form. Substances such as naphthenic acid, linseed oil, and colophony, which prevent the coagulation of tung oil, merely reduce the tendency of the sol to pass into the gel form. The formation of the gel is favoured by exposure to the air, rise of temperature, and by the addition of a little gelatinised oil. It is also caused by the action of light, with the initial formation of α -elaeostearin (*cis* form) and β -elaeostearin (*trans* form), which are respectively soluble and insoluble in acetone. The β -glyceride easily polymerises to a substance insoluble in the usual organic solvents. Tung oil dries, with the formation of crystalline masses of β -elaeostearin, but heated (i.e. polymerised) tung oil, on the contrary, dries evenly, as β -elaeostearin is in this case not present (J. Marcusson, Z. Deuts. Oel. u. Fettind. 1923, 43, 162-163; Chem. Zentr. 1923, 94 [iv.] 297; J. Soc. Chem. Ind. 1923, 42, 938 A). On exposure to the light the oil also becomes solid. The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents for oils, and shows no tendency to melt again on being heated to 250°. The gelatinisation is not due to oxygen absorption, since it takes place when air is excluded. Chapman (Analyst, 1912, 37, 543) has made a critical examination of various polymerisation tests, and has shown that greater importance should be attached to the hardness of the jelly obtained under standard conditions than to the time required to effect the polymerisation. The time, however, is the basis of the so-called Browne method, which is commonly employed by varnish chemists, and is officially adopted by the American Society for Testing Materials (Analyst, 1912, 37, 410). It consists in heating 5 c.c. of the oil at 282° and noting the time required for complete solidification. This should not take more than 12 minutes for a pure oil. Jameson (Analyst, 1920, 45, 328) has shown that the time is increased by the presence of free fatty acid, which frequently occurs to the extent of from 1.9 to 4.6 p.c. When tung oil is heated with lead oxide or red lead, the oil

gelatinises within 15 mins. to a light brown mass.

If a saturated solution of iodine in chloroform or any other solvent be dropped on to the oil it is immediately solidified; and if the oil has been previously dissolved in chloroform, a jelly is obtained. Bromine has no such action on the oil.

When a solution of 1 grm. of the oil in 5 c.c. of chloroform, is stirred with 5 c.c. of a saturated solution of iodine in chloroform, the whole is converted into a stiff jelly after about 2 mins. With 2 grms. of the oil the jelly is so stiff that it can be granulated.

Investigation of the effect of glycerol, oleic acid, resin, 'ester gum,' paracoumarone resin, and linseed oil on the rate of gelatinisation of tung oil shows that their efficiency in preventing this change falls in the order given. Tung oil containing 6 p.c. of glycerol can be 'bodied,' e.g. at 280°C., without difficulty. Tung oil containing lead linoleate equivalent to 0.02 p.c. of lead, when treated in this way and dissolved in turpentine, dried rapidly to a smooth tough, transparent film (F. H. Rhodes and T. J. Potts, Chem. and Met. Eng. 1923, 29, 533; J. Soc. Chem. Ind. 42, 1923, 1081 A).

In China and Japan tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, as a common adulterant of lacquer, and also for lighting. Large quantities are also consumed for water-proofing paper and all kinds of tissues. The oil is further employed in admixture with powdered lime as a mortar. The lamplack of the best kinds of Chinese ink are obtained by burning the oil with a regulated amount of air. The cold-drawn oil is stated to be used in medicine as an emetic and also as a purgative. It should be noted that the raw oil is poisonous. J. L.

TUNGSTEN. Sym. W. At.w. 184.1. Although found in most of the tin deposits throughout the world, the mineral *wolfram* which furnishes the bulk of the tungsten of commerce and its products, appears to have been regarded, until the middle of the eighteenth century, rather as a constituent of *cassiterite* than as an associated mineral. The term 'wolfram' was, in fact, apparently applied to it on account of its causing loss of tin in smelting, in the same sense that antimony was called 'the wolf' by the alchemist because it devoured the base metals when employed in the refining of gold.

The word 'tungsten' is of Scandinavian origin and signifies 'heavy stone,' in allusion to the high specific gravity of wolfram.

In 1781, Scheele obtained a yellow powder (which he termed tungstic acid) by acid treatment of the aqueous extract from the fusion of a certain heavy lime mineral with potassium carbonate. The production of a yellow colouring matter by direct acid treatment of this mineral (afterwards termed *scheelite*) had been previously noted by Woulfe, who did not, however, explain its nature. Scheele's work was confirmed and amplified by Bergman in 1782, and the following year, his former pupils, the brothers D'Elhuyart, are stated to have shown the presence of tungstic acid in wolfram and to have produced metallic tungsten from it.

Scheelite CaWO_4

80.55 p.c. of WO_3) is also an important tungsten mineral, but its common association with rare metals (molybdenum, &c.) and base metals (antimony, &c.), from which it is difficult to effect a separation, has resulted in a smaller output and a lower price as compared with wolfram. Among other minerals may be mentioned *reinite*, a variety of ferberite, FeWO_4 , *cupro-scheelite* $\text{CaWO}_4 \cdot \text{CuWO}_4$, *stolzite* or *raspite* PbWO_4 , and *tungstite* (*tungsten ochre*) $\text{WO}_3 \cdot \text{H}_2\text{O}$ and *ferritungstite* $\text{Fe}_2\text{O}_3 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$. The last-named minerals are commonly found as an incrustation produced by the weathering of tungsten minerals, but occasionally occur massive, and the author has an interesting piece of the former which was sent to England as *scheelite*, but is almost pure tungstic acid, apparently of colloidal origin.

The principal countries where tungsten minerals are found are (in order of importance) United States (chiefly west of the Rocky Mountains), Burma (mainly from Tavoy, south of Rangoon), Bolivia, Portugal, Australia, Japan, South China, Spain, South Africa (including Rhodesia), Austria, Germany, France, and England (Cornwall). The world's production (mostly wolfram, although notable quantities of *scheelite* are mined in United States, Australia, New Zealand, and South Africa) is estimated at nearly 20,000 tons in 1917 against about 8,000 tons in 1913. The largest producers are United States (about 4,700) followed by Burma and Bolivia with about 3,000 and nearly 4,000 respectively. The British Empire produces about 30 p.c. of the total world's production. For a useful summary of the occurrence of tungsten ores, see S. J. Johnstone, J. Soc. Chem. Ind. 1918, 37, 29 R. and later.

Although their value mainly depends on the amount of tungsten which they contain, almost the whole of the output being absorbed in the manufacture of the metal and its alloys, the minerals are invariably sold on their tungstic acid content. The best concentrated or hand-picked material contains up to 74 p.c. WO_3 , but the usual value of that sold in bulk varies between 65 and 72 p.c., the latter being considered high grade. The sale of the ores was, before the war, more often a matter of private treaty, although schedules, covering ores of various percentages and showing limits for P, S, and other impurities, were published by several firms in the United States. The home consumption of ores of tungsten was comparatively small before the war, when most of the ore produced within the Empire was bought and smelted by the Germans, who separated it and exported to this country the manufactured tungsten metal. At the outbreak of war, the then existing makers of the commercial metal ('tungsten powder') and ferro-tungsten in England very largely increased their output, and other concerns commenced the manufacture, notably one organised by an association of the large steel interests. The price of wolfram and *scheelite* rapidly rose to more than double that obtaining before the war, until all ores of tungsten produced within the Empire were commandeered, by agreement between the Imperial and Colonial governments, and a maximum price fixed. The basis price fixed

was 55s. (afterwards raised to 60s.) for each unit WO_3 (i.e. for each 1 p.c. per ton of ore) at 65 p.c. or over, 3d. deduction being made by the buyer for each unit or part of a unit below 60 p.c., and 6d. per unit below 60 p.c. down to 55 p.c. Ore containing lower percentages is saleable at approximately the same rate of penalisation, and, if the impurity is chiefly tinstone, the tin is paid for if over 4 p.c., as it then usually pays for electro-magnetic separation and recovery of the tin. A large proportion of the wolfram ore imported into this country is 'concentrated' at the mine by hand-picking, but in some centres it is separated from the gangue by finer crushing and wet dressing. In the case of the Burmese and Bolivian production, the wolfram is more frequently associated with tinstone. Below 2 p.c. tin (metal) the concentrate is sold direct to the smelters; above that amount (and the ores or concentrates sometimes contain as much as 30 p.c. Sn and over) it is separated. For methods of analysis of ores and concentrates, see Hutchin, *Analyst*, 1911, 36, 398, and *Inst. Min. and Met.* 1918; also Frantmann, *Zeitsch. angew. Chem.* 1911, 24, 2142.

The treatment of the mined ore varies according to its nature and the associated impurities. In Cornwall, where the ores are frequently arsenical and the recovery of the wolfram is chiefly subsidiary to the tin, the treatment consists usually in wet-dressing the crushed ore on tables, roasting the first rough concentrates, re-grinding and concentrating, and finally dry-dressing by means of electro-magnetic separators. The last-named operation, which depends upon the fact that wolfram is weakly magnetic to an electro-magnet, provides the only available means of mechanically separating wolfram from tinstone and other heavy minerals which accumulate during the concentration. Three or four products are commonly produced, viz. fairly clean wolfram (from 60 to 65 p.c. WO_3), an intermediate or tinny wolfram, which is returned to the plant for re-treatment, a strongly magnetic iron oxide, which is valueless, although commonly containing 3 or 4 p.c. WO_3 , and a fairly clean tin concentrate containing usually less than 2 p.c. WO_3 . Much of the imported ore or concentrate from Burma or Bolivia contains wolfram in a less fine state of division, and electro-magnetic separation is carried out on the material with no preliminary treatment other than crushing and grading into various sizes. In this case, only two final products are obtained, viz. wolfram containing from 65 to 73 p.c. or even 74 p.c. WO_3 , and a non-magnetic 'reject' containing from $\frac{1}{2}$ to 2 p.c. WO_3 and from 60 to 70 p.c. tin (metal), according to the concentration of the original material. In the United States most of the wolfram occurs free from tin and in a gangue of a comparatively low specific gravity composed chiefly of silicious matter. In this case a simple concentrating plant consisting of crusher, jigs, and shaking table is sufficient. Wolfram, is, however, extremely friable and liable to slime on crushing, and great care must be exercised to minimise the losses which are in any case considerable. No satisfactory method has yet been devised for the mechanical separation of an ore contain-

ing both wolfram and scheelite with tinstone, such as is found in the Shan States (Burma) and elsewhere. Scheelite is heavy and non-magnetic, and remains with the tinstone when either wet-dressing or electro-magnetic separation is employed. It is invariably present in wolfram ores, although frequently in more traces.

For the estimation of tin in wolfram, see O. F. Lubatti (*Chem. Soc. Trans.* 1923, 123, 1409-1411).

For estimation of molybdenum in tungsten, see W. J. King (*J. Ind. Eng. Chem.* 1923, 15, 350).

The composition of selected specimens of the principal tungsten minerals of the nature of wolfram is shown in the following table, compiled from published and private sources, including Dr. W. F. Hillebrand of the United States Geological Survey, and H. E. Wood of the Colorado Scientific Society, etc. :—

	Wolfram.		Ferberite.		Hübnerite.	
	Colo-rado	Burma	Slam	Corn-wall	Spo-ken	Colo-rado
	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.
WO_3	74.10	75.41	75.00	73.16	75.0	75.9
FeO	11.07	17.33	15.05	22.78	18.0	23.0
MnO	14.35	7.13	8.26	3.06	3.0	0.6

The above analyses are all those of picked specimens, any silica, lime, alumina and other gangue matter being ignored. Traces of columbium, tantalum and other rare metals, as well as of tin, copper, and bismuth, are commonly present in actual combination, even in selected crystals.

Estimation of tungsten in low-grade ores.—

Two grms. of ore are fused with 4 parts of sodium peroxide in a nickel crucible. The fused mass is leached with 100 c.c. of water, the liquid filtered, and the precipitate well washed. The filtrate is heated, acidified with nitric acid, and made alkaline with ammonia; the precipitate is left to settle and filtered off. The hot filtrate, faintly acidified with nitric acid, is treated with excess of mercurous nitrate solution followed by ammonia until the precipitate gets black; the liquid, however, should remain faintly acid and contain mercurous nitrate. The precipitate is filtered off, washed with boiling water and dried, and the paper ashed separately. The precipitate is ignited to constant weight in a platinum crucible and fused with potassium bisulphate, and the cold mass is treated with hot water and a fragment of ammonium carbonate; if the resulting solution is not perfectly clear, the flocculent precipitate (silica or alumina) is filtered off, ignited, and weighed, and the weight subtracted from the first, tungstic acid being obtained by difference (*E. Jünger, Zeitsch. anal. Chem.* 1923, 63, 438; *Analyst*, 1924, 49, 298).

Estimation of tungsten in tungsten-steels.—

Two to three grms. of the steel are dissolved in 80-100 c.c. of 1:1 hydrochloric acid and the solution is evaporated to 40 c.c. Nitric acid is added drop by drop until all the iron is oxidised and the insoluble material assumes a yellow colour. The solution is cooled below 40°, then gently evaporated to 15 c.c., and boiled with 5 c.c. of strong hydrochloric acid and 4 or 6 drops of strong hydrofluoric acid. 80 c.c. of cold water are added and the solution is boiled for 3 min. and filtered through a pulp filter.

The precipitate is washed with hot dilute hydrochloric acid till free from iron, ignited, and weighed as tungsten trioxide (K. Swoboda, *Oesterr. Chem. Ztg.* 1924, 27, 53; *J. Soc. Chem. Ind.* 1924, 43 B. 435).

Manufacture of tungsten.—The manufacture of tungsten (by the soda fusion method) and ferro-tungsten (by the thermit or electric furnace method) demands an ore or concentrate as free from impurities as possible, and, while makers' requirements differ in normal times, this is only because those whose requirements are less stringent are themselves prepared to carry out the necessary purification. Objectionable impurities, inasmuch as they affect either or both the quality of the resultant product and the yield, are Sb, As, Bi, Cu, Sn, P, S, and Si, and they should be removed, so far as possible, before the chemical or metallurgical treatment. In the sodium carbonate fusion method, arsenic, phosphorus, and silica are highly objectionable, owing to the formation of soluble tungstates; freedom from tin, copper, and bismuth is not so important as it is in the thermit process, when these metals, if present, appear in large proportion in the ferro-alloy. In the electric furnace method of reduction these metals are objectionable, but are to some extent volatilised in the process. Wolfram is preferred to scheelite by the users of the soda fusion method, but a mixture of the two minerals is an advantage in the thermit and electric furnace treatment. Some users object to hübnerite, or wolfram containing an excess of manganese over iron, but no discrimination is made in the market; wolfram, ferberite, hübnerite, and scheelite, all fetching the same price per unit of WO_3 .

The treatment of tungsten ores for the manufacture of metallic tungsten ('tungsten powder' or of its oxides or salts) comprises a series of operations which, although chemically and metallurgically simple, require extreme care and experience, and result in heavy losses even under the best conditions. The first step is the production of sodium tungstate by the 'Oxland process', patented in 1847 and still used with practically no modification. It consists in heating, in a reverberatory furnace, the finely powdered ore with from 5 to 10 p.c. more than the theoretical amount of sodium carbonate (sometimes with the addition of about 5 p.c. sodium nitrate). The charge is maintained at a bright red heat for from two to three hours and rabbled occasionally by hand. The mass is not allowed to fuse beyond a pasty condition, in which state it is withdrawn when the reaction is completed. Sodium sulphate in place of the carbonate was proposed by Oxland, but its necessities a higher temperature and results in irregularity in the furnace and in the nature of the product, and has met with no general application. The fritted charge or 'melt' is broken up when cold, reduced to powder and dissolved by means of live steam in a boiler provided with stirrers. The tungstate solution and residual mud (consisting mainly of oxides of iron and manganese) is pumped through a filter press and the liquor concentrated to the required strength. For the preparation of pure tungstate the solution is crystallised and re-crystallised in vats.

For the manufacture of tungstic acid, the second step in the production of metallic tung-

sten, the hot concentrated solution of sodium tungstate is run direct from the evaporator into boiling hydrochloric acid (strongest commercial HCl, sp.gr. about 37°Tw.), the granular, yellow tungstic acid being washed by decantation, pressed and calcined. The strength of the solution of both tungstate and acid and the method of admixture and washing, require the most careful supervision. Under the best conditions, both temporary and permanent, losses are heavy, partly from the production of a soluble acid tungstate and partly from the formation of colloidal tungstic acid. The production of both is minimised by the use of pure ores, by precipitation with a large excess of acid at the highest possible temperature, and by washing rapidly with dilute acid. Any arseno- or phospho-tungstates which may have been formed are not decomposed by HCl, and silico-tungstates also result in loss of WO_3 , by remaining partly in solution or, if decomposed, hinder settlement and introduce SiO_2 into the precipitated WO_3 . In order to recover any tungstate or tungstic acid in solution, it is usual to treat all filtrates and wash waters with lime, the precipitated calcium tungstate being either mixed with a fresh furnace charge or put aside for special treatment.

The third and final step in the manufacture of tungsten consists in the reduction of the calcined tungstic acid with carbon, which is usually carried out in crucibles, either in coke wind furnaces or regenerative gas furnaces of the Siemens type. The calcined tungstic acid is finely ground and intimately mixed with the purest anthracite, in the proportion of slightly less carbon than is theoretically required for the reduction of the metal with production of carbon monoxide. The temperature is raised slowly until it reaches about 1100°C. at which it is maintained for some hours, when the crucible is cooled in a reducing atmosphere. The partly sintered mass is removed from the crucible, finely ground in a ball mill, washed free from undecomposed oxide, free carbon and particles of crucible, heated with a weak solution of sodium carbonate to remove remaining traces of oxide, and finally dried as a fine-grained but distinctly granular powder. Proposals have been made from time to time to carry out the reduction by means of producer gas, while hydrogen is always used when the pure carbon-free metal is required.

Metallic tungsten may also be prepared by the direct reduction of sodium tungstate with carbon at a heat sufficient to volatilise the sodium which is simultaneously produced, or by similarly reducing calcium tungstate and dissolving out the lime which remains with the resultant powdered metal, or by reducing tungstic acid with metallic zinc. The metal obtained thus and by many other apparently simple processes is, however, always impure, and the only commercial methods known consist in the reduction of tungstic acid by the processes already referred to.

The melting-points of tungsten-molybdenum alloys lie on a straight line connecting the melting-points of the elements, and the microstructures are all homogeneous. The two form a continuous series of mixed crystals. The electrical conductivity temperature coefficients

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confirm this; this coefficient may be used to determine small proportions of molybdenum in tungsten (W. Geiss and J. A. M. van Liempt, *Zeitsch. anorg. Chem.* 1923, 128, 355-360; *J. Soc. Chem. Ind.* 1923, 42, 1227 A).

The accepted standard specification for tungsten powder in England is as follows:—

	p.c.
Tungsten	96-99
Carbon	0.6
Silicon	0.3
Manganese	0.3
Sulphur	0.06
Phosphorus	0.02
Arsenic	Trace
Tin	0.05
Copper	Trace
Calcium	0.1

	1 P.c.	2 P.c.	3 P.c.	4 P.c.	5 P.c.	6 P.c.	7 P.c.
Tungsten	83.36	84.82	80.74	85.72	81.79	98.51	96.45
Carbon	0.54	0.027	0.04	0.75	0.53	0.109	0.129
Silicon	1.06	1.96	0.99	0.130	0.49	0.25	0.28
Manganese	0.81	0.21	0.815	0.395	1.33	0.035	0.03
Copper	0.03	0.022	0.22	Nil	Trace	0.012	0.18
Tin	0.276	0.177	0.214	0.196	0.285	0.059	0.029
Phosphorus	0.019	0.055	0.031	0.009	0.016	0.003	0.004
Sulphur	0.005	0.007	0.035	0.005	0.022	0.004	0.046
Lime	0.02	0.134	0.0164	0.021	Nil	0.041	0.164

Nos. 1, 2, and 3. Ferro-tungsten produced by the aluminium or 'thermit' process. Balance, metallic iron.

Nos. 4 and 5. Ferro-tungsten produced by the electric furnace.

Nos. 5 and 6. Tungsten powder produced by reduction of WO_3 by carbon. Iron is usually about 0.5 or 0.6 p.c. (For analytical methods, see Arnold, *Zeitsch. anorg. Chem.* 1914, 88, 748, and R. Fieber, *Chem. Zeit.* 1912, 36, 334.)

Ferro-tungsten is an alloy usually containing from 80 to 85 p.c. W. It is made on a large scale by the 'thermit' process (*q.v.*) and in the electric furnace. By the former method two qualities are made by at least one English firm, viz. one very low in carbon and containing about 2 p.c. silicon, for the manufacture of magnet and other steel, and the other containing about 0.5 p.c. carbon and about 1 p.c. silicon for high-speed tool steels. In the electric furnace the ore is commonly smelted with carbon as a reducing agent, and the resulting alloy decarburised and refined. It is stated that one American firm smelts scheelite with iron sulphide and carbon in the electric furnace producing an alloy low in carbon.

The loss of tungsten is high in all methods of reduction. It is estimated that yields of 91½, 87, and 88½ p.c. respectively are obtained in the thermit, electric furnace, and soda fusion processes, but these figures vary considerably in different works and are probably not on the low side. In the case of ferro-tungsten, losses in the slags may be partly recovered by re-treatment. In the electric furnace there is also loss by volatilisation.

With the exception of a very small amount (probably under 1 p.c.), the whole of the world's output of tungsten is used in the manufacture of alloy steels; chiefly in those known as 'high-

and for ferro-tungsten:—

Tungsten	75-80
Carbon	1.0
Manganese	1.5
Silicon	1.5
Calcium	0.5

In the event of manganese and silicon not exceeding 1 p.c. each, calcium may be 1 p.c.

Copper	0.35
Tin	0.35
Sulphur	0.07
Arsenic	0.06
Phosphorus	0.06

The following table shows the composition of a number of typical varieties of tungsten powder and ferro-tungsten as made in England at the present time (iron omitted):—

speed' tool steels. The original 'self hardening' steel of Mushet, first made in 1857, contained about 6 p.c. W. The modern high-speed steels contain between 16 and 20 p.c. W. and from 2 to 4 p.c. Cr., and have the property of red-hardness, i.e. ability to retain their temper at the dull red heat which is reached when cutting metal at a high speed. Arnold and Read (*Proc. Inst. Mech. Engs.* March, 1914) attributed this property to the presence of tungsten carbide. They showed that with about 11½ p.c. W present in the steels they examined the whole was present as WC displacing Fe_3C . With less tungsten the two carbides Fe_3C and WC were present, and with more tungsten the excess was present as a tungstide (Fe_2W). Tungsten may be introduced into steel in the form of metallic powder or ferro-tungsten alloy. The prejudice against ferro-tungsten, which formerly existed among high-speed steel makers, due in some measure to the impurities present (high carbon, &c.) and irregularity of the tungsten content, appears to be largely disappearing under the influence of the excellent products which are now being manufactured in this country, and the scarcity of the powder in the early days of the war certainly helped the manufacturer of the ferro-alloy. Tungsten powder is preferred by a number of the English steel makers, and to-day probably the use is equally divided between the two. There is considerable loss by oxidation in the case of both, but users of the ferro-tungsten claim there is less danger of loss than with tungsten powder, and that it is cheaper. For particulars concerning alloys and the effect of tungsten upon the hardening and tempering of high-speed tool steel, see R. A. Hadfield, *Iron & Steel Inst.* 1903, 64, 14; Edwards & Kikkawa, *ibid.* Sept. 1915; and C. A. Edwards, *The Physico-Chemical Properties of Steel*, 1916,

Pure metallic tungsten, such as is used for the production of ductile tungsten, &c., is produced on a relatively small scale but has some highly important uses. A very high degree of purity is required, and the usual method of manufacture is by reduction with hydrogen, in electric resistance furnaces, of tungstic acid, purified by solution in ammonia, crystallisation of the ammonium tungstate, and re-precipitation by hydrochloric acid. The reduction is carried out at a temperature between 1000° and 1100°C. The metal powder is pressed in a hydraulic press into the form of rods, which are then sintered at a temperature of 1300°C in a current of hydrogen. The metal bar, which is still extremely brittle, is worked by hammering and rolling at a temperature of 1500°C. in a special machine through which hydrogen is flowing. Owing to the ease with which tungsten oxidises at a high temperature, cooling must take place in hydrogen. In the case of wire, the bar is worked down to about 30 mils ($\frac{3}{16}$ in.), when it becomes ductile at the ordinary temperature. The finer sizes are drawn while red hot through diamond dies. For a description of the methods for preparing ductile tungsten and filaments, see R. E. Myers, *Trans. Amer. Inst. Chem. Eng.* 1911, 3, 172; R. W. Moore, *Mot. & Chem. Eng.* 1914, 3, 186; also *Electrical Rev.* 1914, 74, 595.

Tungsten as ordinarily obtained is a powdered or semi-fused, crystalline, brittle metal, harder than glass, and having a sp.gr. of between 16.5 and 17. That obtained by Moissan in the electric furnace had a sp.gr. of 18.7 and was softer than glass. A method for causing small crystals of tungsten to grow into large single crystals by taking advantage of the thermal dissociation of tungsten hexachloride is described by van Arkel (*Physica*, 1923, 3, 76; *J. Soc. Chem. Ind.* 1924, 43, B. 427). The properties of pure wrought tungsten are entirely different from those of the powdered or ordinary cast metal. It is grey-white, lustrous, tough, and non-magnetic, and can be rolled into thin sheet, welded at a yellow heat, and drawn into wire considerably thinner than one-thousandth of an inch. It melts at $3100^{\circ} \pm 60^{\circ}$. Pifani and Meyer (*Ber. Deut. Phys. Ges.* 1912, 14, 326), $3540 \pm 30^{\circ}$. Langmuir (*J. Franklin Inst.*, 1915, 490), 3645° – 3665° , Worthing (*Zeitsch. Physik.* 1924, 22, 9; *Chem. Soc. Abstr.* 1924, 126, ii, 289). Its tensile strength increases as the drawing proceeds. Wire of 5 mils diameter has a tensile strength of 460,000 lb. per sq. in., that of 1.2 mils rises to 580,000; hard drawn piano wire having a tensile strength of 507,000 lb. The sp.gr. of the pure wrought metal is from 19 up to about 19.5 in the finest wire. Tungsten has the lowest coefficient of expansion of any known element except the diamond within the range of ordinary temperatures (Worthing, *Phys. Rev.* 1917, 638). The hard drawn wire has an electric resistance of 6.2 microhms per cubic centimetre at 25°, the temperature coefficient for 0° to 170° being 0.0051. The corresponding figure for annealed wire is 5.0. The spectrum of tungsten has been investigated, among others, by W. S. Gorton (*Phys. Rev.* 1916, 7, 203); Bayen (*Compt. rend.* 1924, 180, 57); Bloch (*ibid.* 133); and Lemon (*Nature*, 1925, 215, 802). The radiation of

heat and light from tungsten at high temperatures has been studied by Zwicker (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 409; *Chem. Soc. Abstr.* 1925, 128, ii, 1041; see also Worthing, *Zeitsch. Physik.* 1924, 22, 9; *Sci. Abstr.* 1924, 27, 528).

Emission of positive ions from hot tungsten.—Tungsten at temperatures approaching the melting-point emits positively charged ions. The positive ions are not due to the presence of residual traces of gas; they only appear at temperatures above 2500°, and they are very heavy or very slow-moving particles, little affected by a magnetic field of 400 gauss, and probably consist of charged atoms or molecules of tungsten. The positive emission is much smaller than the electron emission at the same temperature and, like the electron emission, increases rapidly as the temperature is raised. At the highest temperatures the positive emission decreases rapidly with time. A tungsten spiral which has been made to give a large electron emission gives a larger initial positive emission when the potential tube is reversed (W. A. Jenkins, *Phil. Mag.* 1924 [vi], 47, 1025–1047; *Chem. Soc. Abstr.* 1924, ii, 443).

Tungsten is unaffected by water or air at ordinary temperatures, but when heated in air above 300°C. it oxidises rapidly and burns at a bright red heat. Molten sulphur or phosphorus attacks it slowly, while at a red heat their vapours rapidly convert it into the sulphide or phosphide. It is attacked by fluorine at ordinary temperatures with incandescence, and by chlorine at 250° to 300°C. It dissolves very little hydrogen and shows no tendency to react with nitrogen at temperatures up to 1500° (Sieverts and Bergner, *Ber.* 1911, 44, 2394). Tungsten is readily attacked by fused oxidising salts, such as alkaline nitrates and peroxides. Fused bi-sulphates and alkalis or alkaline carbonate also attack it, but their solutions have no action. It is readily oxidised when heated with oxidising agents such as lead peroxide, potassium chlorate, &c. At ordinary temperatures it is unaffected by bromine, iodine, and sulphuretted hydrogen. Sodium hypochlorite has a considerable solvent action on the fine powder, which is also soluble in an ammoniacal solution of hydrogen peroxide. Strong or weak hydrochloric acid has no action upon it at ordinary temperatures, but the strong acid slowly attacks it at the boiling-point and produces a coating of black sub-oxide. Boiling dilute sulphuric acid has no action, but the hot strong acid attacks it slowly. Concentrated nitric acid has but little action, but the dilute acid produces a yellow coating of tungstic acid which, as is also the case with *aqua regia*, appears practically to prevent further action. Hydrofluoric acid does not affect the metal even when hot, but dissolves it readily when mixed with nitric acid.

Tungsten combines directly with silicon and boron at or near the melting-point. It has been alloyed with many metals such as aluminium, copper, manganese, and nickel, but the alloys are not yet in extensive use. It enters into the composition of 'steelite,' the new cobalt-chromium alloy used in cutting steel. Irman (*Metall. und Erz.* 1915, 12, 358) investigated nickel-tungsten alloys and found

that with 18 p.c. W the alloy was very ductile and very resistant to dilute sulphuric acid. An alloy of tungsten with 1 p.c. thorium and 0.2 p.c. platinum is said to produce a tough, ductile alloy (U.S. Pat. 1167827, 1916). Schirmeister (Stahl und Eisen, 1915, 996) finds tungsten increases the tensile strength of aluminium, and that the hardness of the hot-rolled alloys increases at first but becomes constant at 1 p.c., the ductility falling slowly. For properties of tungsten at high temperatures, see Langmuir, Phys. Rev. 1916, 7, 302.

As a winder for electric furnaces tungsten wire is cheaper and said to be superior to platinum. Owing to its high melting-point, heat conductivity and hardness, tungsten appears to be eminently suitable for electrical contact devices, and is superior to platinum as a material for the targets in Röntgen (X-ray) tubes. Owing to its high melting-point (over 3000° as compared with 1755° for platinum) it can be placed directly at the focus of the cathode rays, and radiographs of sharper definitions can be obtained with much shorter exposure than with platinum (Coolidge, J. Ind. Eng. Chem. 1912, 4, 2). Tungsten has been suggested as a catalyst for the production of ammonia from atmospheric nitrogen (Eng. Pat. 1161, Jan. 15, 1912, and U.S. Pat. 1916, 175693), and has also been used for valves of aeroplane engines and ultra-violet ray electrodes, and valves for wireless telegraphy. There is reason to think that a considerable future use for this metal lies in the manufacture of laboratory and other utensils, as, although not so resistant to certain reagents as platinum or tantalum, there are many purposes for which its special resistance to such reagents, coupled with its greater cheapness, will render it of special value.

It is now generally recognised that tungsten is one of the most important metals other than those commonly spoken of as commercial metals. The saving which has been introduced by its employment in the manufacture of high-speed steel and in the form of fine-drawn wire in the electric light industry shows very remarkable figures. A recent bulletin issued by the United States Geological Survey (F. L. Hess, Bull. 652), states that one man and one lathe can do as much work with high-speed tungsten steels as five men and five lathes could formerly do with simple carbon steels, and that hundreds of millions of dollars' worth of labour is saved annually by this means. The 'Mineral Resources,' 1910, estimated that, assuming the present lamp consumption to require 80 million 25-watt tungsten lamps per annum, the saving in current effected by employing tungsten lamps in place of the old carbon lamps would result in an annual saving of between £40,000,000 and £50,000,000. Since that time lamps filled with nitrogen have been placed on the market, and other improvements have been added which have made the incandescent electric lamp more efficient and the saving very largely increased. It is stated that in 1916 about 200,000,000 lamps were manufactured in the United States alone. For a description of the manufacture of filament lamps, see Coolidge, U.S. Pat. 6028933, 1913; also Elec. Rev. 1914, 74, 595, and J. Soc. Chem. Ind. 1914, 1083.

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COMPOUNDS OF TUNGSTEN.

Oxides.—Tungsten is said to form a number of oxides the separate existence of which is not definitely settled. Thus, when sulphuric acid acts on metallic tungsten under varying conditions, the blue oxides, WO , W_2O_3 , W_4O_9 , W_5O_{11} , are formed; sulphurous acid acts on tungsten forming the oxide W_2O_4 , and a beautiful purple oxide with a yellow metallic lustre, W_2O_5 , is obtained by heating ammonium metatungstate to a bright red heat or by fusing tungstic acid with potassium iodide (Desi, J. Amer. Chem. Soc. 1897, 19, 213). On heating tungstic oxide with carbon a blue or purple oxide is produced at 650° to 850°, a chocolate-brown mixture of oxides at 900° to 1050°, and metallic tungsten above 1050° (Davis, J. Ind. Eng. Chem. 1919 11, 201).

The hydroxide $W_5O_{11} \cdot H_2O$, a dark blue powder with a purple lustre, is formed when tungstic acid is reduced with stannous chloride and hydrochloric acid, or by heating the acid with hydrogen iodide in a sealed tube at 200°. With ammonia it yields ammonium tungtate and the hydroxide $W_2O_3 \cdot H_2O$ (Allen and Gottschalk, Amer. Chem. J. 1902, 27, 323).

The only oxides which are definitely known are WO_2 , W_2O_3 , WO_3 .

Tungsten dioxide WO_2 may be prepared by the reduction of the trioxide or an alkaline metatungstate with zinc and hydrochloric acid (Pfordten, Ber. 1883, 16, 508) or by heating the trioxide to a dull redness in hydrogen (Riche, Ann. Chim. 1857, [iii.] 50, 29; Greenwood, Chem. Soc. Trans. 1908, 1493). It may be obtained crystalline by reducing lithium paratungstate with hydrogen (Hallopeau, Compt. rend. 1898, 127, 512).

Tungsten dioxide may be formed by heating an intimate mixture of tungsten trioxide and $\frac{1}{10}$ its weight of glycerol, ethylene glycol or similar hydroxyl compound, to a bright red heat for some hours (Eng. Pat. 18922, 1907; J. Soc. Chem. Ind. 1908, 22; see also Van Liempt, Zeitsch. anorg. Chem. 1923, 126, 133).

Tungsten dioxide, prepared in the wet way is of a copper red colour, prepared in the dry way it is a brown powder. It is readily oxidised to the trioxide; heated in chlorine it yields a yellow oxychloride WO_2Cl_2 . When amorphous it is soluble in hydrochloric and in sulphuric acid, but is quite unacted on when crystalline.

Blue tungstic oxide W_2O_5 , formed when tungsten trioxide is reduced with hydrogen at 250°–300° (Malaguti, Compt. rend. 1835, 1, 292) or by electrolysis fused sodium tungstate (Smith, Ber. 1880, 13, 753), is readily oxidised to the trioxide.

Tungsten trioxide (tungstic oxide or anhydride) WO_3 occurs naturally as wolframite and as tungstite or meymacite (Walker, Amer. J. Sci. 1908, [iv.] 25, 305), also in the form of tungstates in wolfram and scheelite. It may be prepared by calcining in contact with air, the lower oxides, the metal, a sulphide or its hydrate (tungstic acid), v. below.

Tungsten trioxide forms large bright yellow needles which may be obtained by heating the amorphous metal to a very high temperature in air or by fusion of tungstic acid with borax in a porcelain vessel (Nordenfjeld, Pogg. Ann.

1861, 114, 612); or by passing hydrogen chloride over tungstic acid or a mixture of sodium tungstate and sodium carbonate at a white heat (Debray, *Compt. rend.* 1862, 55, 287). The green or blue colour which it occasionally exhibits is probably due to reduction at ordinary temperatures by traces of organic matter. The yellow colour may be restored by heating in oxygen. Its sp.gr., when amorphous, varies between 5.27–7.13, when crystalline between 6.30–6.38. It melts at 1473° and is insoluble in water. According to Matignon, tungstic oxide does not melt at 2130° (*Compt. rend.* 1923, 177, 1290; *Chem. Soc. Abstr.* 1924, 126, ii. 48). When heated in hydrogen it gives the blue oxide at 250°, the dioxide at a red heat, and the metal if the latter action is prolonged. It is also reduced when heated with zinc and certain other metals (Delépine, *Bull. Soc. chim.* 1900, [iii.] 23, 675). When heated with chlorine or sulphur monochloride, it is converted into a volatile oxychloride and in the former case also into the hexachloride (Smith and Fleck, *J. Amer. Chem. Soc.* 1899, 21, 1008; Bourion, *Compt. rend.* 1908, 146, 1102; Defacqz, *ibid.* 1319).

The oxide is soluble in hydrofluoric acid, but not in hydrochloric or nitric acids or in *aqua regia*. See also Ehrenfeld, *J. Amer. Chem. Soc.* 1895, 17, 381.

Plastic masses of tungsten oxide for incandescent lamp filaments may be prepared by treating the oxide or hydrated tungstic acid with ammonia at -20° or below, or when in alcoholic suspension with gaseous ammonia (*Eng. Pat.* 14850; *J. Soc. Chem. Ind.* 1908, 1198, 1104). According to J. A. M. van Liempt (*Zeitsch. anorg. Chem.* 1923, 127, 215–220), temperature has little effect on the precipitation of tungsten trioxide by mineral acid, but concentration of the acid has considerable influence. The oxide is precipitated as a mixture of the white and yellow forms, together with an absorption compound with water, and in order to obtain the precipitate in an easily manipulated form, it is advisable to use hydrochloric or nitric acid in high concentration and in excess (*J. Chem. Soc. Ind.* 1923, 42, 1174 A).

Tungstic acids.—Tungsten trioxide forms two well characterised acids, $\text{WO}_3 \cdot \text{H}_2\text{O}$ or H_2WO_4 and $(\text{WO}_3)_2 \cdot \text{H}_2\text{O}$ or $\text{H}_2\text{W}_2\text{O}_{13}$. In addition the salts of a number of polytungstic acids are known (Schaefer, *Zeitsch. anorg. Chem.* 1903, 38, 142).

For the hydrosols of tungstic acid, see Lottermoser (*Verh. Ges. deut. Naturforsch. Aerzte*, 1910, ii. 70); Müller (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 93). For the hydrates of tungsten trioxide, see Hüttig and Kurre (*Zeitsch. anorg. Chem.* 1922, 122, 44).

Tungstic acid H_2WO_4 may be obtained by precipitating a solution of a tungstate with excess of hot acid. If cold acid is used, the white hydrate $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ is formed, from which the acid may be obtained by boiling. The comparative rates of precipitation of tungstic acid from sodium tungstate by different acids has been investigated by van Liempt (*Rec. trav. chim.* 1924, 43, 30; *Chem. Soc. Abstr.* 1924, 126, ii. 194). It is prepared by digesting a tungsten mineral with hydrochloric acid, then with *aqua regia* until the brown powder has

become yellow, when the iron and manganese have been dissolved out. The residue is well washed and then shaken with ammonia which dissolves the free tungstic acid. On filtration and evaporation the tungstic acid crystallises out. The finely powdered mineral may be fused with calcium chloride or with alkali carbonates or sodium chloride. The mass is lixiviated and the calcium or other metallic tungstate residue is then decomposed with nitric or hydrochloric acid.

Tungstic acid may be prepared from wolfram or other mineral containing tungsten, by heating the mineral under pressure with a concentrated solution of potassium hydroxide, lime or baryta being added to form insoluble compounds with some of the impurities.

The tungstic acid is then separated from the solution either by fractional precipitation with acid, the impurities separating first, or the whole of the precipitate formed by adding sufficient acid is fractionally redissolved by alkali. The process is said to be economical, convenient, and to give very pure acid (*Fr. Pat.* 359040, 1908; *J. Soc. Chem. Ind.* 1908, 939).

A continuous process for the manufacture of sodium tungstate and tungstic acid from wolframite ore by fusion with soda-ash and sodium nitrate is described by Gordon and Spring (*J. Ind. Eng. Chem.* 1924, 16, 555; *J. Soc. Chem. Ind.* 1924, 43, B. 631).

Tungstic acid may be purified by treating tungsten trioxide with carbon tetrachloride vapour at a red heat. The resulting volatile chlorine compound is sublimed, condensed and treated with *aqua regia*; the tungstic acid formed is then further purified by solution in ammonia and reprecipitation with dilute nitric acid (*U.S. Pat.* 926084; *J. Soc. Chem. Ind.* 1909, 794).

Tungstic acid is a yellow powder insoluble in water and almost so in all acids except hydrofluoric acid, in which it dissolves to the extent of 44.7 p.c. at 25° , 55.3 at 50° , using 50 p.c. hydrofluoric acid (Rosenheim and Bernhardt-Grisson, 7th Inter. Congr. Appl. Chem., 1909, Sect. x. 120). It is readily soluble in alkalis.

A colourless alcoholic hydrochloric acid solution of tungstic acid when electrolysed by a graphite anode, first becomes deep blue (containing sexa- and quinquevalent tungsten), then green (containing only quinquevalent tungsten), which on further reduction changes to olive green (mixture of quinque- and quadrivalent), then to brown (quadrivalent). When polished platinum is used as cathodes only green solutions are produced; with mercury cathodes of 0.025 amp. per sq. cm. of cathode surface, quinquevalent tungsten is formed, whilst with 0.07 amp. and over, trivalent tungsten was produced. With lead cathodes the results were similar to those with mercury, except that the tervalent tungsten formed violet-red solutions. Zinc cathodes also give rise readily to the tervalent form (see also Collenberg and Racker, *Zeitsch. Elektrochem.* 30, 230; *Sci. Abstr.* 1924, 27, 775).

Freshly prepared tungstic acid dissolves in aqueous solutions of most aliphatic amines forming substituted ammonium tungstates such as $(\text{NMeH}_2)_2\text{W}_2\text{O}_{13} \cdot 6\text{H}_2\text{O}$, which crystallise on evaporation. When heated they are de-

composed forming the amine, tungstic acid and the blue oxide of tungsten (Ekeley, J. Amer. Chem. Soc. 1909, 31, 664). It also gives crystalline precipitates with pyridine and quinoline (Rosenheim and Bernhardt-Grissom, *l.c.*).

Colloidal tungstic acid may be prepared by adding hydrochloric acid to concentrated sodium tungstate solution until it has an acid reaction. The white gelatinous precipitate formed, protected from currents of air, is washed by decantation several times at 0° to 5°: 15 parts of the acid are then dissolved in 1 part of concentrated oxalic acid by gently warming, and the liquid is subjected to dialysis. If the outer water is changed frequently, the oxalic acid may be completely removed (Pappadà, Gazz. chim. ital. 1902, 32, ii. 22; see Sabanéeff, Zeitsch. anorg. Chem. 1897, 14, 354).

Colloidal tungstic acid may be obtained by dissolving 5 grms. of tungsten tetrachloride in about 50 c.c. of a mixture containing equal volumes of ethyl alcohol and ether; the filtered solution is diluted to 250 c.c. with alcohol and then mixed with an equal volume of water. The colloidal solution thus obtained behaves as a positive colloid; it may be kept for some days without appreciable opalescence being observed, but coagulation occurs more quickly by adding a larger quantity of water, and immediately when small quantities of neutral salts, hydroxides, or strong acids are added. Weak organic acids or rise in temperature exert no effect. If an electric current is passed through, a deep blue precipitate separates at the cathode (Müller, Zeitsch. Chem. Ind. Kolloide, 1911, 8, 93; Lottermoser, Verh. Ges. deut. Naturforsch. Aertze, 1910, 11, 70; Wöhler and Engels, Koll. Chem. Beihefte, 1910, 1, 454; Zeitsch. Elektrochem. 1910, 16, 693).

The colloidal acid is also prepared by dialysing a 5 p.c. solution of sodium tungstate to which sufficient hydrochloric acid has been added to combine with the sodium. Colloidal tungstic acid forms a gum-like mass which may be heated at 200° without becoming insoluble and which at a red heat is converted into the trioxide. The colloidal acid has, probably, the constitution of the *meta* acid.

Tungstic acid and sodium tungstate are used in the production of colour resists for aniline black. 200 grms. sodium tungstate dissolved in 1 litre of gum tragacanth paste constitutes a white resist which may be rendered more lustrous and opaque by passing the printed tissue, after steaming, through a solution of barium chloride. The compound thus formed may be coloured by pigments, such as vermilion, ultramarine blue and chrome green, a series of pale resist colours being formed, along with which the usual albumin and tannic acid colour mixtures may be printed (Scheurer, Bull. Soc. Ind. Mulhouse, 1900, 138; *ibid.* 1898, 122).

Tungstic acid may also be employed in the production of resist effects upon *p*-nitraniline red and of discharge effects upon indigo-dyed tissues. In the latter case, the tissue dyed with the indigo is padded in a solution of sodium tungstate, dried and printed with a steam discharge mixture containing barium chlorate, potassium ferrocyanide and a basic dyestuff able to withstand the oxidising action, such as methamine 6 G, ultramarine, or chrome yellow.

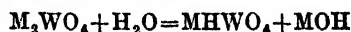
The colours are rendered faster by the addition of albumin together with an alkali citrate or tartrate.

Metatungstic acid $H_2W_6O_{13} \cdot 7H_2O$, first isolated by Scheibler (J. pr. Chem. 1861, [i.] 83, 310), may be prepared by decomposing the lead salt with hydrogen sulphide or the barium salt with dilute sulphuric acid. It crystallises in small yellow octahedra, very soluble in water, giving a bitter solution, and loses its water of crystallisation at 100°. (*Cf.* Rosenheim and Kohn, Zeitsch. anorg. Chem. 1911, 69, 247; *ibid.* 1916, 96, 139). For its photochemical properties, see Vasilieva (J. Russ. Phys. Chem. Soc. 1912, 44, 819). For its behaviour on electrolysis, see Leiser (Zeitsch. Elektrochem. 1907, 13, 690).

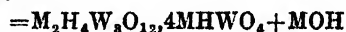
Paratungstic acid, the acid corresponding to the salts of the formula $12WO_3 \cdot 5M_2O \cdot Aq$, has been prepared in dilute solution by mixing barium paratungstate with a quantity of dilute sulphuric acid not quite sufficient for complete decomposition. The solution cannot be concentrated even *in vacuo* without decomposition, and when boiled it yields tungstic acid (Hallopeau, Compt. rend. 1895, 121, 61).

Tungstates.—Tungstic acid forms three series of salts: normal tungstates $R_2WO_4 \cdot xH_2O$; paratungstates $3R_2O \cdot 7WO_3 \cdot xH_2O$, or $5R_2O \cdot 12WO_3 \cdot xH_2O$

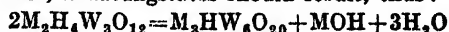
and metatungstates $R_2O \cdot 4WO_3 \cdot xH_2O$. Copaux (Compt. rend. 1913, 156, 1771) regards the paratungstates as hydrotungstates and represents them by $M_3[H(W_2O_7)_3]$. They may also be considered as compounds of 1 mol. of the tritungstate with 4 mols. of the hydrogen tungstate. Their derivation from normal tungstates may be expressed thus:



and



If, from analogy to the vanadates and molybdates, the action of hydrogen ions proceeds still further, hexatungstates should result, thus:



and the so-called metatungstates are in reality the hexatungstates (Prandtl, Ber. 1915, 48, 692). The alkaline tungstates $M_2WO_4 \cdot Aq$ are prepared by fusing a naturally occurring tungstate with sodium or potassium hydroxide or carbonate, preferably with the addition of a silicious or other flux. The alkali tungstate falls to the bottom and may be tapped off, or, after cooling, the slag may be removed (J. Soc. Chem. Ind. 1885, 116; *ibid.* 1900, 542; *ibid.* 1899, 171; Eng. Pats. 30053, 1897; 6045, 1900).

The *sodium salt* crystallises in thin prisms, soluble in 4 parts of cold, in 2 parts of hot water, the solution having a bitter taste and an alkaline reaction. It has m.p. 698° (Parravano, Gazz. chim. ital. 1909, 39, ii. 55).

The *potassium salt* forms large prismatic crystals, m.p. 894°. The ammonium salt is very unstable.

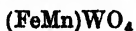
Calcium tungstate $CaWO_4$ occurs native as *scheelite* and may be prepared artificially by the interaction of calcium chloride and a normal tungstate. If the amorphous white precipitate so obtained is mixed with lime and heated in a current of hydrogen chloride, it is obtained

crystalline. The corresponding *barium tungstate* was prepared by Rousseau for use instead of white lead (Schoen, J. Soc. Chem. Ind. 1900, 740).

The so-called di- and tri-tungstates of sodium, barium, and calcium do not appear to exist.

Lead tungstate occurs native as *stolzite* and crystallises in red tetragonal pyramids.

Ferrous tungstate occurs as *wolfram*

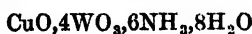


forming dark grey or brownish-black prisms.

Manganese tungstate is found as *hübnerite*. Granger (Compt. rend. 1898, 127, 106; *ibid.* 1905, 140, 935) has proposed the employment of the tungstates in the ceramic industry.

Ammonio copper tungstate $\text{CuWO}_4 \cdot 4\text{NH}_3$, deep blue crystals, readily decomposed. A similar zinc salt is also known (Briggs, Chem. Soc. Trans. 1904, 675).

The copper compound



has been obtained by the interaction of an ammoniacal solution of copper sulphate and ammonium tungstate. It forms small blue needles (Briggs, *l.c.*).

Sodium paratungstate $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot \text{Aq}$ is known commercially as tungstate of soda and may be prepared on a large scale by roasting wolfram with soda ash and lixiviating the fused mass. The boiling solution is then nearly neutralised with hydrochloric acid and allowed to crystallise when large triclinic crystals of the salt separate. It is sometimes used as a mordant instead of sodium stannate in dyeing and calico printing. It also renders cotton, linen, &c., non-inflammable. The corresponding potassium salt is formed in glistening scales when normal potassium tungstate is boiled with a little water.

Sodium tungstate is much used both by itself and in conjunction with other fire-retarding compounds. In some experiments on its protective action recorded by Sibley (J. Ind. Eng. Chem., No. 8, 1921), impregnation of cotton fabrics with a 3 p.c. solution was found to be equally as efficacious as treatment with a more concentrated solution. For the protection of tulle, muslin, and other delicate fabrics impregnation with a solution containing 10 grms. tungstate, 125 grms. ammonium phosphate, and 7 grms. boric acid per litre has been proposed. This solution is added to the finishing medium (gum, starch, or dextrin) in the proportion 1 : 4. Ammonium chloride, ammonium sulphate, and aluminium acetate may also be combined with sodium tungstate. A medium particularly recommended for artificial silk can be prepared by diluting a mixture of the following solutions: 100 parts aluminium acetate (sp.gr. 1.13), 10 parts acetic acid (sp.gr. 1.06), and 200 parts sodium tungstate (sp.gr. 1.40). Water-resistance can be imparted by using an excess of the acetate (Eng. Pat. 175746 of 1920). According to Mond (Eng. Pat. 4457 of 1915) zirconium hydroxide may be applied to fabrics as a hydrogel, prepared by steeping in a solution of the aceto-nitrate containing magnesium sulphate, draining, heating to 65°C., and finally washing. One litre of the steeping medium

should contain 200 grms. magnesium sulphate and 20 grms. of the aceto-nitrate, prepared by evaporating zirconium nitrate with acetic acid. To enhance the fire-retarding effect, the treated fabric may be allowed to absorb phosphoric acid. Another method is to impregnate the material with a solution of precipitated zirconium phosphate in concentrated oxalic acid (Pharm. J. 1924, 691).

For various paratungstates, see Hallopeau, Ann. Chim. 1900, vii. 19, 19, 92; Taylor, J. Amer. Chem. Soc. 1902, 24, 629.

Metatungstates $\text{M}_2\text{W}_2\text{O}_{11} \cdot \text{Aq}$ were discovered by Marguerite (Ann. Chim. 1846, [iii.] 17, 475). The alkali salts are readily formed when the normal tungstates are boiled with tungstic acid until the filtrate no longer gives a precipitate on addition of hydrochloric acid. The other metatungstates are best prepared by double decomposition of the barium salt with the required sulphate or carbonate. The metatungstates have a bitter taste, are generally readily soluble in water and deposit tungstic acid on prolonged boiling. A large number of them are known but there is considerable difference of opinion as to their constitution (Copaux, Compt. rend. 1909, 148, 633; Zeitsch. anorg. Chem. 1911, 70, 297; Rosenheim, *ibid.* 418; *ibid.* 1911, 69, 247; 1912, 75, 141; Just, Ber. 1903, 36, 3619).

Pertungstates $\text{M}'\text{WO}_4 \cdot \text{Aq}$ are formed by boiling a paratungstate with hydrogen peroxide (Péchar, Compt. rend. 1891, 112, 1060); or by electrolysis of a slightly acid solution of sodium tungstate (Thomas, J. Amer. Chem. Soc. 1899, 21, 373). More highly oxidised compounds are formed by treating the pertungstates with hydrogen peroxide (Melikoff and Pissarjewsky, Ber. 1898, 31, 632; Pissarjewsky, J. Russ. Phys. Chem. Soc. 1902, 34, 472).

Tungsten bronzes are compounds of the alkali metals with tungsten and oxygen, which, owing to their colour and insolubility in acids and alkalis have been employed as substitutes for bronze powders. Their exact constitution is not known, although they are generally regarded as compounds of the tungstates with tungsten dioxide. They may be obtained by the reduction of the tungstates heated to redness with hydrogen, coal gas, zinc, iron or tin.

Tungsten bronzes may be prepared electrolytically by fusing tungstic acid with the calculated amount of metallic carbonate and electrolysis of the mass. A series of brightly coloured mixed alkali and alkaline earth tungsten bronzes of various compositions are described by Engels (Zeitsch. anorg. Chem. 1903, 37, 125) and Schäffer (*ibid.* 1904, 38, 148).

Four *tungsten sodium bronzes* are known. $\text{Na}_3\text{W}_2\text{O}_{11}$ of a golden yellow colour, $\text{Na}_2\text{W}_2\text{O}_{11}$ of a blue colour, $\text{Na}_3\text{W}_3\text{O}_{15}$ of a purple red colour, and $\text{Na}_4\text{W}_5\text{O}_{15}$ which forms red-yellow cubes and yields a brown-yellow powder (Philipp, Ber. 1882, 15, 499).

Potassium forms one bronze, $\text{K}_2\text{W}_2\text{O}_{11}$ (Knorre and Schäffer, *ibid.* 1902, 35, 3407).

Blue lithium bronzes are described by Hallopeau (Compt. rend. 1898, 127, 512).

Tungstates of the rare earths are described by Hitchcock (J. Amer. Chem. Soc. 1895, 17, 453).

TUNGSTEN AND THE HALOGENS.

Tungsten hexachloride WCl_6 is prepared by heating metallic tungsten in excess of pure dry chlorine, particular care being taken to exclude all traces of air and moisture in order to avoid the formation of the oxychloride (Roscoe, *Annalen*, 1872, 162, 349). A small quantity of the latter is formed at the beginning of the reaction, however, in spite of all precautions. It should be driven off beyond the portion of the tube where the chloride is to be collected. Tungsten hexachloride forms dark violet opaque crystals, which are very stable when pure but are readily decomposed by moist air or water, if the slightest trace of the oxychloride is present. It has m.p. 275° , b.p. $346.7^\circ/759.5$ mm.

On heating the hexachloride in a stream of nitrogen with powdered aluminium and quartz, extracting the product with hydrochloric acid, concentrating the reddish-yellow extract and saturating it with hydrogen chloride, it yields $HWCl_4 \cdot 4H_2O$ in slender yellow needles, which rapidly lose hydrogen chloride on exposure to air (Lindner, *Ber.* 1922, 55 [B], 1458).

The salt $K_2W_2Cl_8$ and a number of corresponding salts of tervalent tungsten form green solutions and are powerful reducing agents (Collenberg and Sandved, *Zeitsch. anorg. Chem.* 1923, 130, 1; *Chem. Soc. Abstr.* 1924, 126, ii, 51).

Tungsten pentachloride WCl_5 is formed by the incomplete reduction of the hexachloride in a current of hydrogen. It is volatile and when redistilled forms long, pure black shining crystals, m.p. 248° , b.p. 275.6° . It is hygroscopic and dissolves in water forming an olive-green solution, but most of it decomposes into the blue oxide and hydrochloric acid (Roscoe, *l.c.*).

Tungsten tetrachloride WCl_4 forms the non-volatile residue in the production of the pentachloride. It may also be prepared by the distillation of the latter or of the hexachloride, or better, a mixture of the two chlorides in a current of hydrogen. It forms a greyish-brown crystalline powder (Roscoe, *l.c.*). It is hygroscopic, infusible, is partially decomposed by water and is reduced by hydrogen to the metal.

Tungsten dichloride WCl_2 is best prepared by heating the tetrachloride in a current of carbon dioxide at the temperature of a moderately hot zinc bath. It is a grey non-volatile powder partly decomposed and partly dissolved by water forming a brown solution (Roscoe, *l.c.*).

Tungsten dioxydichloride WO_2Cl_2 , obtained by passing chlorine over the dioxide, forms light lemon-yellow scales. Heated with ammonia it forms the compound $W_2O_4N_2H_2$ (Smith and Shinn, *Zeitsch. anorg. Chem.* 1893, 4, 381).

Tungsten oxytetrachloride $WOCl_4$, beautiful red needle-shaped crystals, m.p. 210.4° , b.p. 227.5° , is formed by the interaction of the trioxide and phosphorus pentachloride (Schiff, *Annalen*, 1879, 197, 185); or by passing the vapour of the hexachloride over the heated trioxide.

Tungsten hexabromide WBr_6 , obtained by heating tungsten with dry bromine vapour in an atmosphere of nitrogen, forms blue-black needles which decompose when heated to a high temperature, give a colourless solution in aqueous ammonia, fume in air and give a royal

blue oxide when treated with water (Schaeffer and Smith, *J. Amer. Chem. Soc.* 1897, 18, 1098).

Tungsten pentabromide, prepared by passing dry hydrogen bromide over tungsten hexachloride at 300° , or better by the action of excess of bromine on tungsten, forms fern-like aggregates of dark needles with green reflex, m.p. 276° , b.p. 333° . It is very hygroscopic, yields the blue oxide when treated with water and dilute acids and is decomposed by alkalis, alkali nitrates, carbonates and bisulphates (Defacqz, *Ann. Chim.* 1901, [vii.] 22, 247).

Tungsten oxybromides WO_2Br_2 , $WOBBr_4$ and the compounds WCl_2Br_2 , $WCl_4 \cdot 3WBr_6$ are also known (Defacqz, *Compt. rend.* 1899, 129, 515).

Tungsten tetriodide WI_4 , obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at 110° , is a black crystalline substance of sp.gr. 5.2 at 18° , decomposed by water, alkali-hydroxides and carbonates. Soluble in absolute alcohol (Defacqz, *Compt. rend.* 1898, 127, 510).

Tungsten diiodide WI_2 , obtained by the action of hydrogen iodide on tungsten hexachloride at 400° , is an amorphous, insoluble, infusible, non-volatile brown powder of sp.gr. 6.9 at 18° (Defacqz, *ibid.* 1898, 126, 962).

Tungsten hexafluoride WF_6 may be obtained by the interaction of tungsten hexachloride with anhydrous hydrofluoric acid or with arsenic trifluoride, or, best of all, antimony pentafluoride. It has m.p. 2.5° and b.p. 19.5° . Is readily soluble in alkalis, attacks glass and most metals and forms double salts with alkali fluorides. When acted on by water it yields tungstic acid (Ruff, *Zeitsch. anorg. Chem.* 1907, 52, 256).

Tungsten oxytetrafluoride WOF_4 , obtained by the interaction of the oxytetrachloride and anhydrous hydrogen fluoride, forms small colourless hygroscopic plates, m.p. 110° , b.p. $185-190^\circ$, is decomposed by water forming tungstic acid and absorbs large quantities of ammonia in the cold (Ruff, *l.c.*).

Tungsten dioxydifluoride is known in an impure state. For various double fluorides, see Maignat (*Ann. Chim.* 1863, [iii.] 69, 63); Marchetti (*Zeitsch. anorg. Chem.* 1895, 10, 66); Miolati and Rossi (*Real. Accad. Lincei*, 1896, [v.] 5, ii, 223); Ephraim and Heymann (*Ber.* 1909, 42, 4456).

TUNGSTEN AND SULPHUR.

Tungsten disulphide WS_2 may be prepared by passing hydrogen sulphide over tungsten hexachloride at $375-550^\circ$, or by fusing an intimate mixture of pure dry potassium carbonate, flowers of sulphur and tungsten trioxide. It is a grey-black crystalline powder, insoluble in water, fairly stable, and has sp.gr. 7.5 (Defacqz, *Compt. rend.* 1899, 128, 609).

Tungsten trisulphide WS_3 , best obtained by treating a sulphotungstate with excess of sulphur, is a brown powder which becomes black when dried, is slightly soluble in cold water, more so in hot water, and readily in alkali hydroxides and carbonates (Corleis, *Annalen*, 1893, 232, 344). It has been obtained in the colloidal state by Winsinger (*Bull. Assoc. Sci. Belg.* 1893, 16, 390).

The compounds, $WCl_2 \cdot 3WS_2$ (*Ann. Chim.* 1901, [vii.] 22, 238) and $WO_2 \cdot S$ (Winsinger,

(*l.c.*) and a number of metallic sulpho- or thio-tungstates, M_2WS_4 (Coriols, *l.c.*), have been described. A *di-* and *tri-selenide* (Uelsmann, J. 1860, 92) and a *trithuride* are also known.

Tungsten nitrides W_2N_3 , W_3N_4 , a number of oxynitrides, nitretamido and oxynitretamido compounds, and also a hydroxylamine tungstate have been obtained (Wöhler, Annalen, 1850, 73, 190; *ibid.* 1858, 105, 258; Rideal, Chem. Soc. Trans. 1889, 41; Wöhler, *ibid.* 1851, 3, 171; Desi, *l.c.*; Allen and Gottschalk, *l.c.*).

Tungsten cyanides have also been prepared by Rosenheim and Dehn (Ber. 1914, 47, 392; Olsson, Ber. 1914, 47, 912).

TUNGSTEN AND PHOSPHORUS.

Tungsten combines directly with phosphorus when heated to redness, forming a dark green phosphide W_2P_4 .

Tungsten diphosphide WP_2 , produced by heating tungsten hexachloride at 450° in a current of hydrogen phosphide forms a black crystalline mass insoluble in water, sp.gr. 5.8. The phosphorus is readily displaced by the halogens and by sulphur and nitrogen at high temperatures. It may be reduced by heating with hydrogen, zinc or copper (Defacqz, Compt. rend. 1900, 130, 915).

If tungsten diphosphide is heated with a large excess of copper phosphide in a graphite crucible in a wind furnace and the product treated with dilute nitric acid, it yields the *monophosphide* WP , grey lustrous prismatic crystals, sp.gr. 8.5 (Defacqz, *ibid.* 1901, 132, 32).

Another phosphide W_2P is formed by reducing a mixture of phosphorus pentoxide (2 mols.) and tungsten trioxide (1 mol.) in a charcoal crucible at a high temperature (Wöhler, Chem. Soc. Trans. 1853, 5, 94).

Phosphotungstic acid.—Tungstic acid combines with phosphoric and also with arsenic, antimonie and vanadic acids to form complex compounds of varying composition, $M_2O_5 : WO_3 = 1:7$ to $1:24$ analogous to the molybdates. Phosphotungstic acid is used as a reagent for the precipitation of alkaloids, proteins and some of their products of hydrolysis, also for the detection of potassium and ammonium salts with which it gives insoluble precipitates. It may be prepared by acidifying a solution of 4 parts of sodium tungstate and 1 part of sodium phosphate with sulphuric acid and extracting the phosphotungstic acid with ether (Winterstein, Chem. Zeit. 1898, 22, 539).

Some new series of phosphotungstates are iber by F. Kehrman and R. Mellet (Helv. Acta, 1922, 5, 942), including the simple $3M_2O_3.P_2O_5.6WO_3.aq.$, of which the potassium, and ammonium salts have been prepared in the pure state.

Literature on phosphotungstic acids and the phosphotungstates: Kehrman, Zeitsch. anorg. Chem. 1891, 1, 428; Soboleff, *ibid.* 1896, 12, 16; Rogers, J. Amer. Chem. Soc. 1903, 25, 298.

Arsenotungstovanadates

$18(NH_4)_2O.As_2O_5.21WO_3.4V_2O_5.13H_2O$;

$6Ti_2O_3.As_2O_5.21WO_3.5V_2O_5.13aq.$; and

$6BaO.As_2O_5.17WO_3.5V_2O_5.4aq.$

are described as red crystals by Cannevi (Gazz.

chim. ital. 1923, 53, 773; Chem. Soc. Abstr. 1924, 126, ii. 117).

Tungsten arsenide WAs_3 , prepared by heating tungsten hexachloride in a current of hydrogen arsenide at 150° – 360° , is a black crystalline insoluble powder of sp.gr. 6.9 at 18° .

Tungsten chloroarsenide W_2AsCl_4 , obtained by heating the above substances in a sealed tube at 60° – 70° , forms hygroscopic bluish-black crystals, decomposed by water and acids (Defacqz, Compt. rend. 1901, 132, 138).

For *arseniotungstic acids and tungstates*, see Kehrman and Rüttimann (Zeitsch. anorg. Chem. 1899, 22, 285). *Vanadotungstates* Friedheim, *ibid.* 1894, 6, 11; Rogers, *l.c.*; Friedheim and Henderson, Ber. 1902, 35, 3242). *Antimoniotungstates* (Hallopeau, Compt. rend. 1896, 123, 1065). *Zirconotungstates* (*ibid.* 1896, 122, 1419). *Alumino- and alumino-phospho- and arseno-tungstates* (Daniels, J. Amer. Chem. Soc. 1908, 30, 1846).

Tungsten boride WB_2 , prepared by fusing the two elements together in an electric furnace, crystallises in hard octahedra, sp.gr. 9.6 (Tucker and Moody, Chem. Soc. Trans. 1902, 16).

TUNGSTEN AND CARBON.

When tungsten trioxide is fused with calcium carbide in an electric furnace, it forms an iron-grey carbide, CW_2 , which is harder than corundum and has sp.gr. 16.06 at 18° . In the presence of a large excess of iron, the carbide W , an iron-grey crystalline powder of sp.gr. 15.7 at 18° , is formed (Moissan, Compt. rend. 1897, 125, 839; Williams, *ibid.* 1898, 126, 1722).

Tungsten carbides are formed when the finely divided metal or its oxides are heated in carbon monoxide, or in a mixture of methane and hydrogen. At 1000° W_2C_4 is formed in carbon monoxide, and WC in a mixture of methane and hydrogen (1:1) at 80° (Hilpert and Ornstein, Ber. 1915, 46, 1669).

W_2C has been formed by heating tungsten in a carbon electric furnace; it melts above 2700° and solidifies as a homogeneous substance (Ruff and Wunsch, Zeitsch. anorg. Chem. 1914, 85, 292). Voigtländer and Lohmann (D. R. P. 286184, 1914) claim tungsten carbide to have a hardness of 9.8 compared with the diamond at 10.

Two carbides of tungsten, W_2C and WC , are formed when naphthalene vapour acts on incandescent tungsten filaments. These compounds at temperatures from $2400^\circ K.$ to $2790^\circ K.$ lose all their carbon, the tungsten filament regaining the same conductivity as before carbonisation. Incandescent tungsten may be carbonised by almost any hydrocarbon vapour. Alcohol will also carbonise the filament, but at only $\frac{1}{2}$ the rate at which acetylene effects the carbonisation. The electrical resistivity of cold W_2C is about 15 times that of tungsten, but the temperature coefficient of resistance is very much less. The conductivity of a partially carbonised filament at any temperature is in agreement with that calculated from the amounts of tungsten and W_2C present (M. R. Andrews, J. Phys. Chem. 1923, 27, 270).

Chromium tungsten carbide $OW_2.3Cr_2O_3$, is formed by heating a mixture of chromic oxide, tungstic acid and carbon in a carbon crucible in

an electric furnace for five minutes with a current of 400 amperes at 75 volts and treating the product with warm hydrochloric acid, then with concentrated ammonia solution. It forms small hard stable crystalline grains of sp.gr. 8.41 at 22°. By the addition of tungsten to chromium steels, the formation of this stable hard carbide might give rise to the production of new steels with special qualities (Moissan and Kouznetzow, *Compt. rend.* 1903, 137, 292).

Iron tungsten carbide $3W_2C \cdot 2Fe_3C$, a magnetic substance, sp.gr. 13.4 at 18°, has also been prepared (Williams, *ibid.* 1898, 127, 410; Carnot and Goutal, *ibid.* 1899, 128, 207).

TUNGSTEN AND SILICON.

Tungsten silicide WSi_2 has been prepared by heating copper silicide with amorphous tungsten in an electric furnace, using a current of 800–900 amperes and 50 volts, the resulting product is then washed successively with nitric acid, caustic potash, warm hydrofluoric acid and water. It may also be prepared by reducing a mixture of silica and tungstic anhydride with sulphur and alumina. It forms brilliant, grey crystals, of sp.gr. 9.4, which are not magnetic and are very stable (Dofacqz, *Cefmpt. rend.* 1907, 144, 848; Hönigschmidt, *Monatsh.* 1907, 28, 1017).

The silicide WSi_2 is obtained by heating the trioxide with silicon in the electric furnace, after which the mass is suspended in dilute hydrochloric acid (1 in 10) and electrolysed. The excess of metal dissolves and the silicide is removed, washed with *aqua regia*, then with ammonia, and is finally separated from carbon silicide gravimetrically by suspension in methyl iodide (Vigouroux, *Compt. rend.* 1898, 127, 393). It forms beautiful steel grey crystals with a metallic lustre, sp.gr. 10.9. See also Frilley, *Rev. de Metallurgie*, 1911, 8, 457; *J. Soc. Chem. Ind.* 1911, 1018.

Tungsten aluminium silicide forms black hexagonal crystals (Manchot and Kieser, *Annalen*, 1904, 337, 360).

Silicotungstic acids of the formulæ,



$H_8W_{12}SiO_{42} \cdot 20H_2O$, $H_8W_{12}SiO_{42} \cdot 29H_2O$, &c., were discovered by Marignac (*Ann. Chim.* 1864, [iv.] 3, 5). The acid corresponding to the last formula is formed by precipitating its salts with mercurous nitrate and decomposing the mercury salt with hot hydrochloric acid. It crystallises in large tetragonal prisms, is readily soluble in water, alcohol, and ether, and forms a valuable reagent for alkaloids. The salts, most of which are soluble in water, are prepared by boiling gelatinous silicic acid with metallic polytungstates (Wyrouboff, *Bull. Soc. franc. Min.* 1896, 19, 219; Friedheim and Henderson, *l.c.*).

ORGANIC SALTS OF TUNGSTEN.

of tungstic acid are described by Smith and Dugan (*J. Amer. Chem. Soc.* 1899, 21, 1016); *alkali tungsten tartrates* by Henderson and Barr (*Chem. Soc. Trans.* 1896, 1456); *citrates* by Henderson, Orr and Whitehead (*ibid.* 1899, 547); *tungsten oxalates* by Rosenheim (*Ber.* 1893, 26, 1191); *tungsten cyanides* by Rosenheim and Dehn (*Ber.* 1914, 47, 392; *ibid.*

1915, 48, 1167; Olsson, *Ber.* 1914, 47, 917; *Zeitsch. anorg. Chem.* 1914, 88, 49).

Tungsten forms ozosalts which are readily soluble and difficult to obtain free from the normal salts used in their preparation. The following have been described:—

Sodium ozotungsten oxalate



and also the corresponding ammonium and calcium salts which have only 1 mol. of water of crystallisation (Mazzucchelli and Inghilleri, *Atti. R. Accad. Lincei*, 1908, [v.] 17, ii. 30).

Complex compounds of the tungstic acids with organic acids have been obtained by Grossmann and Kramer (*Zeitsch. anorg. Chem.* 1904, 41, 43); and by Mazzucchelli and Bonghi (*Gazz. chim. ital.* 1910, 40, ii. 241); and additive compounds of the tetra-, penta-, and hexachloride with organic esters by Rosenheim and Loewenstamm (*Ber.* 1902, 35, 1115).

Oxalotungstites, *Chlorotungstites* and other derivatives of quinquevalent tungsten have been obtained by Collenburg (*Zeitsch. anorg. Chem.* 1918, 103, 247).

Gerber (*Mon. Scient.* 1917 [v.] 7, 73–219) finds evidence for the existence of a new element, *netungsten*, at wt. 187, associated with tungsten, and which, as it is spectroscopically indistinguishable from tungsten, he suggested may be an isotope of that metal (*cf.* Barbe, *Mon. Sci.* 1919, [v.] 9, i. 73).

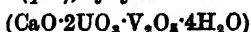
TUNGSTENITE. Tungsten sulphide WS_2 , corresponding with molybdenite (MoS_2), which it closely resembles in physical characters. It occurs in some quantity intimately intermixed with pyrites, fahlore, and galena in a compact ore at the Emma mine in the Little Cottonwood district, Salt Lake Co., Utah. Under the microscope it is seen in this ore as feathery flakes resembling graphite in appearance. It is lead-grey and opaque with a metallic lustre, and soft enough to mark paper; sp.gr. about 7.4. The mineral is not oxidised by roasting in air, and is not attacked by hydrochloric or nitric acids, but is decomposed by *aqua regia* (R. C. Wells and B. S. Butler, *J. Washington Acad. Sci.* 1917, 7, 596). L. J. S.

TUNGSTITE or **TUNGSTIC-OGHRE**. A yellow, earthy mineral frequently observed in small amounts as an alteration product of wolframite and scheelite, and long supposed to be anhydrous tungsten trioxide WO_3 . The original tungstic-oghre of B. Silliman (1822) and the 'wolframine' from Cornwall were, however, never analysed, and in the text-books the characters of the artificial orthorhombic crystals of the anhydrous oxide have been assumed for the natural mineral. A mineral of similar appearance has been described under the name meymacite (A. Carnot, 1874) with the composition $WO_3 \cdot 2H_2O$. T. L. Walker (*Amer. J. Sci.* 1908, 25, 305) suggests that these are really identical and that the correct formula is $WO_3 \cdot H_2O$. He describes a golden-yellow mineral occurring with wolframite in veins of gold-quartz near Salmo in British Columbia. Minute crystals from cavities possess a perfect cleavage in one direction and are optically biaxial; sp.gr. 5.517; soluble in ammonia or sodium hydroxide, but not in acids.

Another 'tungstic ochre' occurring with

wolframite in the Germania tungsten mine, Deer Trail mining district in the State of Washington, was found by W. F. Schaller (Amer. J. Sci. 1911, 32, 161) to be a hydrated ferric tungstate, $\text{Fe}_2\text{O}_3 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$, for which the new name *ferritungstite* was proposed. This is pale-yellow to brownish-yellow and crystallised in minute hexagonal scales. L. J. S.

TURANITE. Hydrated copper vanadate, $5\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, forming compact, spongy, or radially fibrous aggregates and reniform crusts of an olive-green colour. It is found with alaite (*q.v.*), ferganite (*q.v.*), tyuyamunite



malachite, &c., in the oxidation zone of the uranium and vanadium deposits which occur in limestone at Tyuya-Muyun in Fergana, Russian Central Asia. L. J. S.

TURANOSE. A sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, obtained by heating melezitose with acetic acid. Is not hydrolysed by any of the ordinary enzymes and is consumed very slowly by yeast. Rotatory power $[\alpha]_D = +71.8$ shows no birotation (Tanret, Compt. rend. 1906, 1424) (*v.* CARBOHYDRATES).

TURBIDIMETRY. See NEPHELOMETRY.

TURF. *v.* FUEL.

TURGITE *v.* TURITE.

TURICINE *v.* BETAINES.

TURITE, TURGITE or HYDROHÆMATITE.

A hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, containing, according to the formula Fe_2O_3 , 94.7, (Fe 66.2), H_2O 5.3 p.c. It is sometimes soft and earthy with a bright red colour, being then included (together with earthy hæmatite) under red-ochre. It may also be massive and compact; with sometimes a radially fibrous structure and a smooth and brilliant mamillated or botryoidal surface, being then very similar to the kidney-iron-ore (more strictly the *Ger. Rother Glaskopf*) variety of hæmatite. Such material is dark red to black with a sub-metallic lustre. Sp.gr. 4.29–4.49; H. 6½ (harder than limonite). A characteristic feature is the dark cherry-red streak, which is of a lighter shade than that of hæmatite. Crystals are not known, but the fibrous material is birefringent with straight optical extinction. Few analyses show exactly the theoretical amount of water; there seems rather to be a gradual passage on one side to hæmatite (Fe_2O_3) and on the other to limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, with 14.5 p.c. H_2O). Compact or earthy red hæmatite often contains 1–2 p.c. H_2O . The existence of turite as a distinct mineral species has therefore been doubted, and it has been regarded as a colloidal material forming a stage in the hydration of hæmatite to limonite, or of the dehydration of limonite. Turite, however, when heated in a bulb-tube decrepitates with surprising violence, and in this respect it differs from both hæmatite and limonite. Its dehydration curve is quite distinct from those of limonite and goethite. Occurrences of fibrous mamillated turite and limonite at Salisbury in Connecticut and Bridgeville in Nova Scotia show a sharp line of demarcation between the two minerals. Turite was first described from the Turinaky¹ copper mines near Bogdolovak in the Urals, and it has since

been recorded with iron ores from many other Russian localities. It is no doubt a mineral of common occurrence elsewhere with hæmatite and limonite ores (L. J. Spencer, Min. Mag. 1919, 18, 339). L. J. S.

See also *Iron oxides*, art. IRON.

TURKEY-RED OILS *v.* OILS, FIXED, and FATS.

TURMERIC (*Indian saffron*; *Terra merita*). The so-called turmeric root of commerce is the underground stem or rhizome of *Curcuma longa* (Linn.), or of various species of *Curcuma*—e.g. *C. tinctoria*, *C. viridiflora* (Roxb.), &c. These plants, belonging to the *Scitamineæ*, are indigenous to Southern Asia, and are there largely cultivated, being exported from China, Madras, Bengal, Java, Malabar, Batavia and Barbadoes. Those varieties which are derived from the central rhizomes are more or less round (*Curcuma rotunda*, Linn.), while the lateral rhizomes are long and finger-shaped (*C. longa*). When of good quality these commercial varieties are hard, and possess a dull, waxy, resinous fracture, the external colour being yellowish-grey, and internally orange-brown, but producing, when ground, a somewhat bright yellow powder, having a strong characteristic odour and a peppery bitter taste.

The rhizome of *Canna speciosa*, a West African plant, is said to be exactly similar to East Indian turmeric in taste, smell, and chemical reactions (Daniell, Pharm. J. 19, 258). It is cultivated in Sierra Leone, and furnishes the so-called 'African turmeric.'

According to Pelletier and Vogel (Annalen, 44, 297), turmeric contains cellulose, gum, starch, mineral matter, a strong-smelling volatile oil, a brown colouring matter, and a characteristic yellow colouring matter named by them *Curcumin*. Pectin and pectic acid are also present (Schützenberger). Kachler (Ber. 3, 713) found a notable quantity of potassium binoxalate.

Pelletier and Vogel's method of isolating the curcumin consisted in first removing the fatty, resinous, and other impurities by extracting pulverised turmeric with water and carbon disulphide, then dissolving out the colouring matter with boiling alcohol, and purifying it by successive solution in ether and alcohol, precipitation with lead acetate, subsequent treatment with hydrogen sulphide and extraction of the product with ether. It was thus obtained as an amorphous yellow powder.

Lepage adopted a similar method, but after extraction with carbon disulphide the colouring matter was dissolved in alkali, precipitated with acid, and finally purified by means of ether.

Daube was the first to obtain curcumin in the crystalline state. He removed essential oil by passing a strong current of steam over the coarsely-ground turmeric, then thoroughly extracted it with hot water, and finally treated the dried residue with boiling benzene. On cooling the solution thus obtained, crude curcumin separated as bright orange-red crystalline crusts, which were pressed between blotting-paper, and dissolved in cold alcohol. After filtering off some yellow flocculent substance, the solution was precipitated with an alcoholic solution of neutral lead acetate, adding finally a little basic lead acetate in order to neutralise

¹ Hence the name, from the adjacent Tura river. The German spellings *turgite* and *turjit* are mistranslations of the Russian *тырма*, turite.

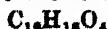
almost entirely the liberated acetic acid and prevent thereby any solution of the colour-lake. The brick-red precipitate was washed with alcohol, suspended in water, and decomposed with hydrogen sulphide. The liberated curcumin was extracted from the precipitate with boiling alcohol, from which it crystallised on slow evaporation.

Benzene is very suitable for the isolation of pure curcumin, for although it is very little soluble in this liquid, the resinous impurities are not dissolved thereby.

Gajewsky (Ber. 3, 265) obtained crystalline curcumin by first extracting turmeric root with carbon disulphide, then dissolving out the colouring matter with ether, and purifying it by fractional crystallisation from ether or benzene. He detected the presence of another colouring matter and also traces of an alkaloid. This chemist obtained an increased yield of colouring matter by washing the dry ethereal extract with dilute ammonia to remove resin, then dissolving the brittle residue in boiling concentrated ammonia solution and precipitating with carbon dioxide; 250 grms. ethereal extract gave 100 grms. flocculent curcumin, m.p. 140°. Jackson (Ber. 14, 485) also obtained crystallised curcumin by first removing the oil by long extraction with carbon disulphide (sixty hours), then thoroughly extracting (sixty hours) with ether, and after washing the orange-coloured product thus obtained with cold alcohol or ether, crystallising from hot alcohol.

Perkin (Chem. Soc. Trans. 1904, 85, 63) precipitates an alcoholic turmeric extract with lead acetate, washes the lead compound first with alcohol then with water, and decomposes it with dilute sulphuric acid. From the mixture of lead sulphate and curcumin the latter is removed with boiling alcohol and the extract evaporated and poured into ether, which causes the separation of tarry impurities. The ethereal solution, after evaporation to a small bulk, is treated with carbon disulphide and allowed to stand, the crystals which separate from time to time being removed. 0.56 p.c. of curcumin was thus obtained from turmeric.

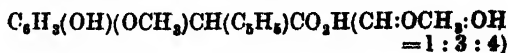
Curcumin crystallises from alcohol in orange-coloured prisms, m.p. 165° (Daube), 172° (Gajewsky), 178° (Jackson), and 183° (Ciamician and Silber, Ber. 30, 192), and is soluble in ether, forming a green fluorescent liquid. Alkaline solutions dissolve it with a reddish-brown colour, which when neutralised passes to yellow, and on this account it is useful in the form of 'turmeric paper' as a reagent for alkalis. Whereas Daube assigned to curcumin the formula $C_{18}H_{16}O_8$, Gajewsky ($C_{18}H_{16}O_8$), probably



Jackson considered that $C_{18}H_{14}O_8$ or $C_{18}H_{12}O_8$ were more reasonable expressions, and of these Jackson and Menke (Amer. Chem. J. 6, 78) preferred the former, and prepared the following derivatives harmonising with this view:—

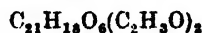
Dihydrocurcumin $C_{18}H_{18}O_8$, brownish-white powder, m.p. 100° ca.; *dihydrocurcumin anhydride* $C_{18}H_{16}O_7$, dirty white powder, m.p. 120° ca.; *disilylcurcumin* $C_{18}H_{20}O_8$, brownish tar; *p-bromobenzylcurcumin* $C_{18}H_{17}BrO_8$, pale yellow crystals, m.p. 76°–78°; *acetylcurcumin* $C_{19}H_{18}O_8$, brownish mass; *diacetylcurcumin* $C_{21}H_{20}O_8$,

yellow rhombic crystals, m.p. 154°; *curcumin-tetrabromide* $C_{18}H_{14}O_8Br_4$, powder, m.p. 185° ca.; *tetrabromocurcumin* $C_{18}H_{12}O_8Br_4$, red powder; *pentabromocurcumin dibromide* $C_{18}H_{10}O_8Br_5$, red powder, m.p. 120° ca.; *potassium curcumin* $KC_{18}H_{12}O_8$, red powder, and *dipotassium curcumin* $K_2C_{18}H_{10}O_8$, red needles. By fusion with alkali curcumin gives *protocatechuic acid*, when oxidised with permanganate *vanillin*, and the diethyl ether by similar treatment yields *vanillic acid ethyl ether*. Jackson and Menke represented curcumin by the following formula:—



Heller (Ber. 1914, 47, 2998) has obtained *dihydrocurcumin*, now shown to possess the formula $C_{22}H_{24}O_8$, by catalytic reduction, as colourless needles, m.p. 95°–96°.

Ciamician and Silber (Ber. 30, 192), as the result of methoxy determinations, assigned the formula $C_{22}H_{20}O_8$ or $C_{19}H_{14}O_8(OCH_3)_2$ to curcumin, and prepared *diacetylcurcumin*



needles, m.p. 170°–171°; and *curcumin dimethyl ether* $C_{18}H_{16}O_8(OCH_3)_2$, yellow needles, m.p. 135°. Digested with hydroxylamine hydrochloride in alcoholic solution curcumin gave the compound $C_{22}H_{22}NO_8$ (i.e. $C_{22}H_{20}O_8NOH-H_2O$), needles, m.p. 178°, whereas phenylhydrazine gave a substance crystallising in colourless needles.

Perkin (Chem. Soc. Trans. 1903, 83, 140; 1905, 85, 63), by means of alcoholic potassium acetate, obtained from curcumin the monopotassium salt $C_{22}H_{19}O_8K$, fine orange-red needles. A *benzoyl-curcumin*, pale yellow needles, m.p. 176°–178°, was also prepared, and gave by the cryoscopic method numbers harmonising with Ciamician and Silber's formula.

Molecular weight determinations, according to Jackson and Clarke (Ber. 1905, 38, 2712), indicated the correctness of the formula



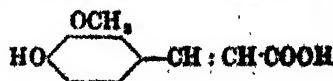
and again (*ibid.* 1906, 39, 2269) these authors pointed out that unless special care is employed, Zeisel's method gives erroneous figures with curcumin. When heated with hydriodic acid at 120° a correct result is given, but above this temperature curcumin gives a colourless oil rich in iodine (75.75 p.c.) which reacts with the alcoholic silver nitrate solution.

Von Kostanecki and Lampe (*ibid.* 1910, 43, 2163) consider that Ciamician and Silber's formula $C_{22}H_{20}O_8$ correctly represents curcumin, and describe *dicarbomethoxycurcumin*



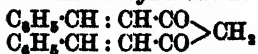
yellow prisms, m.p. 150°, and *dicarbomethoxycurcumin*, yellow leaflets, m.p. 149°–150°.

When curcumin is boiled with potassium hydroxide solution, *vanillic acid* and *ferulic acid*



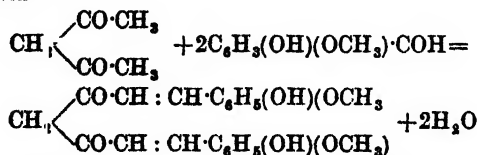
are produced. As a result these authors con-

which on hydrolysis splits off acetic acid with formation of dicinnamoyl-methane—



This compound, which crystallises in yellow prismatic needles, m.p. 144°, dissolves in sulphuric acid to form an orange-red solution possessing a yellow fluorescence. Both in its chemical and physical properties it closely resembles curcumin, and dyes cotton yellow shades which, however, are weaker than those given by curcumin itself.

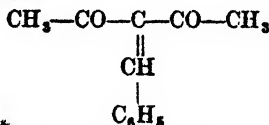
In 1914 (Ber. 47, 887) Heller described a stereoisomeride of curcumin which he named *iso-curcumin*, and this he obtained as a reddish-yellow crystalline solid, sintering at 140° and melting near 180°, by condensing vanillin with acetylacetone in the presence of hydrochloric acid—



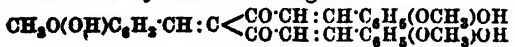
Ryan and Dunlea (Proc. Roy. Irish Acad. 1915, 32, B, 657), however, criticised this statement. They find that the first product of the action of benzaldehyde on acetyl-acetone in this way is not benzylidene-acetone



but a chlorinated compound which on heating *in vacuo* gives



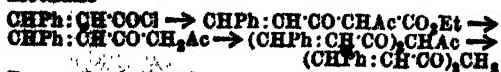
Iso-curcumin thus may be the trivanillin condensation product, with which indeed Heller's analytical results agree—



Heller (Ber. 1914, 47, 2998), however, states that this criticism of Ryan and Dunlea is unjustified in that *iso-curcumin* is a chlorine free colouring matter. *Iso-curcumin* shows a faint reaction with ferric chloride, and is to be regarded as a mixture of ketone with a little enol, whereas curcumin is decidedly enolic. *Ethyl-carbamato-iso-curcumin* melts at 142°. See also Ber. 1917, 50, 1244, and Ber. 1921, 54, 1118.

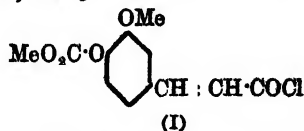
Ghosh (Chem. Soc. Trans. 1919, 292), by the simple conversion of curcumin into *iso-curcumin*, confirms Heller's view that the two substances are geometrical isomerides.

Curcumin has been synthesised by an application of the method employed for the synthesis of dicinnamoyl-methane (Lampe and Milobedzki, Ber. 1913, 46, 2235). In this cinnamoyl chloride was condensed with ethyl acetoacetate and the product hydrolysed, when cinnamoyl-acetone resulted. Condensation of this product with a second molecule of cinnamoyl chloride and hydrolysis of the product gave dicinnamoyl methane



By employing carbomethoxyferuloyl chloride (I)

in the place of cinnamoyl chloride, the dicarbomethoxy-derivative of curcumin was obtained. It gave curcumin on hydrolysis (Lampe, Ber. 1918, 51, 1347)



It is well known that a mixture of boric and hydrochloric acids imparts to turmeric paper a red colour which is turned blue by alkalis. This reaction was investigated by Schlumberger (Bull. Soc. Chem. [ii.] 5, 194), who found that when an alcoholic extract of turmeric is heated in a sealed tube with boric acid, a red crystalline boric acid derivative is produced, soluble in alkaline solutions with a purple-violet colour. Boiling water decomposes this compound with elimination of boric acid, and formation of *pseudo-curcumin*, a yellow powder. In the alcoholic solution of the boric acid compound is digested with strong hydrochloric acid, a black substance separates, whereas boric acid remains in the liquid.

On extracting the black powder with a mixture of alcohol and acetic acid, the filtrate deposits green iridescent crystals of rosocyanine.

Rosocyanine is readily soluble in alcohol containing a trace of mineral acid and dissolves in ammonia solution with a blue colour. It is, according to Schlumberger, an unstable substance, and if boiled for a long time with alcohol, is converted into *pseudo-curcumin*.

Jackson and Clarke (l.c.) prepared rosocyanine by heating a solution of curcumin in dilute alcohol with boric and sulphuric acids, and describe it as a purplish-red powder, closely resembling powdered rosaniline. These authors considered it to be isomeric with curcumin $\text{C}_{14}\text{H}_{14}\text{O}_4$, and described an *ammonium salt* $\text{C}_{14}\text{H}_{13}\text{O}_4\text{NH}_4$, and a *potassium salt* $\text{C}_{14}\text{H}_{13}\text{O}_4\text{K}$, both of which possess an intense blue colour.

The tinctorial properties of curcumin are of special interest, for not only is it a strong colouring matter towards mordants, but with cotton, wool, and silk it behaves also as a substantive dyestuff. In the latter case it is only necessary to add the material to a boiling decoction of the colouring matter. Though considerably employed up to within recent years by the wool and silk dyer in the formation of olives, browns, and other compound colours, turmeric is now but rarely used for dyeing purposes in England. In India, however, it appears to be still in vogue.

Cotton is usually dyed in a decoction of turmeric rendered slightly acid by the addition of a little acetic acid, or alum may be employed. The colour does not resist either the action of light or of alkalis, and readily acquires a brownish-red tint. Wool may be dyed without any addition, keeping the temperature about 80°. By previously mordanting with alum a brighter effect is produced, whereas tin mordant gives a more orange colour. Potassium dichromate and ferrous sulphate employed in a similar manner yield respectively olive and brown-coloured shades.

Silk is preferably dyed in an acid bath, and is sometimes previously mordanted.

Turmeric oil is the thick orange-coloured aromatic oil present to the extent of 3.23 p.c. in turmeric from which it can be extracted by means of carbon disulphide. Bolley examined the portion distilling over at 230°-250°, and considered it to be identical with carvol, whereas Gajewsky (l.c.) found the portion distilling over at 220°-228° contains less carbon and more hydrogen than that which passes over at a higher temperature. On oxidising the latter portion with chromic acid, an acid oil is obtained which contains valeric, caproic, and terephthalic acids. Jackson and Menke (l.c.) analysed that portion which distils over at 285°-290°, and gave it the formula $C_{15}H_{18}O$, and the name *turnerol*, and obtained *turnerol chloride* $C_{15}H_{17}Cl$, *sodium turnerol* $C_{15}H_{17}ONa$, and *turnerol iso-butyl ether* $C_{15}H_{27}O \cdot C_4H_9$. With permanganate turnerol gave *terephthalic acid*, *turmeric acid* $C_{11}H_{14}O_2$, and *apoturmeric acid* $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$. According to Rüpe (Ber. 1907, 40, 4909), when turmeric oil is boiled with dilute sodium hydroxide solution a substance, b.p. 156°/12 mm., apparently not identical with Jackson and Menke's turnerol, is produced. Stronger alkali yields an optically active ketone $C_{15}H_{18}O$, *curcumone*, b.p. 119°-120°/8 mm., which gives a semicarbazone, m.p. 119°-120°-5°, an oxime, b.p. 159°/11 mm., and condensation products with aromatic aldehydes. With permanganate the ketone gives *p-methylacetophenone* and *terephthalic acid*, and with alkaline hypobromite the acids $C_{12}H_{16}O_8$, m.p. 150°, and $C_{12}H_{16}O_2$, m.p. 33°-34°. By the further action of permanganate the latter yields a dicarboxylic acid $C_{12}H_{14}O_4$, m.p. 228°. Rüpe, Luksch, and Steinbach (Ber. 1909, 42, 1515) were unable to isolate from turmeric oil the turnerol of Jackson and Menke, having sp.gr. 0.9388 at 20° and $[\alpha]_D^{20} = -27.46$. By digestion with alcohol and 30 p.c. potassium hydroxide solution the ketone $C_{15}H_{18}O$, *curcumone*, was obtained, which has b.p. 121°/10 mm., sp.gr. 0.9566 at 20°, $n_D^{20} 1.50526$, $[\alpha]_D 80.55$, and yields the *p-bromophenylhydrazone*, m.p. 71°. It condenses with benzaldehyde to form the compound $C_{15}H_{16}O : CH \cdot C_6H_5$, m.p. 106°, and with piperonal and anisic aldehydes similar compounds melting respectively at 86° and 77°-78° are produced.

The acid $C_{12}H_{16}O_2$ (l.c.), m.p. 33°-34°, is called *curcumatic acid*, and appears to be identical with Jackson and Menke's turmeric acid (Rüpe and Steinbach, Ber. 1910, 43, 3465). By oxidation with permanganate it gives terephthalic acid, *p*-tolyl methyl ketone, and the acid $C_{12}H_{14}O_4$, m.p. 226°-228° (l.c.), and this possibly consists of *apoturmeric acid* (Jackson and Menke). Although it was considered that curcumatic acid might be γ -*p*-tolylvaleric acid, the synthesis of this latter compound showed that the substances are similar but not identical (*ibid.* 1911, 44, 584). Again, curcumatic acid is not *p*-tolyl- α -methylbutyric acid (Rüpe and Bürgin, *ibid.* 1218). Rüpe and Steinbach (l.c.) consider that curcumone is to be regarded as a benzene derivative containing two parasubstituents, one being methyl, and the second, one or other of the groups



whereas in curcumatic acid the group COMe is replaced by COOH. See also Schimmel & Co. Ber. April, 1911).

A. G. P.

TURMERIC ACID v. TURMERIC.

TURMERINE v. PRIMULINE AND ITS DERIVATIVES.

TURMERYL CHLORIDE v. TURMERIC.

TURNBULL'S BLUE. A variety of Prussian blue, probably a ferricyanide, v. CYANIDES.

TURNER'S YELLOW. *Patent yellow.* Lead oxychloride $3PbO \cdot PbCl_2$.

TURNIP. A biennial, cruciferous plant, producing in the first year a large root stock containing a store of carbonaceous and nitrogenous matter intended for the formation of flower-stem and seeds in the second year. This 'root' is the chief valuable product for which the crop is grown. Many varieties, differing in the shape, size, and colour of the root, are known, but they may all be classed as belonging to two species—the 'white turnip,' or simply 'turnip,' *Brassica rapa* (Linn.), or *B. rapa rapifera* (Metzger), and the 'Swedish turnip,' or 'Swede,' known often as 'ruta-baga' in America, *Brassica campestris rutabaga* (Linn.), or *B. napus esculenta* (DC.). There are many varieties of each, but as a rule 'turnips' have rougher leaves, of greener colour, and the root has white, or, in some cases, yellow flesh; whilst 'swedes' possess smoother leaves of a bluish-green colour, and the roots have yellow flesh. The leaves of the turnip spring directly from the root, whilst those of the swede arise from a distinctly marked 'neck.'

Both types grow best in cool, damp climates; in hot, dry countries the roots tend to become very woody and fibrous. Swedish turnips resist frost better, and can be grown in stiffer soils than the white varieties; they also keep better after gathering.

According to König, the following figures represent the average composition of the two types—

	Pro-	Other	
	Water	N-free	
	tein	Fat	Sugar ext. Fibre Ash
White turnips	90.67	1.12	0.24 2.55 3.55 1.11 0.76
Swedes	88.88	1.39	0.18 3.02 4.35 1.44 0.74

Great variations in composition, however, have been observed, the most important factors, in order of importance, being apparently, season, variety, size of root, district, and soil. Even with the same variety, grown under the same conditions, and with roots of approximately the same size, considerable variations in the composition of individual roots are found, especially in the amount of sugar. Thus, Collins (J. Soc. Chem. Ind. 1920, 20, 536) found in 25 individual roots of XL All swedes, the proportion of sugar varied from 4.5 to 7.8 p.c., with an average of 6.27 p.c.

The variation with season is considerable; Collins, as the average of 12 varieties of swedes grown in 1900, found a sugar content of 6.26 p.c., while the same varieties, in 1901, gave an average of only 4.05 p.c. of sugar. Analogous to the effect of season is that of local climate; even in Britain this effect is seen. In 1904 several varieties of swedes were grown simultaneously in Cambridgeshire, Norfolk (2 centres), and Ross-shire (4 centres), and the resulting

crops were examined for dry matter and sugar content.

The following figures show the sugar contents of 5 varieties, as grown at the various centres—

Variety	Cam-bridge			Norfolk			Ross-shire		
	1	2	Mean	1	2	3	4	Mean	
Fell's Bronzetop.	6.5	6.1	8.0	7.0	7.2	7.3	7.1	8.0	7.4
New Arctic	6.1	6.0	8.1	7.0	6.9	7.2	7.1	7.9	7.3
Magnum Bonum	6.3	5.7	7.6	6.6	6.8	7.2	6.6	8.1	7.2
XL All	6.0	6.0	7.4	6.7	6.8	6.8	6.7	7.5	7.0
Carter's Elephant	6.3	5.8	7.0	6.3	6.7	6.9	6.8	7.4	7.0
Average	6.2	5.9	7.6	6.7	6.9	7.1	6.9	7.8	7.2

These results clearly show that the roots grown in the moist, cool climate of Ross-shire were, on the average, richest in sugar, while those grown in the hot, dry climate of Cambridgeshire were the poorest (Guide to Expts. 1906, Dept. of Agric. Univ. of Cambridge).

So, too, Hendrick (Bull. 1, Coll. Agric. Univ. of Aberdeen, 1904) found, as the average of analyses of 21 varieties of swedes, grown in Aberdeenshire, 11.7 p.c. of dry matter, and 5.15 p.c. of sugar, while 9 varieties of turnips yielded an average of 9.48 p.c. of dry matter, and 4.55 p.c. of sugar; and Wood (Guide to Expts. Dept. of Agric. Univ. of Camb. 1906) found as the mean of the analyses of 5 varieties of swedes, grown in Cambridgeshire (1 centre, and Norfolk (2 centres), 10.8 p.c. of dry matter and 6.6 p.c. of sugar, and for 7 varieties of white turnips 7.81 p.c. of total dry matter, and 4.24 p.c. of sugar.

The effect of soil upon the composition of the roots, although perceptible, is not great. That of manuring is very great upon the yield, but is comparatively small upon the composition, except in so far as it affects the size of the roots.

The effect of size of root, in any variety, is considerable, small roots being invariably richer in solid matter, especially sugar, than large ones. This is well seen from the following analyses by Hendrick (J. Soc. Chem. Ind. 1897, 16, 213) of two samples of 'Achilles' turnips—

Average wt.	Dry		Water		Sugar		Total N		Alb. N		Ash	
of 1 root	Water	matter	Water	matter	Sugar	Total N	Alb. N	Ash	Water	matter	Sugar	Total N
5lb. 10z.	92.8	7.2	3.93	0.102	0.108	0.56						
2lb. 14oz.	91.3	8.7	4.62	0.148	0.076	0.64						

In view of these many circumstances affecting the composition of the roots, it is obviously of little value to attempt to give any representative composition of turnips.

It may, however, be of interest to quote the figures given by Kellner and by Warrington as representing the average composition of turnips and swedes.

Kellner gives—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Swedes	87.8	1.5	0.2	8.2	1.3	0.9
Turnips	91.5	0.9	0.1	6.0	0.8	0.7

Warrington's figures are—

	Water	Proteids etc.	Amides, Fat	N-free extract	Crude fibre	Ash
Swedes	89.3	0.7	0.7	0.2	7.2	1.1
Turnips	91.5	0.5	0.5	0.2	5.7	0.9

The protein, i.e. total N \times 6.25, in the above analyses, contains a considerable and variable quantity of non-proteid substance. König states that from 35 to 55 p.c. of the total nitrogen is present, partly as amides or amino acids,

partly as nitrates. Warrington estimates the non-albuminoid nitrogen in turnips at 49 p.c. of the total nitrogen, but gives as the average digestible albuminoids 0.2 p.c. in swedes, and 0.1 p.c. in turnips. Collins (l.c.) found, in 'Monarch' swedes, the real albuminoids varied from 0.47 to 0.63 p.c., while the amides, &c., ranged from 0.34 to 0.61 p.c. Hendrick (l.c.) found the proportion of non-albuminoid nitrogen to total nitrogen varied from 27 to 42 p.c. in yellow turnips, and from 23 to 59 p.c. in 'Best of All' swedes. In the days when the 'nitrogenous substances' or 'albuminoids' in food-stuffs were estimated by multiplying the total nitrogen by 6.25, turnips, in common with other roots, gave results on analysis which indicated that they possessed greater feeding value than actual experience showed them to have. If, however, distinction is made between true proteids and amino compounds, amides and nitrates, the nutritive value of turnips, as assessed by analysis, seems, in most cases, to be much less than their actual efficiency as foods (v. Ingle, Trans. High. & Agric. Soc. Scotland, 1910, 22, 178; also Hendrick, *ibid.* 150). It would seem, in fact, that either the true albuminoids in turnips are much more digestible than has hitherto been admitted, or, more probably, that the amino compounds may, under certain conditions, behave like albuminoids, in building up animal tissue.

For a study of the hydrolysis of the soluble protein of swedes, v. Williams (J. Agric. Sci. 1917, 8, 182).

The sugars present in turnips are dextrose, lævulose, and sucrose, the invert sugars largely predominating. The other N-free extractives include pectins, pentosans, and cellulose.

The ash of turnips varies greatly in composition and amount. According to figures compiled by König, the whole ash varies from 4.9 to 14.0 p.c. of the dry matter, while the potash in the ash may range from 26 to 62 p.c., the lime from 5 to 15.9 p.c., and the phosphorus pentoxide from 5.5 to 18.9 p.c. The mean of 32 analyses of the ash gave—

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂	Cl
	45.4	9.8	10.6	3.7	0.8	12.7	11.2	1.9	5.0

The upper half of a root is richer in solid matter than the lower, and due allowance must be made for this fact in sampling turnips for analysis.

Turnip leaves are sometimes used for feeding purposes; according to Kellner they contain, on the average—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
88.4	2.2	0.5	5.3	1.5	2.1

Turnips, like other plants of the genus *Brassica*, contain thio compounds, and when they decay or even suffer slight decomposition by boiling, they evolve unpleasant-smelling sulphur compounds, among which mercaptans are probably included.

Turnips require liberal supplies of phosphates, and phosphatic manures, generally superphosphates, are almost invariably used for this crop. For a study of the destination of phosphates and nitrogen when applied as a manure to turnips, v. Somerville and Smith (J. Soc. Chem. Ind. 1897, 16, 19), H. I.

TURPENTINE v. OILS, ESSENTIAL: also TURPENTENS.

The production of turpentine and rosin in France during the last 10 years has been as follows:—

Year.	Turpentine metric tons.	Rosin metric tons
1913 . . .	25,000	85,000
1914 . . .	19,000	64,000
1915 . . .	15,000	51,000
1916 . . .	17,000	60,000
1917 . . .	17,000	60,000
1918 . . .	20,000	60,000
1919 . . .	25,000	85,000
1920 . . .	35,000	120,000
1921 . . .	31,000	105,000
1922 . . .	32,000	118,000

For the temperature coefficient of refractive index of American turpentine, see G. Thompson (Chem. News, Jan. 12, 1923, 126, 20-21).

About 75 p.c. of the world's supply of turpentine is produced in the United States, chiefly from the southern longleaf yellow pine (*Pinus palustris*), but other species, such as the Cuban or slash pine (*P. caribæa* or *heterophylla*), the rosemary pine (a variety of the Loblolly pine, *P. taeda*), and the western yellow pine (*P. ponderosa*) are also tapped; most of the remaining 25 p.c. is obtained in the south-western coast regions of France from the maritime or cluster pine (*P. pinaster* or *maritima*). The following States contribute to the American supply: Florida, 37 p.c.; Georgia, 19 p.c.; Louisiana, 15 p.c.; Alabama, 12 p.c.; Mississippi, 9 p.c.; Texas, 7 p.c.; North and South Carolina, which formerly produced the bulk of the world's supply, now furnish less than 1 p.c.

The oleo-resin is obtained by scarifying or 'chipping' the living trees. A V-shaped cut is made about once a week immediately above the last cut, thereby forming a 'face' down which the gum exuding from the cut flows, collects in galvanised iron or baked clay cups holding 1 to 2 quarts. The tapping season lasts from early spring to late autumn, the oleo-resin being removed from the cups about once a month and taken to the stills in barrels.

The distillation plant is simple and has not been improved materially during the last 50 to 60 years. It consists of a copper still of 500 to 1000 gallons capacity, with a still-head (generally removable) connected to a large copper condensing-coil cooled in water. From 7 to 14 barrels of oleo-resin go to make a charge, depending on the size of the still and the nature of the oleo-resin.

The oleo-resin contains some water and the distillate at the beginning consists of about 45 p.c. of turpentine and 55 p.c. of water. When the water decreases to about 30 p.c., a small stream of water is admitted to the still. The yield of turpentine varies from 16 to 22 p.c. It is mostly shipped in wooden casks holding 50 to 53 U.S. gallons (231 cub. in.), treated internally with glue to prevent absorption of turpentine by the wood. Tank cars of 5000 to 10,000 gallons capacity are used in the Western States (F. P. Veitch and V. E. Grotliach, U.S. Dept. Agric., Bureau of Chem. Bulletin No. 898, 1920, in abstract, J. Soc. Chem. Ind. 1921, 165 R.).

Ordinary American turpentine is able to

attack iron in the presence of air, thus acquiring a deep red colour. This appears to be due to organic acids of high molecular weight (Levy and Defries, J. Soc. Chem. Ind. 1923, 42, 472 T.; 1924, 43, B. 103).

Wood turpentine is obtained from stumps, sawmills slab, &c., by destructive distillation or by steam distillation; the crude product is redistilled over soda-ash, and when thus refined, can scarcely be distinguished from the volatile portion of the oleo-resin exuded from the living tree (spirits of turpentine.) Refined wood-turpentine has the following characteristics: sp.gr. at 15° 0.863; n_D^{20} 1.468; initial b.p. 153°; distillation range 91 p.c. below 170°; acidity, trace. About 70 p.c. distils below 160°, and this portion has been identified as α -pinene (Lambert, J. Ind. Eng. Chem. 1922, 14, 491; Analyst, 1922, 406).

The following are suggested by the U.S. Dept. of Agric. as specifications for three standard grades of turpentine:—

Standard or No. 1 turpentine should have a sp.gr. at 20° of from 0.862 to 0.870; a refractive index at 20° of from 1.468 to 1.476; 95 p.c. should distil below 170°, and a layer of not less than 200 mm. should be required to equal in colour the Lovibond yellow glass No. 1. On polymerisation with 38-normal sulphuric acid the residue should not exceed 1 p.c., should be reddish in colour and viscous, and its refractive index at 20° should be from 1.500 to 1.520. An unadulterated turpentine which does not agree with these requirements may properly be regarded as not of standard or No. 1 quality.

Second quality or No. 2 turpentine should have a sp.gr. at 20° of from 0.862 to 0.875; a refractive index at 20° of from 1.468 to 1.480; 90 p.c. should distil below 170°, and a depth of not less than 100 mm. should be required to equal the Lovibond yellow glass No. 1. The polymerisation residue must not exceed 1 p.c., and must have a refractive index of not less than 1.50.

Third quality or No. 3 turpentine should have a sp.gr. at 20° of from 0.865 to 0.880; a refractive index at 20° of from 1.468 to 1.485; 60 p.c. should distil below 170°, and a depth of not less than 50 mm. should be required to equal the Lovibond yellow glass No. 1. The polymerisation residue must not exceed 1 p.c., and must have a refractive index of not less than 1.500.

The following are the tests for adulteration:—

'Straight' wood turpentines are readily distinguished from gum turpentines by their odour, or when they have been very carefully refined by the odour of the first fraction, or of the residue from fractional distillation. One or both of these portions have the peculiar 'sawmill smell,' and the residue has a camphoric and somewhat nauseating odour characteristic of wood turpentine, which is quite different from the mild, sweet fragrance of gum turpentine.

Destructively distilled wood turpentine and also rosin spirits are more readily distinguished from gum spirits by their odour than is wood turpentine prepared by steam distillation, and they also give distinguishing colour reactions when mixed with sulphurous acid or with hydrochloric acid. When steam-distilled wood turpentine has been carefully refined so that 95 p.c.

95 p.c. of it distils at from 155° to 170° , both of these colour tests are practically useless.

At the present time a number of highly refined grades of pine wood oil ("kienöl"), obtained as a by-product from the manufacture of sulphate wood pulp, are on the market and employed for the adulteration of true turpentine oil. An extremely simple test for this adulteration is obtained with the ferric ferricyanide reagent. Two solutions are made up (a) with 0.5 grm. of potassium ferricyanide in 250 c.c. of water and (b) 0.1 grm. of ferric chloride in 250 c.c. Four c.c. of each of the two solutions are mixed together and 3-5 drops of the sample to be tested are added. With impure turpentine oils the formation of Prussian blue is observed within a few minutes. Pure turpentine oil within 3 minutes produces only a faint green coloration, or at the most slightly blue colour at the line between the oil and aqueous layer (H. Wolff, Zeitsch. angew. Chem. 1923, 36, 233; J. Soc. Chem. Ind. 1923, 42, 730 A).

Turpentine adulterated with more than 10 to 20 p.c. of coal-tar oils, or of gasoline or kerosene which have not been deodorised, may usually be readily detected by the characteristic odour of the mixture. The odour of rosin spirits, while quite distinctive, is difficult to detect in mixtures with turpentine. The presence of petroleum oils is also indicated by bubbles or 'beads' persisting for a few moments on the surface of the turpentine shaken in a partly filled bottle.

The presence of more than 10 p.c. of kerosene or similar mineral oils is readily detected by the spot which a few drops of the sample placed on white paper leaves on drying. Gasoline and other light mineral oils do not leave this spot.

It is possible so to adulterate turpentine that neither the specific gravity, refractive index, or flash-point is materially altered. Such careful adulteration is rare, but as adulterants cannot invariably be detected by making these determinations, and further, as mineral oil is the most probable adulterant, it is more rational at once to polymerise the suspected sample, note the volume, colour and consistency of the unpolymerised residue, and determine its refractive index.

If rosin spirits is present in notable quantities, it may be detected by the amount of residue on polymerisation in conjunction with lowered initial boiling-point and the deep coloration produced by mixing portions of the original turpentine of the first fraction with sulphurous acid and with hydrochloric acid.

If the initial distilling temperature of the turpentine is less than 154° and the original sample gives a reddish colour with sulphurous acid and a greenish-red with hydrochloric acid, and the residue from polymerisation is less than 5 p.c., it is probable that the sample is adulterated with rosin spirits. An odour of rosin spirits in the sample, or in any fraction, would be confirmatory, and all tests should be repeated on the first fraction obtained with a fractionating column. At best the detection of small amounts of rosin spirits is very difficult, and the procedure outlined may often fail to detect its presence.

The presence of marked quantities of coal-tar oils, benzol, toluol, and xylol is detected by the odour, the lower initial distilling temperature,

i.e. between 80° and 155° , and by further examination of the first fractions which distil below 155° . The rise of temperature on shaking during polymerisation is also indicative of the nature of the sample. Coal-tar and petroleum oils do not raise the temperature more than 35° or 40° when mixed with sulphuric acid. When the temperature of turpentine mixed with 38-normal sulphuric acid does not rise above 50° or 60° , mineral oil, coal-tar oil, or some other oil than turpentine is present in large quantities. The older the sample of turpentine, the greater, or at least the more rapid, the rise of the temperature of the mixture.

Benzene in turpentine may also be detected by the precipitate of $\text{Ni}(\text{Cy}_3\text{NH}_2)_2\text{C}_6\text{H}_6$, which it forms with nickel ammonium cyanide (Pritzke and Jungkunz, Chem. Zeit. 1924, 48, 555; Analyst, 1924, 49, 450).

Non-volatile oils are easily detected by a distillation test (J. Soc. Chem. Ind. 1911, 30, 559).

For the constituents of Indian turpentine from *Pinus longifolia*, Roxb., see J. L. Simonsen and M. G. Rau (Chem. Soc. Trans. 1923, 123, 549-560); J. L. Simonsen (Chem. Soc. Trans. 1923, 123, 2642-2666).

Oil of turpentine from *Pinus laricio* of Spain contains over 90 p.c. of *l*-pinene (Dupont and Barraud, Bull. Soc. Chem. 1924, 35, 784; J. Soc. Chem. Ind., 1924, 43, B, 720).

Venice Turpentine.—The production of Venice turpentine (trementina) in Italy is confined to the Province of Venetia Tridentina, formerly Austrian Tyrol territory, in the northern part of Italy. In this region that species of pine known as larch is found in abundance on the slopes of the Apennines, and the distillation of turpentine from the wood of this tree forms an important industry. There seems to be no monopoly of the industry as, according to the Journal of the Royal Society of Arts, quoting a United States Consular report, the production of Venice turpentine (known to the producers as olio greggio di larice or Tyrol larch turpentine) is divided among a great number of individuals and small concerns. In some cases the municipal government owns and operates distillation plants for the production of turpentine—an unusual occurrence in Italy. Venice or Tyrol larch turpentine is sold by weight (Pharm. J. Sept. 8th, 1923).

TURPETH or TURBITH MINERAL. An old name for basic mercuric sulphate $\text{HgSO}_4 \cdot 2\text{HgO}$, sometimes called Queen's yellow, v. MERCURY.

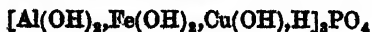
TURPETH or TURBITH ROOT. The root of the convulvulaceous plant *Ipomoea Turpethum* (R.Br.) [*Operculina Turpethum* (Peters)], found in India and Australia. It contains a volatile oil and a drastic resin, turpethin $\text{C}_{27}\text{H}_{44}\text{O}_{10}$, isomeric with jalapin and scammonin. When treated with dilute mineral acids this substance is hydrolysed into glucose and turpetholic acid $\text{C}_{16}\text{H}_{28}\text{O}_8$ (v. Bonttron-Charlard, J. Pharm. Chim. 8, 131; Spirgatis, J. pr. Chem. [i.] 92, 97).

TURPETHIN v. GLUCOSIDES.

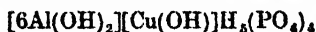
TURQUOISE or CALAITE (Turkic, Ger.). A gem-stone which has often been regarded as a hydrated aluminium phosphate



accidentally coloured by copper and iron phosphates. It has been shown, however, by S. L. Penfield (Amer. J. Sci. 1900, 10, 346) that the latter enter into the constitution of the mineral, and he writes the formula



representing a derivative of orthophosphoric acid with the hydrogen atoms largely replaced by the univalent radicles $Al(OH)_2$, &c. In some analyses approximately two-thirds of the hydrogen atoms are so replaced, and the formula becomes $R_2'HPO_4$. The amount of copper ranges from 2.0 to 8.5 p.c. CuO , and the iron from 0.1 to 4.0 p.c. Fe_2O_3 . The mineral is soluble in hydrochloric acid without discoloration; when heated it loses water and blackens. It is opaque (or translucent in thin chips) with a sky-blue to green colour, and on the polished surface shows a soft, waxy lustre; sp.gr. 2.6-2.8; H. 6. Turquoise occurs as cryptocrystalline masses, sometimes with nodular or stalactitic surfaces, in crevices in rocks, more especially in those of volcanic origin. The best quality of material has for centuries been mined near Nishapur in Persia, and being exported to the west through Turkey it came to be known as turquoise. Deposits in the Sinai Peninsula were worked by the ancient Egyptians. Ancient mines, worked in prehistoric times, are also known in Mexico and in the state of New Mexico. Considerable quantities (17 tons in 1909, and 8½ tons in 1910) are now obtained from Nevada, New Mexico, Arizona, California, and Colorado (D. B. Sterrett, Min. Res. U.S., Annual Reports for 1910 and earlier). Minute crystals of turquoise have been described from Campbell Co., Virginia; these are triclinic and isomorphous with chalcosiderite. Analysis of them gave the formula $CuO \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 9H_2O$; written in the form of Penfield's formula this becomes



(W. T. Schaller, Amer. J. Sci. 1912, 33, 35).

Turquoise has been imitated by subjecting to pressure a mixture of aluminium and copper phosphates. Very clever imitations are also made of glass; these may be detected by the bright, glassy, conchoidal fracture when chipped at the edges—the fracture of turquoise being dull and finely granular.

Bone-turquoise or **odontolite** is fossil bone or ivory coloured by the iron phosphate vivianite, or perhaps sometimes artificially stained by a copper solution. It can be recognised under the microscope by its organic structure. It effervesces with acid, and gives a smell of burning when heated.

L. J. S.

TUSSOL. Antipyrine mandelate.

TUTENAG or **TUTENAGUE.** Chinese silver. *Packfong.* An alloy resembling German silver.

TUTOCALINE. A local anæsthetic of the novocaine type (cf. Vol. vi. p. 637). Its action is more powerful than that of novocaine (Schulemann, Lancet, 1924, 206, 965; Pharm. J. 1924, 113, 46; Wagner, Arch. Exp. Path. Pharm. 1925, 109, 64; Chem. Soc. Abstr. 1925, 128, i. 1503).

TYLCAISIN (*kalmopyrin*). Trade name for calcium acetyl salicylate.

TYLLITHIN (*appron*). Trade name for lithium acetyl salicylate.

TYLNATIN. Trade name for acetyl-o-

coumaric acid, used in the treatment of inoperable cancer.

TYLNATRIN. Trade name for sodium acetyl salicylate.

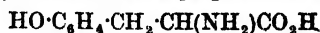
TYNDALLMETER. See NEPHELOMETRY.

TYPE METAL v. TIN.

TYRAMINE. Trade name for *p*-hydroxyphenylethylamine hydrochloride, v. ERGOT.

TYRIAN PURPLE v. PURPLE OF THE ANCIENTS. In Costa Rica a dyestuff apparently of the 'Tyrian purple' class is obtained from shell-fish, and is used for dyeing silk thread a fast purple colour.

TYROSINE, *p*-hydroxyphenylalanine, *p*-hydroxy-β-phenyl-α-aminopropionic acid



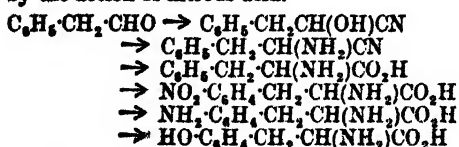
was so named by Leibig, who first obtained it by fusing freshly prepared cheese (*rupós*) with caustic potash (Annalen, 1846, 57, 127). It occurs widely spread both in the animal and vegetable kingdoms, forming one of the most common products of proteid hydrolysis, and occurring in the free state in the seedlings and young shoots of the vetch (*Vicia sativa*) (Gorup-Besanez, Ber. 1877, 10, 781); the gourd (*Cucurbita pepo*) (Schulze and Barbieri, *ibid.* 1878, 11, 710, 1233); the lupins (*Lupinus luteus*, *L. albus*) (Schulze, *ibid.* 1878, 12, 1924; Wassilieff, Landw. Versuchs Stat. 1901, 55, 45); in the tubers of potatoes (*Solanum tuberosum*) (Schulze, Ber. 1879, 12, 1924), the swede (*Brassica rapa*), the dahlia (*Dahlia variabilis*) (Borodin, Botan. Zeit. 1882, 590; Leitgeb, Chem. Zentr. 1888, 1397; Bertrand, Compt. rend. 1896, 122, 1215); in the tubercules of *Stachys tubifera* (Planta and Schulze, Ber. 1890, 23, 1698); in the juice of sugar beet (*Beta vulgaris*) (v. Lippmann, *ibid.* 1884, 17, 2835), in celery (*Apium graveolens*) (Bamberger and Landsiedl, Monatsh. 1904, 25, 1030); in the unripe seeds of the French bean (*Phaseolus vulgaris*) (Pfenninger, Ber. Deut. bot. Ges. 1909, 27, 227), the pea (*Pisum sativum*) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1910, 65, 431); in the green pods of the broad bean (Bourquelot and Hérissé, J. Pharm. Chim. 1898 [vi.] 8, 385); in the juice of elderberries (*Sambucus nigra*) (Sack and Tollens, Ber. 1904, 37, 4115); in fungi (Winterstein, Zeitsch. physiol. Chem. 1899, 26, 438). In the animal kingdom, tyrosine is found in caterpillars, crabs, spiders, and beetles (v. Lippmann, *l.c.*) and in cochineal (Warren de la Rue, Annalen, 1848, 64, 1); in the larva of *Lucilia Caesar* (Gessard, Compt. rend. 1904, 139, 644); it occurs in Emmenthaler and in Roquefort cheeses (Benecke and Schulze, Landw. Jahrbücher, 1887, 16, 317; Winterstein and Thöny, Zeitsch. physiol. Chem. 1902, 36, 28; Dox, J. Amer. Chem. Soc. 1911, 33, 423). Under normal conditions, tyrosine is not found in the liver or blood of men and animals, but occurs under certain pathological conditions (Frerichs and Staedeler, J. 1856, 702; Hoppe-Seyler, Zeitsch. physiol. Chem. 1881, 5, 348; Neuberg and Richter, Deut. med. Wochensach. 30, 499; Huber, Archiv. Heilkunde, 18, 485; Wyss, Schweiz. Zeitsch. Heilkunde, 1864). The presence of tyrosine in muscle and in all other organs which do not normally contain products of digestion suggests putrefaction (Pietre, Compt. rend. 1914, 158, 1934); v. Juge (J. Pharm. Chim. 1913, [vii.] 8, 559) for its presence

in urine. It can be detected by the Frerichs-Städeler method in normal or pathological urines, in quantities of 0.2 gram in 400 c.c. of urine and by Lippich's method in quantities of 0.01-0.02 gram in 100 c.c. Tyrosine is sometimes present in cases of acute yellow atrophy (Schumm and Papendieck, *Zeitsch. physiol. Chem.* 1922, 121; 1).

Preparation.—Tyrosine is most conveniently prepared from silk by hydrolysing with fuming hydrochloric acid, and evaporating the product under reduced pressure to dryness; the residue is dissolved in water and a stream of ammonia passed through the solution; it is then again evaporated to dryness, and the residue treated with cold water, when the tyrosine is left undissolved; or the whole residue may be boiled with water and animal charcoal, and from the filtrate pure tyrosine crystallises out quantitatively: one kilo of silk yielding 50.65 grms. of tyrosine (Abderhalden, *Zeitsch. physiol. Chem.* 1912, 77, 75; Abderhalden and Teruuchi, *ibid.*, 1906, 48, 528). Marshall (J. Biol. Chem. 1913, 15, 85) recommends obtaining it from the pancreatic digestion of caseinogen; the liquid on cooling deposits an abundant crystalline yield of tyrosine.

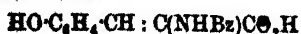
For the preparation of tyrosine from peptones, see Beijerinck (*Chem. Weekblad*, 1919, 16, 1494).

Synthesis.—Staedeler (*Annalen*, 1860, 116, 57) was the first to show that tyrosine was an aromatic compound, since it yielded chloranil (tetrachloroquinone) on treatment with chlorine; but its constitution as *p*-hydroxy- β -phenyl- α -aminopropionic acid was not established until 1882 when Erlenmeyer and Lipp (*Ber.* 1882, 15, 1544; *Annalen*, 1883, 219, 161) prepared racemic tyrosine from phenylacetaldehyde by the following series of reactions: *phenylacetaldehyde* on treatment with hydrogen cyanide gave *phenyllactonitrile*; this was converted by ammonia into the *nitrile* of *phenylalanine* which, on hydrolysis, gave *phenylalanine*; *p*-nitro-*phenylalanine* on reduction gave the corresponding amino compound from which *p*-hydroxyphenylalanine (*r*-tyrosine) was produced by the action of nitrous acid.

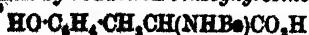


A more convenient method of synthesis is that due to Erlenmeyer jun., and Halsey (*Annalen*, 1899, 307, 138), in which *p*-hydroxybenzaldehyde and hippuric acid condense in the presence of acetic anhydride and anhydrous sodium acetate to form the *acetyl* derivative of the *lactimide* of *p*-hydroxy- α -benzoylamino-

cinnamic acid, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C} \begin{smallmatrix} \text{NBz} \\ \text{CO} \end{smallmatrix}$. This, on hydrolysis with alkali, gives *p*-hydroxy- α -benzoyl-aminocinnamic acid

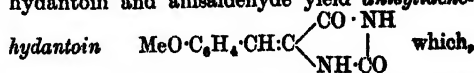


from which by reduction *benzoyltyrosine*

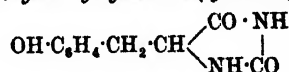


is obtained and converted by hydrolysis with

acids into *r*-tyrosine. Another method of synthesis which can also be extended to the preparation of halogenated derivatives of tyrosine is described by Wheeler and Hoffmann (*Amer. Chem. J.* 1911, 45, 368; cf. Wheeler, Hoffmann and Johnson, *Bio-Chem. J.* 1911, 10, 147; Johnson and Bengis, *J. Amer. Chem. Soc.* 1912, 34, 1061). This method consists in condensing a suitable aldehyde with hydantoin, reducing and hydrolysing the product; thus hydantoin and anisaldehyde yield *anteylidene-*



when boiled with hydrogen iodide is converted into *tyrosine* together with a small quantity of 4-*p*-hydroxybenzoylhydantoin (*tyrosinehydantoin*)

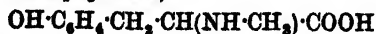


from which tyrosine can be obtained by boiling with baryta water; *dl*-tyrosine may also be synthesised by condensing ethyl phthalimino-malonate with *p*-methoxybenzyl bromide and hydrolysing the product (Stephen and Weizmann, *Chem. Soc. Trans.* 1914, 105, 1152).

Properties.—*l*-Tyrosine, the natural product, is also obtained by the resolution of *dl*-benzoyltyrosine through its brucine salt and subsequent hydrolysis of the *l*-benzoyltyrosine. It crystallises in long flexible silky needles, soluble in 2491 parts of water at 17° (Erlenmeyer and Lipp, *l.c.*), more readily soluble in hot water; dissolves in 13,500 parts of cold 90 p.c. alcohol (Staedeler, *l.c.*), insoluble in acetone, ether or absolute alcohol. It melts and decomposes at 314°–318° (corr.) when rapidly heated (Fischer, *Ber.* 1899, 32, 3638); at 295° (Cohn, *Zeitsch. physiol. Chem.* 1896, 22, 166); at 272° (Habermann and Ehrenfeld, *ibid.* 1902, 37, 18); 287° (*Trans. Guinness Lab.* 1903, i. 57). *l*-Tyrosine is levorotatory both in acid and in alkali solution; the specific rotation varies with the concentration. For a 4 p.c. solution in 21 p.c. hydrochloric acid, the natural product has $[\alpha]_D^{16} = -7.98^\circ$ (Mauthner, *Monatsh.* 1882, 3, 345), $[\alpha]_D^{20} = -8.07^\circ$ (Landolt, *Ber.* 1884, 17, 2838); $[\alpha]_D = -8.48^\circ$ (Schulze, *Zeitsch. physiol. Chem.* 1884, 9, 98); the synthetic product has $[\alpha]_D^{20} = -8.64^\circ$ (Fischer, *Ber.* 1899, 32, 3638). In a 4.6 p.c. solution in 4 p.c. hydrochloric acid, the synthetic compound has $[\alpha]_D^{20} = -13.2^\circ$ (Fischer), and the natural product $[\alpha]_D^{16} = -14.6^\circ$ to -16.1° (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1902, 35, 299); in a 5.8 p.c. solution of 11.6 p.c. potassium hydroxide, the natural product has $[\alpha]_D = -9.01^\circ$ (Mauthner, *l.c.*). The molecular heat of combustion is 1071.2 Cal., heat of formation 156.4 Cal. (Berthelot and André, *Compt. rend.* 1890, 110, 884). The affinity constants of tyrosine are: first acid dissociation constant $K_s = 4 \times 10^{-9}$, second acid dissociation constant $K_s = 4 \times 10^{-10}$, basic dissociation constant $K_b = 2.6 \times 10^{-11}$ (Kanits, *Pflügers Archiv.* 1907, 118, 589). The single band ultra violet absorption spectrum exhibited by solutions of tyrosine, is practically identical with that of proteids containing tyrosine;

gelatin, and other proteids that contain no tyrosine show continuous spectra (Blyth, Chem. Soc. Trans. 1899, 1164). Tyrosine is not affected by diazomethane (Geake and Nierenstein, Bio-Chem. J. 1915, 9, 309). For the oxidation of tyrosine, v. Denis (J. Biol. Chem. 1911-12, 10, 73).

L-N-methyltyrosine,



may be obtained from natural *L*-tyrosine by means of the monotoluene sulphonyl derivative; it has $[\alpha]_D^{21} + 19.75$, and it is identical with natural ratatine (Fischer and Lipschitz, Ber. 1915, 48, 360).

d-Tyrosine, obtained by the resolution of *dl*-benzoyltyrosine through its cinchonine salt and subsequent hydrolysis, has $[\alpha]_D^{20} + 8.64^\circ$ in 4.6 p.c. solution of 21 p.c. hydrochloric acid (Fischer); the dextrorotatory tyrosine obtained by v. Lippmann from the white shoots of sugar beet gave $[\alpha]_D = +6.85^\circ$ in 25 p.c. hydrochloric acid; a feebly dextrorotatory tyrosine was found by Winterstein and Thöny (Zeitsch. physiol. Chem. 1902, 36, 28) in a very old Emmenthaler cheese.

dl-Tyrosine prepared by hydrolysis of the synthetic benzoyl derivative crystallises in stout needles, melting and decomposing at 316° (corr.) when rapidly heated (Fischer, *l.c.*); its hydrochloride is much less soluble in concentrated hydrochloric acid than are the salts of the optically active forms, and the racemic compound can thus be separated from admixture with *d*- and *l*-tyrosine. By fermentation with large amounts of yeast in the presence of sugar and nutritive salts, tyrosine is converted to the extent of 60-80 p.c. into *p*-hydroxyphenylethanol (tyrosol) $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, m.p. 93° , b.p. 310° (compare also Hirai, Acta Scholae Med. Univ. Imperial, Kido, 1918, 2, 425). The *dibenzoyl derivative* melts at 111° ; tyrosol is also obtained by the action of yeast on *p*-hydroxyphenylethylamine (Ehrlich, Ber. 1911, 44, 139; Ehrlich and Pishtschimuka, *ibid.* 1912, 45, 1006). According to Teudji (Acta Schol. Med. Kyoto, 1917, 1, 439, from Physiol. Abstr. 1917, 2, 320; 1918, 3, 165) *Bacillus proteus vulgaris* attacks *r*-tyrosine, and 65.7 p.c. of *d*-tyrosine can be isolated. Tyrosine is converted to *p*-hydroxyphenylethylamine to the extent of 78.7 p.c. by the action of *B. coli* in a suitable medium (Sasaki, Biochem. Zeitsch. 1914, 59, 429). Bacterial action degrades tyrosine to phenol by removal of the alanine side-chain. Sieke (Z. Hyg. 1921, 94, 314) describes experimental conditions for the culture of phenol-forming bacteria and the morphological, cultural, and serological behaviour of *Bacillus coli phenologenes* and *B. paracoli phenologenes*. Varieties of *B. coli* capable of forming phenol are widely distributed.

By putrefactive decomposition, tyrosine is successively broken down into hydro-*p*-coumaric acid $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *p*-hydroxyphenylacetic acid $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *p*-cresol and phenol (Baumann, Ber. 1880, 13, 279; Zeitsch. physiol. Chem. 1880, 4, 304). The administration of tyrosine to normal animals causes the production of phenol in the urine, but no excess of hydroxy acids (Blendermann, *ibid.* 1882, 6,

234; Bied. Zentr. 1883, 209; Cohn, Zeitsch. physiol. Chem. 1894, 14, 189), except in one case when a man took 50 grms. of tyrosine in 24 hours, and this produced alcaptonuria, homogentisic acid being found in the urine (Abderhalden, *ibid.* 1912, 77, 454). Inactive tyrosine administered to cats undergoes selective decomposition, so that the urine contains more of the dextro- than of the naturally occurring laevo- variety, and on evaporating the neutral or alkaline urine containing the tyrosine, it is converted into the corresponding uramino acid which, on subsequent treatment with acid, readily loses water, yielding tyrosine hydantoin (Dakin, J. Biol. Chem. 1910, 8, 25). In the case of alcaptonurics, the administration of tyrosine or certain derivatives of tyrosine, such as mono-palmityl-*l*-tyrosine, distearyl-*l*-tyrosine, *p*-aminotyrosine, causes an increase in the amount of homogentisic acid excreted (Abderhalden and Massini, Zeitsch. physiol. Chem. 1910, 66, 140; Wolkow and Baumann, *ibid.* 1891, 15, 228).

Detection and estimation.—Tyrosine develops a red colour when warmed with Millon's reagent, and can be estimated by means of this reaction (Weiss, Biochem. Zeitsch. 1919, 97, 170). When tyrosine is dissolved in a few drops of warm concentrated sulphuric acid, and the diluted solution neutralised with barium carbonate, the filtrate gives a beautiful violet colour with ferric chloride (Pirea, Annalen, 1852, 82, 252). If a few drops of a solution of tyrosine are added to 2 c.c. of sulphuric acid containing 3 to 5 drops of a solution of aldehyde in twice its volume of alcohol of 90° , the liquid acquires a gooseberry red colour, the intensity of which is proportionate, between certain limits, to the quantity of tyrosine present (Denigès, Compt. rend. 1900, 130, 583). When tyrosine is added to a reagent consisting of 1 part of formalin, 45 parts of water and 55 parts of concentrated sulphuric acid, a green coloration is developed on boiling the mixture (Mürner, Zeitsch. physiol. Chem. 1902, 37, 86). Cf. Totani (Bio-Chem. J. 1915, 9, 391).

Tyrosine develops a rose-red colour under the influence of *tyrosinase*, the colour changing to a dirty violet, and finally a black precipitate of melanin is deposited (*v. Tyrosinase, art. FERMENTATION*). See also Raper and Wormal (Bio-Chem. J. 1925, 19, 84); Happold and Raper (Bio-Chem. J. 1925, 19, 92); Gortner (Proc. Soc. Exp. Biol. Med. 1924, 21, 543; Chem. Soc. Abstr. 1925, 128, i. 474).

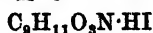
Tyrosine is readily estimated by titration with *N/5* sodium bromate in the presence of hydrochloric acid and sodium bromide, the liberated bromine being absorbed by the tyrosine with formation of dibromotyrosine (Millar, Trans. Guinness Lab. 1903, I. Part 1; Brown and Millar, Chem. Soc. Trans. 1906, 145). For the estimation of tyrosine in proteins, v. Plimmer and Eaves (Bio-Chem. J. 1913, 913, 7, 297); Johns and Jones (J. Biochem. 1918, 36, 319).

For the estimation of tyrosine in the presence of uric acid, see Herzfeld and Klinger (Biochem. Zeitsch. 1918, 88, 283; Fürth and Fleischmann (Biochem. Zeitsch. 1922, 127, 137); Folia and Looney (J. Biol. Chem. 1922, 51, 421).

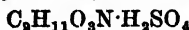
For a microchemical method of estimating

tyrosine, *see* Hanke and Koessler (J. Biol. Chem. 1922, 50, 235).

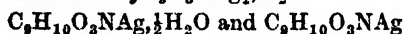
Salts and derivatives.—*L*-Tyrosine forms crystalline salts with mineral acids which dissociate in water, the *hydrochloride* $C_9H_{11}O_3N \cdot HCl \cdot 2H_2O$, *hydrobromide* $C_9H_{11}O_3N \cdot HBr$, *hydriodide*



nitrate $C_9H_{11}O_3N \cdot HNO_3$, and *sulphate*



are described (Haushofer, J. 1883, 1177; Aloy and Rabaut, Bull. Soc. chim. 1908, [iv.] 3, 391; Staedeler, Annalen, 1860, 116, 64); the *platinichloride* $(C_9H_{11}O_3N \cdot HCl)_2PtCl_4$ forms yellowish-brown readily soluble crystals (Gintl, Zeitsch. Chem. 1869, 704); the *picrolonate* blackens and sinters at 260° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127). The following metallic salts have been prepared, those of the heavy metals and the alkaline earth metals are sparingly soluble; the *copper salt* $(C_9H_{10}O_3N)_2Cu$ dissolves in 1230 parts of cold or 240 parts of boiling water (Hofmeister, Annalen, 1977, 189, 24); the *silver salts* $C_9H_9O_3NAg_2 \cdot H_2O$



the *mercury salts*, $C_9H_{11}O_3N \cdot 2HgO \cdot 2H_2O$

$C_9H_{11}O_3N \cdot 2HgO \cdot H_2O$ and $C_9H_{11}O_3N \cdot 3HgO \cdot H_2O$ the *barium salt* $(C_9H_{10}O_3N)_2Ba$; *calcium salt* $C_9H_9O_3N_2Ca$, the *mercury-calcium salt*

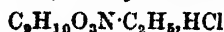


and the *sodium salt* $C_9H_9O_3NNa_2$ (Vintschgau, J. 1869, 895; Baumann, Zeitsch. physiol. Chem. 1880, 4, 320; Causse, Compt. rend. 1900, 130, 1196). Certain mercury salts are of therapeutic application, *v.* Dr. Bayer & Co., D. R. PP. 267411, 267412, and Hoffmann-La Roche & Co., D. R. P. 279957).

L-Tyrosine methyl ester $C_9H_{11}O_3N \cdot CH_3$ forms colourless prisms, m.p. 135°–136° (corr.); $[\alpha]_D^{20} = +25.75^\circ$ in methyl alcohol solution; the *hydrochloride* $C_9H_{10}O_3N \cdot CH_3 \cdot HCl$ forms colourless needles; *L*-tyrosine ethyl ester



has m.p. 108°–109°, $[\alpha]_D^{20} = +20.4^\circ$ in 5 p.c. alcoholic solution; the *hydrochloride*



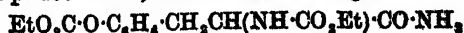
has m.p. 166° (Fischer and Schrauth, Annalen, 1907, 354, 21; Fischer, Ber. 1908, 41, 850; Lilienfeld, Archiv. Physiol. 1894, 383, 555; Röhmman, Ber. 1897, 30, 1978; Fischer, *ibid.* 1901, 34, 433). Tyrosine amyl ester, m.p. 68°–70°, yields a hydrochloride, m.p. 181°–182° (Curtius and Donselt, J. pr. Chem. 1917, [ii.] 95, 327).

L-Tyrosine anhydride $C_{18}H_{18}O_4N_2$ has m.p. 277°–280° (corr.), $[\alpha]_D^{20} = -223.8^\circ$ in N/1 sodium hydroxide (Fischer and Schrauth); *cf.* Graziani (Atti R. Accad. Lincei, 1916, [v.] 25, 1, 500); an anhydride $(C_9H_9O_3N)_2$, slender white crystals, m.p. 278°–279° (uncorr.), and an isomeric anhydride, a powder, m.p. 279°, are described. *d*-Tyrosine anhydride, m.p. 273°, has $[\alpha]_D = +37.59^\circ$ in alkaline solution, and $[\alpha]_D = +93.87^\circ$ in acid solution (Fränkel and Feldsberg, Biochem. Zeitsch. 1921, 120, 218).⁴ *L*-Tyrosineamide $C_9H_{10}ON \cdot CONH_2$ has m.p. 153°–154° and

$[\alpha]_D^{20} = +19.47^\circ$, condenses readily with ethyl chlorocarbonate to form the *monocarbethoxyl*

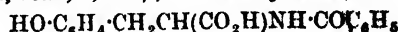


m.p. 155°–157°, and the *dicarbethoxyl*



m.p. 185° (corr.), derivatives; the *dinaphthalene-sulphonyl derivative* $C_{22}H_{18}O_3N_2S_2$ has m.p. 204° (corr.) (Koenigs and Mylo, Ber. 1908, 41, 4427).

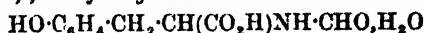
The following *acyl derivatives* of *L*-tyrosine are described: *N*-acetyl-*L*-tyrosine, m.p. 165°, by methylation with methyl sulphate gives *N*-acetyl-*O*-methyl-*L*-tyrosine, m.p. 147°–148°, which on hydrolysis yields *O*-methyl-*L*-tyrosine, m.p. 243° (Karrer, Gisler and others, Helv. Chim. Acta, 1922, 5, 469); the *benzoyl derivative*



m.p. 165°–166° (corr.), $[\alpha]_D^{20} = +19.25^\circ$ in 8 p.c. alkali solution, the *brucine salt* is crystalline; the *dibenzoyl derivative*



has m.p. 211°–212° and forms a *potassium* and a *cadmium salt* (Fischer, Ber. 1899, 32, 3638, 2454); the *formyl derivative*



m.p. 171°–174° (corr.), $[\alpha]_D^{20} = +84.8^\circ$ in 6 p.c. alcoholic solution (Fischer, *ibid.* 1907, 40, 3704); the *palmityl derivative*



m.p. 133°, $[\alpha]_D^{20} = +24.35$ in 1.8 p.c. alcoholic solution; *palmityl-L*-tyrosine-*palmitylether* $C_{41}H_{71}O_5N$, m.p. 95°–96°, $[\alpha]_D^{20} = +15.28^\circ$ in 1.7 p.c. alcoholic solution; *stearyl-L*-tyrosine-*stearylether* $C_{45}H_{79}O_5N$, m.p. 98°–108° (Abderhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61); *glycyl-L*-tyrosine methyl ester, m.p. 123°–124° (Geake and Nierenstein, Bio-Chem. J. 1915, 9, 309); the β -*naphthalene-sulphonyl derivative* forms a *hydrochloride* $C_{21}H_{19}O_3NSCl$, m.p. 170°, a *sodium salt* $C_{21}H_{18}O_3NSNa$, that decomposes at 175°, an *ethyl ester* $C_{21}H_{21}O_3NS$, m.p. 140°–143° (Abderhalden and Funk, *ibid.* 1910, 64, 436); the *di-β-naphthalenesulphonyl derivative* $C_{30}H_{26}SO_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot SO_2 \cdot C_{10}H_7$, m.p. about 120°, forms a *sodium salt*



m.p. 252°–254°, an *ammonium* and a *barium salt* (Fischer and Bergel, Ber. 1903, 36, 2592); the *phenylisocyanate derivative*



has m.p. 104°, and forms a *barium*



and a *silver salt* $C_{18}H_{18}O_4N_2Ag \cdot H_2O$ (Paal and Zitelmann, *ibid.* 1903, 36, 3337); the α -*naphthylisocyanate derivative* melts at 205°–206° (Neuberg and Manasse, *ibid.* 1905, 38, 2359).

For the *hydrazides* of the esters of tyrosine and benzoyltyrosine, *see* Curtius and Donselt (J. pr. Chem. 1917, [ii.] 95, 327).

dl-Tyrosinylcarbamide

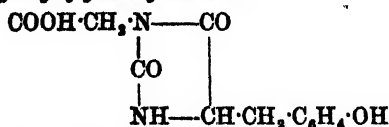


decomposes at 240° (Hugouvenq and Morel,

Compt. rend. 1906, 142, 48); *l*-tyrosinehydantonic acid $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\text{NH}\cdot\text{CONH}_2$, m.p. 218°, forms a crystalline silver salt (Jaffé, Zeitsch. physiol. Chem. 1882, 7, 306).

l-Tyrosinehydantoin $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}$ $\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{NH} \end{matrix}$ melts and decomposes at 242°–245° (Blendermann, l.c.).

Tyrosyl-glycinehydantoin



has m.p. 217°–218° (Johnson and Hahn, J. Amer. Chem. Soc. 1917, 39, 1255).

The alkaloid *surinamine* or *geoffroyine* from *geoffroya* bark is a *methyltyrosine*, in which the methyl has replaced one of the hydrogens of the amino group (Hiller-Bombien, Arch. Pharm. 230, 513; Blau, Zeitsch. physiol. Chem. 1908, 58, 153; Walpole, Chem. Soc. Trans. 1910, 97, 94).

O-Methyltyrosine choline forms a crystalline iodide, m.p. 137°–139°, the aurichloride has m.p. 112°–115°; the platinichloride, m.p. 204°.

Tyrosine-choline yields a crystalline iodide, m.p. 176°, and chloride (Karrer, Gisler and others, l.c.).

Derivatives of *l*-tyrosine containing substituents in the aromatic nucleus are: 3-nitro-*l*-tyrosine $\text{C}_8\text{H}_9\text{O}_5\text{N}_2$, obtained by nitration of *l*-tyrosine, forms yellow needles, m.p. 222°–224° (decomp.); $[\alpha]_D^{25} + 3.21^\circ$, hydrochloride, m.p. 237° (decomp.); cf. Johnson and Kohmann (J. Amer. Chem. Soc. 1915, 37, 1863 and 2598); Waser and Lewandowski (Helv. Chim. Acta, 1921, 4, 657). The barium and silver salts have been prepared, also the nitrate and sulphate (Strecker, Annalen, 1850, 73, 70; Casimir Funk, Chem. Soc. Trans. 1912, 1004). 3-Amino-*l*-tyrosine $\text{C}_8\text{H}_{11}\text{O}_3\text{N}_2$, needles, m.p. 287.5° (decomp.), $[\alpha]_D^{15} - 3.61^\circ$; hydrochloride, prisms, m.p. 175° (decomp.) (Waser and Lewandowski, l.c.), prepared by reducing nitrotyrosine. 3:5-Dinitrotyrosine $\text{C}_8\text{H}_5\text{O}_5\text{N}_2(\text{NO}_2)_2\cdot\text{H}_2\text{O}$, golden yellow crystalline plates, the ammonium and mercury salts, also the hydrochloride and the hydantoin and thiohydantoin derivatives have been prepared (Johnson and Kohmann, l.c. 2164).

Tyrosine sulphonic acid



is strongly acidic and gives a beautiful violet colour with ferric chloride. The ammonium, calcium and barium salts are described (Staedeler, l.c.).

3-Bromotyrosine



has a sweet taste, decomposes at 247°–248°; the hydrobromide decomposes at 190°–191°, the picrate and platinichloride are very soluble in water (Johnson and Bengis, J. Amer. Chem. Soc. 1912, 34, 1061).

3:5-Dibromo-*l*-tyrosine, m.p. about 245°

(decomp.), prepared by the action of bromine vapour on the finely divided tyrosine (Mörner, Zeitsch. physiol. Chem. 1913, 88, 124), is obtained in anhydrous, long, slender needles grouped into bundles or in thin plates hydrated with two molecules of water; it has $[\alpha]_D^{20} + 1.3^\circ$, dissolves in 218 parts of water at 16° or 26 parts of boiling water; the silver salt, the hydrochloride, hydrobromide and sulphate are crystalline, and it forms an unstable perbromide (Gorup-Besanez, Annalen, 1863, 125, 281; Millar, Trans. Guinness Lab. 1903, I. Part 1). 3:5-Di-bromo-*dl*-tyrosine crystallises with one molecule of water in transparent four-edged prisms or thick plates, m.p. about 245° (decomp.); it is nearly twice as soluble in water as the *l*-isomeride, it is not decomposed by concentrated sulphuric acid even on heating (Mörner, l.c.).

Chlorotyrosine, formed by the action of sulphuryl chloride on tyrosine suspended in acetic acid, melts at 257° and forms a benzoyl derivative, m.p. 195°, and a formyl derivative, m.p. 198° (Zeynek, Zeitsch. physiol. Chem. 1925, 144, 246).

3:5-Dichlorotyrosine, m.p. 252° (decomp.), prepared by chlorinating tyrosinehydantoin and decomposing with barium hydroxide the resulting 3:5-dichlorotyrosinehydantoin; the hydrochloride has m.p. 260°–265° (Wheeler, Hoffmann and Johnson, J. Biol. Chem. 1911, 10, 147). 3:5-dichloro-*l*-tyrosine, prepared by the action of chlorine on tyrosine in the presence of glacial acetic acid, has m.p. 256°–260° (decomp.), and the anhydrous hydrochloride gives in 5 p.c. aqueous solution $[\alpha]_D^{20} - 7.8^\circ$ (Zeynek, Zeitsch. physiol. Chem. 1921, 114, 275).

3:5-Di-iodotyrosine, iodogorgonic acid



is not found free in nature but is one of the constituent amino acids of certain proteids; it was first obtained by Dreschel (Zeitsch. Biol. 1896, 33, 85) from *gorgonin*, derived from the horny skeleton of *Gorgonia cavolinii*. This, on hydrolysis with barium hydroxide, yielded an iodo amino acid, hence name *iodogorgonic acid*. It was shown by Wheeler and Jamieson (Amer. Chem. J. 1905, 33, 365) that iodogorgonic acid is a di-iodotyrosine and can be prepared by the direct action of iodine on tyrosine. That it is the 3:5-di-iodotyrosine was shown later by Wheeler and Johns (*ibid.* 1910, 43, 11), for on treatment with methyl iodide and potassium hydroxide it yields the methylether of a di-iodotyrosinetrimethylammonium iodide



which on boiling with sodium hydroxide yields 3:5-diiodo-*p*-methoxyloinnamate. Iodogorgonic acid occurs in a large number of proteids, and has been isolated from *iodo-albacid*, *iodoglidin*, *iodocasein*, *gorgonin* and *spongine* (Oswald, Zeitsch. physiol. Chem. 1911, 70, 310; 71, 200; 74, 290; 75, 353).

3:5-Di-iodo-*dl*-tyrosine, prepared by hydrolysis of the above-mentioned proteids, crystallises from hot water in glassy right-angled plates, from alcohol in hexagonal plates, dissolves in 2164 parts of water at 15°, melts and decomposes at 200°.

3:5-Di-iodo-*l*-tyrosine, prepared by the

action of iodine on *L*-tyrosine, melts at 204° (Oswald), 196°–205° with decomposition (Wheeler and Jamieson); it has $[\alpha]_D^{20} = +2.27^\circ$ in 4.5 p.c. solution of 25 p.c. ammonia (Abderhalden and Guggenheim, *Zeitsch. physiol. Chem.* 1907, 54, 331). The hydrochloride



forms colourless needles, decomposed by water; the sulphate $\text{C}_9\text{H}_9\text{O}_3\text{NI}_2\cdot\text{H}_2\text{SO}_4$ is readily soluble; the silver salt $\text{C}_9\text{H}_9\text{O}_3\text{NI}_2\cdot\text{Ag}_2$ and copper salt $(\text{C}_9\text{H}_9\text{O}_3\text{NI}_2)_2\cdot\text{Cu}\cdot\text{H}_2\text{O}$ form amorphous precipitates. The acetyl derivative



decomposes at 225° (Wheeler and Jamieson, *Amer. Chem. J.* 1905, 33, 365). The methyl ester $\text{C}_9\text{H}_9\text{OI}_2\cdot\text{CH}_3\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{Me}$ decomposes at 192°; its hydrochloride forms colourless needles that decompose at 211° (corr.), and yields the nitrate on treatment with dilute nitric acid (Abderhalden and Guggenheim, *Ber.* 1908, 41, 1237). *Palmityl-3.5-di-iodo-tyrosinepalmityl ether* $\text{C}_{44}\text{H}_{84}\text{O}_8\text{NI}_2$ melts at 55°–60° (Abderhalden and Slavu, *Zeitsch. physiol. Chem.* 1909, 61, 405).

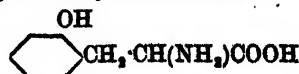
Tyrosinebisazobenzenearsenic acid



is a yellow microcrystalline powder which is insoluble in the usual organic solvents (Pauly, *Zeitsch. physiol. Chem.* 1915, 94, 234).

For the synthesis of *o*-tyrosine, v. Johnson and

Scott (*J. Amer. Chem. Soc.* 1915, 37, 1846). Starting with 2-thiohydantoin *o*-tyrosine-hydantoin is prepared, and this on hydrolysis with barium hydroxide yields *o*-tyrosine



m.p. indefinite; the hydrochloride crystallises from dilute hydrochloric acid in prismatic crystals which decompose at 180°.

A full account of the chemistry and physiological properties of tyrosine will be found in *Biochemisches Handlexikon*, von Abderhalden, vol. iv. part 2, 681–702. M. A. W.

TYSONITE. Fluoride of cerium metals (Ce, La, Di) F_3 , crystallised in the hexagonal system. It is pale wax-yellow with resinous lustre, and a perfect pearly cleavage parallel to the basal plane. Sp.gr. 6.13. The mineral alters very readily to the fluo-carbonate bastnäsité, and the chestnut-brown crystals as usually found are really pseudomorphs of bastnäsité after tysonite with sometimes still a nucleus of the original mineral. Crystals and irregular masses up to several pounds in weight are found at several places in the coarse-grained granite of the Pike's Peak district in El Paso Co., Colorado. P. Geijer (*Geol. För. Förh. Stockholm*, 1921, 43, 19) suggests that tysonite is identical with the Swedish fluorite. L. J. S.

TYUYAMUNITE v. TURANITE.

U

UARANA v. GUARANA.

ULCO. An alloy of lead with small amounts of barium and calcium, used as a substitute for antimonial lead in the manufacture of shrapnel. It is suggested that it may be employed as a bearing metal on account of its high melting-point, excellent structure, and low coefficient of friction.

ULEXINE v. CYTISINE.

ULEXITE (*Boronatrocalcite* of G. L. Ulex, 1849; *Natroborocalcite*). A hydrated borate of sodium and calcium $\text{NaCaB}_5\text{O}_9\cdot 8\text{H}_2\text{O}$, containing 43.0 p.c. B_2O_3 ; sp.gr. 1.65; H. 1; slightly soluble in hot water, and readily soluble in acids. It forms rounded, white masses, 2–3 ins. in diameter, consisting of a loose aggregate of fine, silky fibres; hence the popular name 'cotton-ball.' It occurs abundantly in the borate deposits of Nevada and California, and forms the main mass of those near Iquique in Chile, and Jujuy province in Argentina. L. J. S.

ULLMANNITE. Nickel sulph-antimonide NiSbS , crystallised in the cubic system with tetrahedral symmetry. The antimony is sometimes partly replaced by arsenic; and in the *willymanite* variety, from Broken Hill in New South Wales, half the nickel is replaced by cobalt. The mineral is easily mistaken for galena, since it has a good cubical cleavage. The cleavage is, however, less perfect than in galena, and the colour is steel-grey rather than bluish-grey; further, ullmannite (H. 5½) readily scratches galena. Sp.gr. 6.6–6.7. The mineral is decomposed by nitric acid with separation of antimony oxide and sulphur. It occurs in mineral

veins at several places in the Rhineland, at Lölling and Waldenstein in Carinthia, Mount Ar in the Pyrenees, and as good crystals at Monte Narba in the Sarrabus district of Sardinia. It has been found in small amount in a barytes vein in the New Brancepeth Colliery near Durham. L. J. S.

ULMARENE (*mesoten*). Trade name for salicylic methoxymethyl ester.

ULMITE. A term applied to a form of humus-covering grains of a black friable sandstone found along the coast of New South Wales (Steel, *Proc. Linnæan Soc. N.S.W.* 1921, 46, 213).

ULTRAMARINE. Ultramarine was first artificially made on a commercial scale in 1828, by Guimet, who earned the prize of 6000 francs offered by the 'Société d'Encouragement' of France for its production at a cost not exceeding 90s. per lb. About the same time, Gmelin (*Ann. Chim.* 1828, [ii.] 37, 409) independently discovered how to prepare ultramarine on a laboratory scale. According to Heintze (*J. pr. Chem.* 1891, [ii.] 43, 98), ultramarine was being made by Kottig, director of the laboratory of the Königl. Porzellan-manufaktur in Meissen, at the time when Guimet and Gmelin were claiming the priority of the discovery.

Until 1828 ultramarine was obtained by powdering and washing *lapis-lazuli* (q.v.); its composition was first determined by Clément and Désormes (*Ann. Chim.* 1806, [i.] 57, 317).

Properties.—Artificial ultramarine blue occurs in commerce as a bright, azure blue, impalpable powder, insoluble in water. Its constituent elements are sodium, aluminium, silicon,

sulphur, and oxygen. Heated to 200°–300° with water in a sealed tube, it leaves a colourless residue free from sulphur, while sodium sulphide passes into solution. It also loses its sulphur when heated with mercuric oxide (Chabrie and Levallois, *Compt. rend.* 1906, 143, 222). Ultramarine is quite stable towards alkalis, but is readily decomposed by dilute acids, some sulphur being precipitated and hydrogen sulphide evolved. It is also decomposed by alum solution, owing to the formation of an aluminium derivative. Yellow phosphorus reduces it to a leuco compound, which again becomes blue when heated in air. The preceding reactions seem to indicate the presence of some kind of polysulphide in ultramarine; but it is unaltered by concentrated and fuming sulphuric acid, and also by a mixture of glacial acetic acid and acetic anhydride (Hoffmann and Metzner, *Ber.* 1905, 38, 2482), reagents which instantly decompose polysulphides and thiosulphates. Ultramarine withstands a red heat fairly well, although it loses its brilliancy, and becomes greenish; hence it is difficult to imagine that the blue colour is due to free sulphur, as has been suggested (Paterno and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.] 16, i. 465). Ultramarine blue when strongly heated in hydrogen loses some of its sulphur, but still retains its blue colour. It becomes violet when heated to dull redness in chlorine. It possesses hydraulic properties and increases the binding power of cement (Rohland, *Zeitsch. angew. Chem.* 1904, 17, 609).

When heated with aqueous silver nitrate at 120°–140° in a sealed tube for 15 hours, no silver sulphide is produced, but a dark yellow *silver ultramarine* is obtained, together with silver nitrite and other products (Unger, *Dingl. poly. J.* 1874, 212, 232; Heumann, *Ber.* 1877, 10, 991, 1345, 1888; 1897, 12, 60, 784; *Bull. Soc. chim.* 1877, [ii.] 28, 570; 1878, 30, 326, 327; 1880, 33, 60, 302; *Annalen*, 1879, 189, 253; 1880, 201, 262; Philipp, *Ber.* 1877, 10, 1227; Forcrand and Ballin, *Bull. Soc. chim.* 1878, [ii.] 30, 112; Chabrie and Levallois, *l.c.*). Silver ultramarine is produced by replacement of the sodium in ordinary ultramarine by silver; when fused with various metallic chlorides or iodides the silver is replaced by other metals, and in this way have been obtained *potassium* (blue), *lithium* (blue), *barium* (yellowish-brown), *zinc* (violet), *manganese* (grey), *ultramarines*, &c. Heated with the requisite organic iodide, silver ultramarine is decomposed, yielding *ethyl*, *amyl*, *benzyl*, and *phenyl ultramarines*, and silver iodide (Forcrand, *Compt. rend.* 1879, 88, 30; *Bull. Soc. chim.* 1879, [ii.] 31, 161). Mercurous nitrate solution heated with ultramarine yields a greyish-blue mercurio-ultramarine, which loses mercury on heating and leaves a pure blue residue, which becomes yellow on heating and again blue on cooling, this change being capable of indefinite repetition. Cadmium yields an olive-green product. Lead replaces the sodium completely. Ammonium and calcium ultramarines have also been prepared. Ferrous ultramarine is dark greyish-blue and is readily decomposed by acids. These substances regenerate ultramarine when heated with sodium chloride. They do not evolve hydrogen sulphide when treated with cold hydrochloric acid

(Chabrie and Levallois, *l.c.*). *Selenium* and *tellurium* ultramarines have also been produced, in which sulphur is substituted by either selenium or tellurium (Guimet, *Ann. Chim.* 878, [v.] 13, 102; Plicque, *Bull. Soc. chim.* 877, [ii.] 28, 518; 1878, 29, 522; 1878, 30, 51; Morel, *ibid.* 28, 522). Light blue *boron ultramarine* has been prepared by fusing together anhydrous borax, boric oxide, and either sodium or potassium sulphide, sulphite, or thiosulphate (Hoffmann, *Zeitsch. angew. Chem.* 1906, 19, 1089; 1907, 20, 568; *Chem. Ind.* 1911, 34, 699).

Ultramarine blue crystallises in the regular system, isomorphous with the minerals *hauyn*, *sodalite*, and *nosean*.

Green ultramarine is formed as an intermediate product in the manufacture of ultramarine blue, and is converted into the latter by roasting with sulphur. According to Philipp (*Ber.* 1876, 9, 1109), sulphur is not taken up in the change from green to blue, which can be effected by heating with water in a sealed tube at 100°; a small amount of sodium compound is removed by the water. Heated in chlorine, green ultramarine turns bluish-violet; sodium sulphide solution turns it grey.

White ultramarine is obtained by completely excluding air during the roasting of the materials in the manufacture of ultramarine, and is converted into blue ultramarine when heated in either chlorine, oxygen, or sulphur dioxide (Philipp, *Ber.* 1876, 9, 1109; 1877, 10, 1227; Böttger, *Annalen*, 1876, 182, 311; Hoffmann, *ibid.* 1878, 194, 1).

Red ultramarine was first obtained by Scheffer in the course of preparing the ordinary substance, by heating the materials very strongly in a muffle freely exposed to air; it contains less sodium and more aluminium than the blue variety (Scheffer, *Ber.* 1873, 6, 1450; Büchner, *Dingl. poly. J.* 1879, 231, 446; Zettner, *Ber.* 1875, 8, 259, 353).

Red ultramarine has been prepared by passing chlorine and steam over heated ultramarine blue. It is also obtained by the action of nitric oxide on the blue compound, sulphur being removed in the process. It is decomposed by acids without evolution of hydrogen sulphide, but evolves sulphur dioxide, and is not changed by alum solution. Heated out of contact with air it is changed into a blue product. It now yields hydrogen sulphide with acids.

Yellow ultramarine is obtained by heating the red variety in air for a short time at 360°, or at a little higher temperature (Hoffmann, *Annalen*, 1878, 194, 1). According to Büchner (*Ber.* 1874, 7, 990), both the yellow and red forms are produced by heating blue ultramarine to 300°–400° in oxygen or sulphur dioxide; the colour changes to red and then to yellow. If chlorine is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green and then reddish-yellow (Zettner, *Ber.* 1875, 8, 259, 353).

Violet ultramarine is obtained when the reddish-yellow product previously mentioned is heated with sodium hydroxide (Zettner, *l.c.*). It becomes blue when heated to dull redness or when further heated with an alkali hydroxide, and nitric acid vapours turn it red.

The violet variety was first prepared by

Leykauf in 1859 by allowing moist calcium chloride to react with warm ultramarine blue. In 1872 Wunder prepared it by heating the blue form in chlorine at 300° and treating the product with water. It has been manufactured from ultramarine blue by heating the latter, in thin layers, on earthenware trays at 280°, and passing steam over it to remove sulphur. The temperature was then lowered to 160°, and a mixture of chlorine and steam led over it for 3 hours. For further details, and other methods, v. Wunder, *Chem. Zeit.* 1890, 14, 1119; *ibid.* *Zeitsch. anorg. Chem.* 1912, 77, 209.

Composition.—The various varieties of ultramarine have not yet been satisfactorily shown to possess uniform compositions. In fact, commercial blue ultramarines are manufactured in three different grades, containing different proportions of silica and sulphur. Moreover, it is not possible to obtain products of identical composition even when, in repeated operations, the relative amounts of the different raw materials are maintained constant and the working conditions duplicated as exactly as possible. The following analyses of different samples of ultramarine blue rich in silica indicate its variable composition:—

	Rawlins			Parry and Coste		
	1	2	3	4	5	6
H ₂ O	0.7
SiO ₂	38.9	39.6	42.7	42.3	41.7	42.4
Al ₂ O ₃	29.5	24.0	24.5	26.8	25.2	24.0
Na ₂ O	21.0	19.2	20.0	19.5	18.8	18.7
S	10.8	13.1	13.0	12.0	14.2	15.4

The differences in composition between ultramarines of different colours are shown by the following numbers, taken from Jordan (*Zeitsch. angew. Chem.* 1893, 684):—

	White (Hofma)	Green (Philipp)	Blue (Philipp)	Blue (Philipp)	Violet (Wunder)	Red (Wunder)	Light bl (Wunder)
Na	21.5	17.02	15.66	14.66	11.7	8.1	11.9
Al	16.6	15.81	15.39	12.55	13.1	13.3	13.1
Si	17.0	17.51	16.87	17.29	19.4	19.3	19.7
S	6.4	7.91	5.69	11.38	13.3	15.2	12.7
O	38.4	—	—	—	42.1	43.4	42.0
H	—	—	—	—	0.4	0.7	0.6

The two analyses of ultramarine blue (Philipp) in the table refer to the varieties poor and rich in silica respectively.

The constitution of ultramarine is naturally a matter of great uncertainty, in view of what has been said concerning its composition. It is commonly regarded as a combined silicate and polysulphide of sodium and aluminium, but objections to this view have already been mentioned. For the numerous formulae that have been proposed for ultramarines, v. Rawlins, *J. Soc. Chem. Ind.* 1887, 6, 791; Szilasi, *Annalen*, 1889, 251, 97; Guckelberger, *ibid.* 1882, 213, 182; Dingl. poly. J. 1883, 247, 343; Clarke, *Amer. Chem. J.* 1888, 10, 126; Brögger and Bäckström, *Jahresber. Tech.* 1891, 454; Rohland, *Zeitsch. angew. Chem.* 1909, 17, 609; Abegg's *Handbuch der Anorganischen Chemie*, vol. iii. pt. i.

The blue colour is considered to depend on (1) the presence of an alkali metal; (2) the

direct union of a part of the sulphur with metal; (3) the presence of a part of the sulphur in a lower state of oxidation. Neither aluminium nor silicic acid is essential (Wunder, *Zeitsch. angew. Chem.* 1915, 28, 147; 1917, 30, i. 161; 1920, 33, 23).

The similarity in composition exhibited by ultramarines of quite different colours suggests that the actual colouring material may represent only a small fraction of the total mass; it has been supposed that such a small amount of a coloured substance is present, disseminated throughout a colourless body in a state of solid solution (Rohland, *l.c.*). J. Hoffmann (*Chem. Zeit.* 1910, 34, 823) has suggested that this coloured substance is sulphur; the comparative stability of ultramarine at a red heat does not lend support to this assumption. It is noteworthy, however, that were it not for the presence of sulphur, ultramarine would be expected to be colourless.

Alkali fusion of ultramarine converts the blue colour into a dark red. Since, according to Ostwald, alkali appears to enhance the dispersion of disperse sulphur systems, and since, as in the case of colloidal gold, greater dispersion is accompanied by a change in colour from blue to red, it is considered that the above experimental result is in support of the theory that the colour principle of ultramarine is colloidal sulphur (I. T. Keine, *Chem. Zeit.* 1923, 47, 513).

The silicon dioxide in ultramarine may be displaced by boron trioxide without the disappearance of the blue colour, and the amount of this substance may greatly vary without much alteration in colour. Other solvents for colloidal sulphur manifest a blue colour; thus potassium thiocyanate if dehydrated and heated to redness becomes blue, but it becomes colourless on cooling; phosphoric oxide also acquires a deep blue colour on fusing with sodium sulphide at 900°, but the colour disappears on cooling. The blue colour of the solution obtained by dissolving disulphur trioxide in concentrated sulphuric acid is probably due to the presence of colloidal sulphur.

Uses.—Ultramarine is extensively used in a variety of manufactures. Its large consumption is due to two characteristics: brilliancy as a body colour, and high colouring power. As a body colour it is used in calico-printing, and wall-paper printing, for colouring writing paper and printing-ink, preparing blue pigments, and blueing mottled soap. As a 'whitening' agent it is very valuable, its great strength and purity of tone correcting the yellow tinge in writing and printing papers, cotton and linen goods, paper pulp, whitewash, soap, starch, and ven sugar. It is extensively used in the manufacture of square and ball blue for laundry use.

Tests and analysis.—(i) Dilute 0.1 grm. of a standard sample of ultramarine with 0.6 grm. of pure powdered chalk, and determine the amount of chalk that must be added to 0.1 grm. of the sample under examination in order to match the colour of the diluted standard; this gives an indication of the value of the sample. (ii.) Heat a sample in hydrogen to 400°. A good ultramarine becomes grey and then green, the change taking about half an hour; a bad specimen changes in a few minutes. (iii.) Stir

a little of the powder under examination in a cold saturated solution of alum, and note the length of time required for decolorisation; compare with a standard sample ground equally fine (iv.) Shake up with water and alcohol to detect adulteration with coal-tar dyes.

For the quantitative analysis, the substance may be treated as a silicate readily attacked by dilute hydrochloric acid (*v. ANALYSIS*); in the filtrate from the aluminium the sodium may be determined as the sulphate. The determination of sulphur should be effected on a separate portion, by oxidation to sulphuric acid with *aqua regia* or fuming nitric acid, and subsequent estimation as barium sulphate. See also Andrews, Analyst, 1910, 35, 157.

MANUFACTURE OF ULTRAMARINE.

The only ultramarines prepared on a large scale are the blue and green sodium-sulphur-ultramarines. Three chief varieties of ultramarine blue are found in commerce:—

Glauber salt or sulphate ultramarine, the palest variety. It has a slight greenish tinge, small covering power, and is the form most readily attacked by alum.

Soda ultramarine low in sulphur, a pure blue variety, darker than the preceding, and having more covering power.

Soda ultramarine rich in sulphur and silica, the darkest variety, with a reddish tinge. It has high covering power, and is the form most resistant towards alum; consequently it finds extensive use in paper blueing.

Ultramarine is produced when aluminium silicate is calcined with sodium sulphide; the silicate is employed in the form of china clay, or a similar material, with the addition of silica if necessary; sodium sulphide is produced during the manufacture, either from sodium carbonate, carbon, and sulphur, or from sodium sulphate, carbon, and sulphur. The relative proportions of the ingredients is an important factor in the manufacture of ultramarine, but different authorities recommend different mixtures. With materials of the best quality, the following mixtures are said to be the best for producing the three varieties mentioned above:—

Ultramarine blue	Pale	Medium	Dark
China clay . . .	100	100	100
Soda	9	100	103
Glauber salt . . .	120	0	0
Carbon	25	12	4
Silica (Kieselguhr) .	0	16	16
Sulphur	16	60	117

If the clay employed differs in composition from china clay, the relative proportions of clay and silica must, of course, be suitably adjusted.

The manufacture of ultramarine blue is carried out either by (i.) the *direct* or (ii.) the *indirect* process. All ultramarines rich in silica and a certain amount of the other varieties poorer in silica are made by the former method; but the majority of the ultramarines poor in silica are prepared by the latter method, in which ultramarine green is found as an intermediate product. Both these are dry processes; wet methods have been described and patented, but

do not seem to have been adopted on a large scale (Knapp, J. pr. Chem. 1885, [ii.] 32, 375; 1888, 38, 48; Molvor, Eng. Pat. 9200, 1890; Molvor and Cruickshank, Eng. Pat. 19411, 1892).

For general accounts of the manufacture of ultramarine, *v. Rawlins*, J. Soc. Chem. Ind. 1884, 6, 791; Pichot and Grangier, *ibid.*, 1888, 7, 573; Röhrig, Chem. Zeit., 1883, 567; Wunder, *ibid.*, 1890, 14, 1119; Jordan, Zeitsch. angew. Chem. 1893, 684.

Raw materials.—*China clay*, and French, German, and Bohemian *pottery clays* are used, and always require levigation. The clay must be very finely divided, and free from excessive amounts of iron and manganese oxides. For *soda*, the best soda ash, known as carbonated ash, is employed; it must be stored in a dry place. The *Glauber salt* must be free from acid and iron, and well calcined; it should be ground in stone edge-runner mills before use. *Rod or stick sulphur*, containing very little non-volatile matter, is usually employed, since poorer forms of sulphur produce dirty shades of colour; like the Glauber salt, it is reduced to a fine powder before use. *Carbon* should not contain more than 4 p.c. of moisture; that made from pine trunks is preferred, and is ground in ball mills

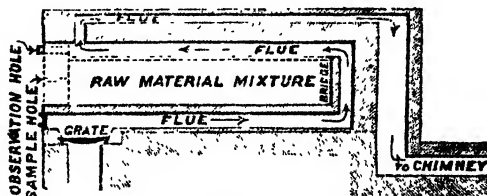


FIG. 1.

and stored in a dry place. Charcoal is sometimes replaced by pitch, tar, colophony, &c. If coal is used, it must be of good quality, and free from sand, stones, and pyrites. *Silica* is usually employed in the form of kieselguhr, but sometimes quartz is used; the latter is ignited and then quenched in water to cause it to break up, being finally dried and ground to powder. Silicious carbon, such as charred rice husks, may partly or wholly replace the carbon and silica (Cross, Eng. Pat. 3174, 1903).

Direct process.—The formation of ultramarine blue by this process is effected by roasting the well-mixed raw materials, allowing access of air during the operation. The successive operations involved are mixing, roasting, lixiviating, wet-grinding, levigating, pressing, drying, and sifting.

The most intimate and cheapest mixture is obtained when the various raw materials have been ground first in edge-runner mills, and then in balance mills. With mixtures containing much sulphur, the other ingredients should first be well mixed, the sulphur then added, and further mixing effected. The mixtures should, in any case, be calcined as soon as they are prepared.

The 'mass' oven, so called from the mixture being treated in a mass, produces directly very good ultramarine if carefully managed. Fig. 1 gives an idea of the arrangement. The raw materials, well mixed and ground, are shovelled

on to the floor of the oven, pushed up to the end with a broad rake, and, after being piled up to nearly the level of the bridge, are nearly flattened, and covered with thin tiles, the joints being filled in with a very thin mortar made with china clay and sand. The oven having been thus filled with about 1 ton of raw material, the front is built up, leaving a hole just above the level of the tiles for observation, fitted with a loose brick. A small hole below this and about opposite the centre of the mass, fitted with a clay stopper, affords a means of taking samples as the burning proceeds. The heat is slowly raised to a bright red, and as it rises small jets of sulphur dioxide are seen to come from the cracks between the covering tiles and burn with feathery flames, increasing in length as the heat becomes greater, and gradually dying away as the reaction is completed. The heat is maintained at its highest point for from 12 to 18 hours, or until the process appears to be finished, when a sample is taken through the small hole by means of a long auger inserted right into the middle of the mass. The sample presents, if sufficiently burnt, a greenish-blue appearance, gives off sulphur dioxide freely without actually burning, and on being spread upon a clean tile quickly loses its heat, and appears a blue colour with a tinge of green. The changes experienced by the mixture are interesting and remarkable. As introduced it is a yellowish-grey, and becomes successively brown, green, and blue. The brown, a dark rich colour, is very unstable, and burns on exposure to air to a greenish half-formed ultramarine, and, even if not exposed, slow combustion goes on until oxidation has taken place. The green is almost equally unstable.

When the drawn sample is found to be sufficiently burnt, the operation is concluded by closing the oven, plastering up cracks, and excluding the air as far as possible. It is then left to cool down, which takes a week or 10 days. On opening, the mass should appear dark blue, the bottom portion not being quite equal in brilliancy to the top owing to the greater degree of heat to which it has been subjected. A loss of about one-third of the original weight occurs, and the mass shrinks considerably.

Charges amounting to 5 tons are treated in stone troughs, 17-20 ft. long and 10-13 ft. wide, placed in a furnace in such a way that they can be reached on all sides by the flame. The troughs are filled to a depth of 12-16 ins. covered with firebricks, and calcined for about 3 weeks.

Ultramarine blue is also prepared directly in shaft furnaces (Fig. 2), described later on (p. 259). Various special furnaces have been patented (Fr. Pata. 410055, 1909; 407098, 403247, 399211, 400103, 1908; 403077, 1909; 425585, 1910).

A rapid process for the direct preparation of the blue has been patented (Fr. Pata. 391770, 391790, 1908). A mixture of china clay (35 parts), carbon (10 parts), sodium alum (40 parts), rosin (8 parts), and sulphur (7 parts) is heated rapidly to 600°-700°, and maintained at that temperature for about 3 hours; the temperature is then raised to 900°, and the mass stirred well for an hour to oxidise it. Powdered sodium

chlorate is then added and the mass stirred for 15 mins.; a further 30 mins. heating then follows. Ultramarine of very superior quality is said to be thus obtained.

Curtius has patented a continuous process. Cast-iron retorts, similar to gas retorts, are employed, lined inside with fire-proof cement. They are set in brickwork, and connected with flues for removing the gases and receivers for condensing sulphur vapour. The charged retorts are closed back and front, but arrangement is made for the admission of air from behind, in order to quickly convert the green ultramarine initially formed into blue. In a modified form of the process, green ultramarine is first produced, discharged into brickwork receptacles beneath the retorts, and directly oxidised to blue (Eng. Pat. 18527, 1890).

The lixiviating, &c. is described later (p. 259).

Indirect process.—The successive stages in

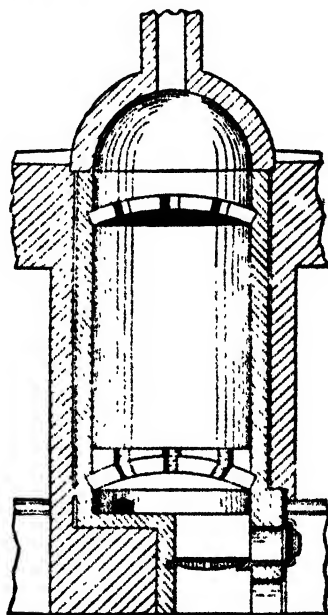


FIG. 2.

this process are mixing, calcining for ultramarine green, crushing, roasting to ultramarine blue, and lixiviating, &c., as in the direct process.

The preparation of the ultramarine green is carried out in either a *crucible* furnace or a *shaft* furnace. The former is a kind of muffle furnace, similar to those used in porcelain works, of square (seldom round) section and lined with firebrick. The ground mixture is filled into tapered crucibles of 12-16 ins. high, the lids are fixed on with a mortar of clay, and the crucibles piled in regular rows in the furnace. A furnace will hold several hundred crucibles, the aggregate charge being 6-8 cwt. of mixture. The temperature is slowly raised until the crucibles are at a bright-red heat, and this temperature is then maintained until the formation of ultramarine green is completed; from 7 to 10 hours are required. It is essential to maintain a uniform temperature throughout the furnace.

When the reaction is finished all openings into the furnace are shut tightly and the furnace allowed to cool down, a process that takes several days.

Shaft furnaces are used for calcining larger quantities, up to 2 tons, of material. These are large, cylindrical, vertical furnaces, lined with firebrick. The furnace is situated at the bottom of the shaft; it is covered in by a firebrick vault, the flat top of which forms the floor upon which the bottom layer of crucibles rests. Numerous openings in the vault allow the heating gases from the furnace to pass up into the shaft. The shaft is filled with crucibles charged with the ground mixture, and arranged layer upon layer. Another vault forms the roof of the shaft proper, and through openings in this the gases pass into a dome and thence into the chimney. Fig 2 shows such a furnace. These furnaces possess many advantages; they require no special fuel, accommodate large charges and permit the heat to be equally distributed in a very satisfactory manner. Soda mixtures low in sulphur must be heated slowly at first in these furnaces, a bright-red heat being only attained in 4 hours.

The green ultramarine thus produced exhibits a blue tinge on the surface, and if required to be sold as such, the blue outer portions must be

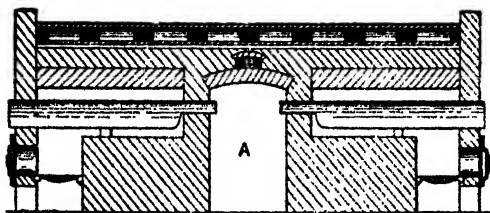


FIG 3.

removed. This is unnecessary if the product is to be directly converted into blue; it must, however, be crushed and ground to powder.

The material is crushed in roller mills to pieces about the size of peas. Glauber salt greens are then ground in dry mills to a degree of fineness that must be determined by preliminary trials, since if ground beyond a certain degree, the brightness of the final ultramarine blue suffers. Soda greens are much softer than Glauber salt greens, and the application of further pressure during the final grinding must be avoided as much as possible. They are usually ground in ball mills, which may be so constructed as to render the preliminary crushing of the raw green superfluous.

The crushed ultramarine green is converted into blue by roasting it with sulphur; the change is completed in a shorter time by this process than if ammonium chloride, hydrochloric acid, chlorine, &c., are used in the place of sulphur. During the process part of the sodium contained in the green becomes converted into sodium sulphate. Two types of furnace are in extensive use (i.) cylindrical or retort furnaces, and (ii.) muffle furnaces.

The former type consists of an arrangement of strong cast-iron tubes, not exceeding 80 in. long by 16 in. diameter, generally arranged in

sets of three, so that the flame entirely surrounds them. They project about 2 in. from the furnace, both at the back and front, and the ends are closed by tight-fitting sheet-iron caps. The arrangement adopted in large works is indicated in Fig. 3; the furnaces are mounted in pairs, back to back. All the gaseous products pass into the narrow corridor A, closed at both ends by doors; through openings in the roof they pass into the flue B, and thence to the chimney.

In the other type of furnace, the muffle is built into the furnace. The hearth is made of strong fireclay plates with lap joints, luted together, the whole surface being then smoothed. The hearth of the muffle forms the cover of the heating chamber; the products of combustion pass from the grate upwards through flues arranged on the sides of the muffle-walls, thence over the arched roof to the chimney. If the muffle is constructed entirely of fireclay, it is built in completely at the back, and a semi-circular hole left in the front, the base of which is on a level with the hearth. This opening, through which the muffle is charged and discharged, can be closed when necessary by a counterpoised iron slide; and since sulphurous gases escape from this opening, it is arched over with a hood for leading these gases to the chimney, an arrangement that is far less convenient and safe than that employed in the cylindrical furnaces. Sometimes the muffle is built with an iron top, and the front of the muffle closed with an iron cap.

The actual roasting process is carried out either (i.) by adding sulphur to the ultramarine green before heating, or (ii.) by heating the green and gradually adding the sulphur during the process. The requisite amount of sulphur is 7 p.c. with soda green, and 9-10 p.c. with Glauber salt green, of the weight of the crude green taken. In carrying out process (i.), the empty retorts or muffles are heated to a medium red heat for soda green, or to bright redness for Glauber salt green. The mixture of green and sulphur is then quickly introduced, and the containing vessels closed. After half an hour, the product is thoroughly mixed and levelled down, a process that is repeated at half-hourly intervals, until all the sulphur has been burnt off. This is indicated by the manner in which the green colour changes to blue. A further 45 mins. heating is given, and then the fire slowly reduced. The retorts and muffles are then tightly closed and allowed to cool. When method (ii.) is employed, the retorts or muffles are charged with ultramarine green, which is raked over and levelled. The successive portions of sulphur added amount to about 1½ lbs. each with retorts (½ cwt. charge), and 4½ lbs. each with muffles (1½ cwt. charge). The first addition of sulphur may be made when a lump of that substance ignites as soon as it is thrown on the ultramarine; the charge is then raked over, and the sulphur allowed to burn away. This operation is repeated until a bright blue product is obtained; samples are withdrawn at intervals and spread out with a steel spatula to examine the colour. The product is then cooled as described under (i.).

The filtering boxes employed in the *lithiation* process are made of pins, 5-7 ft. long.

40–60 in. wide. About 6 or 8 in. above the solid bottom a false bottom is mounted, perforated with many $\frac{1}{4}$ -in. holes, and covered with strong cotton filtering cloth. The cold, calcined ultramarine blue is mixed with a small quantity of hot water (75°–80°) in a vat, thoroughly mixed, and transferred to a filtering box. In this manner all the numerous filtering boxes are charged. The clear filtrates are united, and if sufficiently concentrated (15°B. or more) the liquid is run into crystallising tanks for the recovery of sodium sulphate. Weaker solutions, and the first two or three washings, are concentrated by utilising waste heat from the furnaces. The ultramarine is washed with hot water until quite free from soluble sulphate, of which the crude blue contains about 15 p.c. It is then ground wet in upright mills between hard stones until the requisite fineness is obtained. During this operation sodium silicate passes into solution, and it is therefore necessary to use soft water for the grinding. The whole is then run into a large wooden vat and allowed to settle for 36–48 hours.

The *levigating process* follows next. The top blue liquor is baled out into another vat and left until the extremely finely divided particles of colour have settled; the product is afterwards added to other preparations. The paste remaining in the large vat is distributed in quantities of about 2 cwt. into levigating tanks, three-fourths filled with soft water, and the colour equally distributed throughout the water. The larger particles settle rapidly, and after 2 hours standing the liquids are run into other tanks. The next deposition of ultramarine takes 5 or 6 hours; the liquid is then baled into other tanks, and a further settling of colour for 12 hours is allowed. The liquid now baled off contains extremely finely divided particles; they are precipitated in a fourth series of tanks by the addition of alum, dilute mineral acid, milk of lime or other saline solutions, and the resulting blue paste is pressed. Passing from the first to the fourth series of tanks, the ultramarine becomes successively lighter, finer, bluer, and stronger. The different grades of product are then dried in sheds exposed to air, or on drying hearths heated by waste furnace heat, or in special drying rooms, &c.

The product dries in hard lumps, which must be powdered and sifted; for this purpose ball mills fitted with a continuous sifting device are employed. Very fine brands of ultramarine are sifted in centrifugal sifters or else in a Jasse sifter. It then remains to mix together the various shades and sorts in order to produce the standards of sale; this part of the work is of great importance, as the tinctorial power, fineness of division, depth and purity of colour in each standard, have to be exactly reproduced in bulk.

In making the cheaper brands of ultramarine blue, the pure material is mixed with from 10 to 50 p.c. of gypsum. The latter has an extremely bad effect upon the brightness of certain kinds of ultramarine, which is minimised by incorporating a little glycerol or vaseline into the

competition soon brought this down, and created a demand. Guimet commenced the manufacture in 1828. Between 1830 and 1840 manufactories were established at Cologne and Nuremberg; between 1840 and 1850 nine more were started; 1850–1860 saw nine more; 1860–1870 at least a dozen, and from 1870–1888 four or five, while an equal number of the others had closed down. At the present day there are about a hundred factories, mainly in Germany and France, although a few are in England, Austria, and the United States, and the annual production of ultramarine is between ten and fifteen thousand tons.

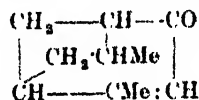
For further information on ultramarine, *v.* Zerr and Rübenkamp's *Treatise on Colour Manufacture*, translated by Mayer (Griffin & Co.); Bersch's *Mineral and Lake Pigments*, translated by Wright (Scott, Greenwood & Son); and Hoffmann's *Ultramarine* (Vieweg u. Sohn, Braunschweig).

ULTRAMARINE, GREEN, *v.* **ULTRAMARINE**; also **CHROMIUM**.

ULTRAMARINE, YELLOW, *v.* **ULTRAMARINE**. The term is also applied to *Barium Chromate*, *v.* **BARIUM**; also **CHROMIUM**.

UMBELLIFERONE *v.* **GUM RESINS**.

UMBELLULARIA CALIFORNICA (Nutt). An evergreen tree indigenous to California, known locally as 'California Laurel,' 'Mountain Laurel,' 'California Bay-tree,' 'Spice-tree,' 'Pepper-wood,' &c. The essential oil is an aromatic liquid possessing a peculiar pungency due to the presence of a ketone *umbellulone* ($C_{10}H_{14}O$)



which forms 60 p.c. of the essential oil; the other constituents are eugenol, 1.7; eugenol methyl ether, 10; *l*-pinene, 6.0; cineol 20.0 p.c.; saffrole and fatty acids, traces (Power and Lees, *Chem. Soc. Trans.* 1904, 85, 629; Tutin, *ibid.* 1906, 89, 1104; 1908, 93, 252).

UMBELLULIC ACID *v.* **HEXDECANOIC ACIDS**.

UMBELLULONE *v.* **LAURUS NOBILIS**.

UMBER. A brown mineral pigment, consisting of a mixture of the hydrated oxides of iron and manganese, mechanically associated with a large proportion of earthy matter of variable character. The material is prepared for the market by grinding and levigation. Raw umber is exported from Cyprus, Turkey, and Umbria in Italy (hence the name). It is also worked to a limited extent in Derbyshire and Pennsylvania.

Sir A. H. Church (*The Chemistry of Paints and Painting*, London, 1901) gives the following analysis of a choice sample of raw umber from Cyprus; water, given off at 100°C., 4.8 p.c.; water expelled at a red heat, including organic matter, 8.8; Fe_2O_3 , 48.5; MnO_2 , 19; CaO , 1.4; MgO , 0.5; Al_2O_3 , 2.1; P_2O_5 , 0.9; SiO_2 , 13.7; CO_2 , &c., 0.3. Part of the manganese probably exists as Mn_2O_3 . For other analyses of umber, *siennas*, and *ochres*, *v.* G. H. Hurst in *Chem. News*, 1889, 59, 172. He found crude Darby-

development of the manufacture of ultramarine has been remarkable. The price in the year of its discovery was about 16s. per lb., but

shire amber to yield the following results: hygroscopic water, 13.47 p.c.; combined water, 5.17; BaSO_4 , 30.10; SiO_2 , 4.43; CaSO_4 , 2.15; CaCO_3 , 2.61; Al_2O_3 , 8.08; Fe_2O_3 , 22.50; MnO_2 , 11.53. A sample of amber, from Caldbeck Fells, Cumberland, as prepared for market by grinding and washing gave: Fe_2O_3 , 47.14; MnO_2 , 11.17; CuO , 3.23; Al_2O_3 , 7.66; SiO_2 , 24.70; combined water, 6.18; CaO , MgO , traces=100.08 (J. Soc. Chem. Ind. 1890, 953, where are given details of the method of preparation).

Hurst regards most ochres as alteration products, formed mainly by the oxidation and hydration of pyrites *in situ*, and mechanically mixed with silica, clay, and other earthy matter. Umbers may have been washed as a fine sediment from deposits of iron and manganese ores. The pigment termed *burnt umber* is merely umber which has been exposed to heat, whereby its colour becomes somewhat reddened. *Cologne umber* is an earthy lignite.

References.—G. P. Merrill, *The Non-Metallic Minerals*, 2nd ed., New York, 1910, 104; chapter on Mineral Paints in *Min. Res. U.S. Geol. Survey*, annual volumes; v. OCHRE.

L. J. S.

UNAL. Trade name for solid hydrochloride of *p*-aminophenol, used as a photographic developer. Rodinal is a concentrated solution of the same compound.

UNDECATOIC ACIDS and **UNDECYLIC ACID** v. **HENDECATOIC ACIDS**.

UPAS ANTIAR v. **ANTIAR RESIN**.

UPAS TIEUTE v. **NUX VOMICA**.

URACIL v. **ERGOT** and **PYRIMIDINES**.

URALITE. A name proposed by G. Rose in 1831 for pseudomorphs of hornblende after augite from the Ural Mountains. (For a *résumé* of the literature, v. A. Wilmore, *Geol. Mag.* 1910, [v.] 7, 357.) Also used as a trade-name for a preparation of serpentine-asbestos, made into the form of boards for fire-proof partitions (v. **ASBESTOS**).

URAMIL v. **PYRIMIDINES**.

URANINITE v. **PITCHBLEND**.

Alfred Schoep (*Bull. Soc. chim. Belg.* 1923, 32, 274–281) has analysed specimens of Katanga pitchblende, estimating total uranium as U_3O_8 and UO_2 in presence of UO_2 by Hillebrand's method of heating the mineral in a sealed tube with dilute sulphuric acid in an atmosphere of carbon dioxide, and volumetric estimation of the dioxide with potassium permanganate. The results lead to the conclusion that the purified mineral (i.e. uraninite) has the formula $(\text{UO}_2)_2(\text{UO}_3)_2$ (cf. Blomstrand, *Chem. Soc. Abstr.* 1884, 1102). This is discussed in comparison with results obtained by other workers for pitchblende from Katanga and other sources, and also for thorianite, and reasons are given for regarding the UO_2 as an oxidation product of the UO_3 , of which the original mineral consisted. Thus the author maintains that the formula of uraninite is UO_3 , as that of thorianite is ThO_2 , the two minerals being isomorphous and analogous in chemical composition. The percentage of the dioxide is greater in fresh specimens of the mineral; some consist of $\text{ThO}_2 \cdot \text{UO}_2$, in which all the uranium compound has undergone oxidation. Thorianite contains

various proportions of UO_2 , and isomorphous mixtures of the two dioxides may be prepared artificially (*Chem. Soc. Abstr.* 1923, 124, ii. 647).

URANITE. An early name for the 'uranium micas' in use before these had been separated into the following species, the most important of which are autunite (calco-uranite) and torbernite (cupro-uranite) (*qq.v.*).

Torbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, tetragonal.

Zeunerite $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, tetragonal.

Autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic.

Uranospinite $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic.

Uranocircite $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic.

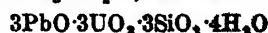
L. J. S.

URAMINO ANTIPYRIN. Trade name for antipyrilurea.

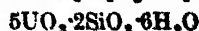
URANIUM. Sym. U. At.wt. 238.2 (238.17 Hönigschmid; 238.5 Richards and Merigold; Lebeau). In 1789 Klaproth prepared from *pitchblende* some compounds of a new element, which he called *uranium* (Crell's *Ann.* 1789, [ii.] 400). The compounds of uranium were studied by Richter, Arfvedson, Berzelius, and others. In 1840 Péligot showed that what had previously been thought to be uranium was really one of its oxides; he prepared the metal by reducing uranous chloride with potassium (*Ann. Chim.* 1842, [iii.] 5, 5). The work of Péligot was confirmed and extended by Ebelmen (*ibid.* 1842, [iii.] 5, 189), Wertheim (*ibid.* 1844, [iii.] 11, 49), Rammelsberg (*Pogg. Ann.* 1842, 55, 318; 56, 125), and Hermann (Ueber einige Uranverbind. Göttingen, 1861).

Occurrence.—Uranium is not very abundant; its chief ore is *pitchblende* or *uraninite*, which consists of impure U_3O_8 , and is found in Cornwall, at Joachimsthal (Bohemia), and other localities. It contains from 40 to 90 p.c. of U_3O_8 (Hermann, *J. pr. Chem.* 1859, [i.] 76, 326; Ebelmen, *Ann. Chim.* 1843, [iii.] 8, 498; Whitney, *Amer. J. Sci.* 1849, [ii.] 7, 434; Gentz, *ibid.* 1857, 23, 421; Zimmermann, *Annalen*, 1886, 232, 300). *Clevite* and *bröggerite* are varieties of pitchblende rich in rare earths. *Carnotite* is a vanadate of potassium and uranium, found in Utah and Colorado (Friedal and Cumenge, *Bull. Soc. chim.* 1899, [ii.] 21, 328). *Samarskite* is a uranotantalite of iron and yttrium, found in Siberia (Miask) and North Carolina (Rammelsberg, *Pogg. Ann.* 1877, 160, 658); *fergusonite* is a complex columbate of yttrium, cerium, uranium, calcium, and iron (Rammelsberg, *ibid.* 1873, 150, 200).

Schoep, of the University of Ghent, has identified several new uranium minerals, to which he has assigned the following formulae: *curite*, $\text{PbO} \cdot 5\text{UO}_2 \cdot 4\text{H}_2\text{O}$; *kasolite*



dewindtite, $\text{PbO} \cdot 2\text{UO}_2 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; *soddite*



becquerelite, $\text{UO}_2 \cdot x\text{H}_2\text{O}$. A uranotitanocolumbate of calcium containing small amounts of rare earth has been designated as *mendeleeffite*; the chemical formula has not been established definitely, but the mineral contains approximately U_3O_8 23.6 p.c., and CaO 15 p.c. It is considered as a variety of *betafite*, but contains

no water of crystallisation (J. Soc. Chem. Ind. 1923, 42, 1061).

Nearly all the phosphates, silicates, and zirconates of the rare earths contain small quantities of uranium, notably *zenotime*, *ascshenite*, *columbite*, *cerite*, and *monazite*. *Thorianite* (v. THORIUM) contains from 10 to 20 p.c. of uranosouranic oxide. See also Szilárd, Le Radium, 1909, 6, 233.

Naturally occurring uranium minerals are radioactive; it was from the pitchblende of Joachimsthal that radium was first prepared, whilst helium was originally obtained from cleveite.

Treatment of uranium minerals; preparation of uranium.—The chief source of uranium compounds is pitchblende, which, after a preliminary roasting, is heated in a reverberatory furnace with sodium carbonate. The product is extracted with warm dilute sulphuric acid and filtered, the residue being used in the preparation of radium salts. The filtrate is worked up commercially for uranium compounds as described under sodium diuranate (p. 265). The following method is due to Wöhler; the liquid is treated with hydrogen sulphide to remove arsenic, antimony, copper, lead, and bismuth, and after oxidising the filtrate with nitric acid, excess of ammonia is added. The washed precipitated iron hydroxide and ammonium uranate are digested at 100° with concentrated ammonium carbonate, containing ammonia in excess, to dissolve the ammonium uranate. The double salt, ammonium uranyl carbonate, crystallises out on cooling the filtered liquid. From the mother liquor a quantity of ammonium uranate can be obtained by precipitating any zinc, nickel, and cobalt with ammonium sulphide, and evaporating the filtrate. Both ammonium uranate and ammonium uranyl carbonate leave the green oxide U_3O_8 when ignited in the air.

Carnotite is fused with potassium hydrogen sulphate and the mass extracted with water; from the solution the double sulphates of uranium and vanadium with potassium sulphate are crystallised out. The crystalline product is reduced with zinc and sulphuric acid, and the vanadium then precipitated with ammonia and ammonium carbonate. From the filtrate the uranium is thrown down as ammonium uranate by boiling (Gin, Chem. Zentr. 1906, ii, 1172; cf. Haynes, Mines and Minerals, 1909, 30, No. 3, 139).

Separation of uranium from thorium and rare earths in pitchblende.—The mineral is dissolved in nitric acid and the silica removed in the usual manner. The filtrate is repeatedly evaporated to dryness for the elimination of free acid. The residue is dissolved in water; the solution in a beaker is neutralised exactly with a few drops of very dilute ammonia, strongly diluted, and boiled for 10 minutes with excess of thiosulphate. After standing 24 hours the precipitate is filtered off, well washed with water containing a little thiosulphate, dissolved in hydrochloric acid, and re-precipitated, after elimination of free acid, as before. If properly performed, the second precipitation removes the last of the cerium. The precipitate, which contains part of the uranium, is dissolved in hydrochloric acid, and the thorium precipitated as oxalate. The

filtrate is evaporated to dryness in a porcelain dish, and the residue cautiously heated with strong sulphuric acid for the decomposition of the oxalic acid; the acid is finally heated until strong fumes appear, and the uranium precipitated with ammonia after cooling and diluting the solution. The filtrate from the thiosulphate precipitate, containing the balance of the uranium is freed from rare earths by means of oxalic acid. The excess of precipitant is destroyed as before, and the iron separated from uranium by precipitation with ammonium carbonate, uranium being again precipitated with ammonia. The united uranium precipitates are ignited and weighed (W. Riss, Chem. Zeit. 1923, 47, 765–766; Analyst, 1923, 48, 626).

Metallic uranium was first prepared by Péligot (l.c.) by reducing the tetrachloride with potassium. Zimmermann (Annalen, 1883, 216, 1) replaced the potassium by sodium (cf. Lely and Hamburger, Zeitsch. anorg. Chem. 1914, 87, 209). It is better to employ the double chloride of uranium and sodium, and magnesium may be used in place of potassium (Moissan, Compt. rend. 1896, 122, 1088). These methods are unsatisfactory, since uranium tetrachloride is extremely hygroscopic. Uranium is best prepared by heating 500 parts of the oxide U_3O_8 with 40 parts of sugar carbon in the electric furnace in a carbon tube. The product, which contains a little carbon, is purified by heating it in a crucible brasqued with uranium oxide, and embedded in another crucible brasqued with titanium, to prevent access of nitrogen to the uranium (Moissan, Compt. rend. 1893, 116, 349). Reduction of uranium dioxide by carbon begins at 1500° (Greenwood, Chem. Soc. Trans. 1908, 93, 1492). The oxides of uranium may also be reduced by heating with aluminium powder (Aloy, Bull. Soc. chim. 1901, [iii.] 25, 153; Stavenhagen, Ber. 1899, 32, 3065; Stavenhagen and Schuchard, *ibid.* 1902, 35, 909; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii, 239; cf. E. Rideal, J. Soc. Chem. Ind. 1914, 33, 673). Uranium may also be prepared by the electrolysis of the fused double chloride of uranium and sodium, in an inert atmosphere, using carbon electrodes (Moissan, Compt. rend. 1896, 122, 1088); and is obtained in the pyrophoric state by heating its amalgam in a vacuum (Féree, Bull. Soc. chim. 1901, [iii.] 25, 622).

According to R. W. Moore (Trans. Amer. Electrochem. Soc. 1923, 96), metallic uranium is conveniently prepared by reducing with metallic sodium the green crystalline tetrachloride, obtained by heating the oxide U_3O_8 to 500°C. for several hours in a current of sulphur chloride, vapour, and subliming the product in a current of chlorine. The resulting mass is broken up in an atmosphere of nitrogen and mixed with metallic sodium that has been distilled *in vacuo* and cut into small pieces under anhydrous benzene. The mixture is heated in a steel bomb in a vacuum, and the reaction product is extracted first with absolute alcohol to remove excess of sodium, then with water to remove sodium chloride, and finally with 2 p.c. acetic acid. The heavy brownish residue of metallic uranium is washed with acetone and dried *in vacuo*. A yield of 90 p.c. of the theo-

retical quantity of metal containing 99.8 p.c. U is readily obtained. The powder is very pyrophoric, but may be pressed into discs in a hydraulic press in an atmosphere of nitrogen, and is then no longer pyrophoric. These discs may be melted by the arc in an atmosphere of rarefied argon to bright, steel-grey, ductile, metallic buttons, which readily tarnish on exposure to the air (J. Soc. Chem. Ind. May 11th, 1923, 406).

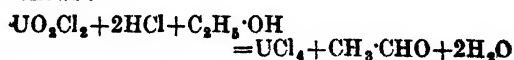
Properties.—Pure uranium is a white metal, which takes a high polish; its density is 18.7, and its specific heat 0.02765 (Zimmermann, *Annalen*, 1886, 232, 310; Ber. 1882, 15, 851). It melts at a white heat, and can be distilled in the electric furnace (Moissan, *Compt. rend.* 1906, 142, 425; cf. *ibid.* 1893, 116, 1429; 1896, 122, 1088). The most prominent lines in the emission spectrum are in the yellow (Thalén, *Ann. Chim.* 1869, [iv.] 18, 239; Hasselberg, K. Svenska. Vet.-Akad. Handl. 1910, 45, 3; Pollok, *Sci. Proc. Roy. Dubl. Soc.* 1909, 11, 331). Most uranium compounds possess marked absorption spectra (Morton and Bolton, *Chem. News*, 1873, 28, 47, 113, 164; Jones and Strong, *Phil. Mag.* 1910, [vi.] 19, 566; Strong, *Zeitsch. physikal. Chem.* 1910, 11, 668) and are fluorescent, the fluorescence spectra having been studied by E. Becquerel (*Ann. Chim.* 1872, [iv.] 27, 539) and H. Becquerel (*Compt. rend.* 1885, 101, 1252; 1907, 144, 459); v. also Becquerel and Kamerlingh-Onnes (*ibid.* 1910, 150, 647) for phosphorescence at low temperatures.

Uranium in the form of powder is unaltered in dry air at ordinary temperatures; it burns in oxygen at 170°. It unites directly with fluorine in the cold, and with chlorine, bromine, and iodine when gently heated. At 500° it combines with sulphur and selenium, and at 1000° unites readily with nitrogen. It forms a crystalline carbide decomposed by water (Moissan, *Compt. rend.* 1896, 122, 1088). It forms alloys with certain metals; that with iron is pyrophoric, this property varying directly with the content of uranium.

Uranium powder decomposes water slowly at ordinary temperatures, more rapidly at 100°. It dissolves readily in hydrochloric, sulphuric, and nitric acids.

Uranium is closely allied to the elements chromium, molybdenum, and tungsten; they all exhibit a maximum valency of six, yield acidic trioxides, and form numerous halogen derivatives in which their valencies vary from two to six. These halogen derivatives in general bear little resemblance to well-defined salts, as is indicated by their volatility, solubility in numerous organic media, and the ease with which they are hydrolysed by water. There are two principal series of uranium salts: (i.) the *uranous* compounds, corresponding to the basic oxide UO_2 ; and (ii.) the *uranyl* compounds, in which the group UO_2 functions as a bivalent metallic radiola. Besides these, there exist *uranates*, *diuranates*, and *peruranates*, analogous to the corresponding chromium derivatives (v. O. de Coninck, *Bull. Acad. roy. Belg.* 1909, 175). The *uranous* salts are usually green or blue, and in solution are readily oxidised to uranyl compounds, even by air, the rate of oxidation being

proportional to the concentration of the solution and inversely proportional to the square of the concentration of the hydrogen ions present (McCoy and Bunzel, *J. Amer. Chem. Soc.* 1909, 31, 367.) They are obtained by the reduction of uranyl compounds (v. Alloy and Auber, *Bull. Soc. chim.* 1907, [iv.] 1, 569; Colani, *Ann. Chim.* 1907, 12, 59). The *uranyl* salts are generally yellow, with a greenish fluorescence. They are highly sensitive to light, and are employed in photography (Niepce de Saint Victor, *Compt. rend.* 1858, 46, 448, 489; Titlestad, *Zeitsch. physikal. Chem.* 1910, 72, 257; Bacon, *Philippine J. Sci.* 1910, 5, 281). Under the influence of light, uranyl salts are converted into uranous salts in the presence of the acid entering into the constitution of the salt and a readily oxidisable substance such as alcohol. The reaction which occurs is as follows:—



Two molecules of acid are necessary for each molecule of uranyl salt. In this way, the fluoride, chloride, bromide, iodide, and sulphate have been prepared, and an aqueous solution of the nitrate. If an insufficient amount of acid is present, basic salts are obtained. If the reaction is allowed to proceed further, a black precipitate of uranous hydroxide is obtained (Bauer, *Schweiz. Chem. Zeit.* 1918, 2, 40; Hatt, *Zeitsch. physikal. Chem.* 1918, 92, 513). Oxidations and reductions brought about by uranium compounds under the influence of light are closely related to the changes which the uranium salt itself undergoes. Thus when alcohol or dextrose is added to a 1 p.c. solution of uranium acetate the former is oxidised and the latter is reduced to the violet oxide $\text{U}_3\text{O}_8\cdot 2\text{H}_2\text{O}$. If in addition methylene blue is added to the above solution the dextrose is oxidised and the methylene blue is reduced, the uranium salt playing the rôle of an oxido-reducing catalyst. Aldehydes and lower fatty alcohols can all be similarly oxidised, and the progress of the reaction can be followed by the reduction of the uranium salt or of methylene blue; the phenols, although readily oxidisable under ordinary circumstances, behave anomalously, owing to the antioxygen character of these substances, and they are not oxidised themselves, nor do they allow the oxidation of other substances to proceed. A red coloration is produced on adding the uranium compound to the phenol solution, but no other apparent change occurs. The solution does, however, contain a certain amount of uranous salt, and the violet oxide can be precipitated from it by heating to 100°C. (Alloy and Valdignié, *Compt. rend.* 1923, 176, 1229; *J. Soc. Chem. Ind.* 1923, 42, 574 A). Uranyl salts are somewhat analogous to basic salts, but they are stable in solution, being only hydrolysed to a slight extent. On electrolysis the uranyl ion UO_2^{2+} migrates to the cathode. Uranyl salts form numerous complex derivatives, especially with salts of organic acids (Dittrich, *Zeitsch. physikal. Chem.* 1899, 29, 449; Ley, *ibid.* 1900, 30, 193; Ber. 1900, 33, 2658; Kohlschütter, *Annalen*, 1900, 311, 1).

Uranium salts are radioactive, emitting α rays, and producing a radioactive element.

called *Uranium-X* (*v. infra*, URANIUM-X and RADIOLOGY).

For the relation of uranium-X to uranium-Z, see Hahn (Zeitsch. physikal. Chem. 1923, 103, 461).

Atomic weight.—This was taken as *circa* 120 until Mendeléeff pointed out the similarity of uranium to chromium, molybdenum, and tungsten, and proposed the value 240 (Annalen, Suppl. 1872, 8, 178; Chem. News, 1880, 41, 39), which assigned to uranium a position in the Periodic Classification in the same Group as the elements just mentioned. The determination of the specific heat of the metal and the vapour densities of uranous chloride and bromide (Zimmermann, Annalen, 1882, 216, 1) confirmed the views of Mendeléeff. The actual value at present adopted (238.5) rests mainly on the work of Zimmermann (Annalen, 1886, 232, 299), Aloy (Ann. Chim. 1901, [vii.] 24, 418); of Richards and Merigold (Proc. Amer. Acad. 1902, 37, 365; Zeitsch. anorg. Chem. 1902, 31, 235); of Lebeau (Compt. rend. 1912, 155, 163); and of Hönigschmid (Compt. rend. 1914, 158, 2004).

OXIDES AND OXYACIDS.

Uranium dioxide or *Uranous oxide* UO_2 is obtained by heating the green oxide or uranyl oxalate in a stream of hydrogen (Berzelius, Péligot, Ebelmen); or by electrolysing uranyl nitrate solution (O. de Coninck and Camo, Bull. Acad. Roy. Belg. 1901, 321); these methods yield a brown pyrophoric powder of sp.gr. 8.2. The reduction of uranyl chloride solution with magnesium or aluminium yields uranous oxide as a black powder (de Coninck, *ibid.* 1909, 744). It is obtained as black, microscopic crystals by reducing crystalline uranic hydroxide in hydrogen (Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368); and as jet black octahedra by fusing the amorphous form with borax, and washing the product with dilute hydrochloric acid (Hillebrand, Zeitsch. anorg. Chem. 1893, 3, 249). It is a basic oxide, and dissolves in concentrated acids to form green uranous salts. It combines directly with chlorine and bromine, forming uranyl chloride and bromine, and burns when heated in air, the oxide U_2O_3 being produced.

On a technical scale it is prepared for the production of ferro-uranium by fusing 35 parts of sodium chloride, 20 parts of sodium uranate, and 1 part of powdered charcoal in a cast-steel pot. The cooled mass is lixiviated with water and the uranium oxide washed by decantation, and is freed if necessary from iron and aluminium by treatment with 5 p.c. hydrochloric acid.

Uranous hydroxide $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ is precipitated by adding an alkali to a solution of a uranous salt and boiling; it forms black flakes, and readily dissolves in dilute acids (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranium trioxide, uranic oxide, uranic anhydride, or uranyl oxide UO_3 is a chamois yellow powder, obtained by heating uranyl nitrate to 250° ; also by heating the hydroxide or double uranyl ammonium carbonate to 250° (Ebelmen, Ann. Chim. 1842, [iii.] 5, 199; de Coninck, Compt. rend. 1901, 132, 204; Bull. Acad. Roy. Belg. 1904, 363, 448; Lebeau, Compt. rend. 1912, 154, 1808). It oxidises to

the green oxide when heated in air, and is reduced by hydrogen to uranous oxide. In contact with water it is transformed into uranic acid $\text{UO}_2(\text{OH})_2$. When heated *in vacuo* at 502° it forms the oxide U_2O_5 .

This oxide is slightly basic, but only one-third of its oxygen can be replaced by acidic radicles; the salts thus produced are of the type UO_2R_2 , and are called *uranyl* compounds. Towards strong bases, uranic oxide behaves as an acid anhydride, similar to chromic anhydride.

For heat of formation see, Mixter, Amer. J. Sci. 1912, [iv.] 34, 141.

Uranic hydroxide or uranic acid $\text{UO}_2 \cdot \text{H}_2\text{O}$ or $\text{UO}_2(\text{OH})_2$ is best prepared by heating a solution of uranyl nitrate in alcohol until no more brown fumes are evolved, and washing the yellow precipitate with boiling water (Malaguti, Ann. Chim. 1843, [iii.] 9, 463). It may also be obtained, mixed with the dihydrate, by evaporating a solution of uranyl nitrate to complete dryness (de Coninck, Compt. rend. 1909, 148, 1462). The *dihydrate* $\text{UO}_2 \cdot 2\text{H}_2\text{O}$, which is obtained as a yellow precipitate by boiling the double uranyl ammonium carbonate with water, loses water at 100° , and yields the hydroxide $\text{UO}_2 \cdot \text{H}_2\text{O}$ (Ebelmen, *l.c.*; for other methods, *v.* Jacquelin, Ann. Chim. 1842, [iii.] 5, 199; Riban, Compt. rend. 1881, 93, 1140; Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368). Uranic hydroxide has a sp.gr. of 5.9; it does not alter in air, and when heated to 300° it is dehydrated. For the preparation of the colloidal hydroxide, *v.* Szilárd, J. Phys. Chem. 1907, 5, 488, 636.

Uranosouranic oxide or Green oxide of uranium $\text{U}_2\text{O}_5 (= \text{UO}_2 \cdot 2\text{UO}_3)$ occurs more or less pure as *pitchblende*. It can be obtained by heating any of the other oxides to a red heat in air, also by igniting ammonium uranate or any uranium salt of a volatile acid. It forms a dark-green, lustrous powder of sp.gr. 7.2, insoluble in water; in concentrated acids it dissolves, forming a mixture of uranous and uranyl salts. This oxide is employed for producing a black glaze on porcelain. It is radioactive, and has been suggested as a suitable standard of α -ray radioactivity (McCoy and Ashman, Amer. J. Sci. 1908, 26, 521).

A violet hydroxide can be obtained by the action of light on aqueous uranyl oxalate or alcoholic uranyl acetate (*v.* Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368; *cf.* Aloy and Rodier, *ibid.* 1920, [iv.] 27, 101). A large number of violet compounds of uranium exist, all of which, by loss of their acid radicles, tend to become transformed into the green hydrated oxide $\text{U}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$. When heated in a current of hydrogen the oxide U_2O_5 shows signs of reduction at 625° , the reduction being complete at 650° , the product being UO_2 . In a vacuum U_2O_5 may be heated to 2000° before it dissociates to UO_2 .

Uranium pentoxide is a black powder, used for producing a black glaze on porcelain. According to Zimmermann (Annalen, 1886, 232, 273) it is a mixture of U_2O_5 and UO_3 .

Uranium peroxide UO_4 is only known in the hydrated form as *peruranic acid* $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. It is obtained by adding hydrogen peroxide to a mixture of uranyl and uranous sulphate in aqueous solution, and drying the precipitate

over concentrated sulphuric acid (de Coninck, Bull. Acad. Roy. Belg. 1909, 692; cf. Fairley, Chem. Soc. Trans. 1877, 31, 133; Zimmermann, Annalen, 1886, 232, 273; Alibegoff, *ibid.* 1886, 233, 123). It forms a yellow powder, which loses oxygen when heated; when treated with alkali hydroxides it yields a mixture of alkali uranate and peruranate.

Other hydrates are also known (Hüttig and von Schroeder, Zeitsch. anorg. Chem. 1922, 121, 243). These substances are probably compounds of uranium trioxide and hydrogen peroxide. It is doubtful if uranium tetroxide exists.

URANATES.

The alkali uranates are formed by precipitating uranyl salts with alkali hydroxides; those of the other metals by adding ammonia to a mixture of a uranyl and a metallic salt. They are yellow, insoluble in water, but soluble in acids. The majority are of the type $M_2O \cdot 2UO_3$, analogous to the dichromates (v. Drenkmann, J. 1861, 255; Patera, J. pr. Chem. 1850, 51, 125; Debray, Ann. Chim. 1861, [iii.] 61, 514; Grandeau, *ibid.* 1886, [vi.] 8, 224; Zimmermann, Annalen, 1882, 213, 290; Ditte, Compt. rend. 1882, 95, 988; de Coninck, Bull. Acad. roy. Belg. 1909, 173, 835).

Ammonium uranate. This is obtained as a yellow, voluminous precipitate by adding ammonia to a solution of a uranyl salt. It is prepared by boiling a solution of uranyl sodium carbonate with ammonium sulphate; or by boiling sodium diuranate (*q.v.*) with concentrated ammonium chloride solution, and forms a fine, deep yellow-coloured powder, that is sometimes used commercially, under the name *uranium yellow*, in the preparation of uranium glass (v. Stolba, Zeitsch. anal. Chem. 1864, 3, 74) and sodium diuranate.

Potassium uranate K_2UO_4 , obtained by fusing uranyl chloride with a mixture of potassium and ammonium chlorides (Zimmermann, *l.c.*), forms yellow, rhombic crystals.

Potassium diuranate $K_2U_2O_7$ is obtained in the form of a trihydrate by precipitating a uranyl salt with potassium hydroxide and drying the product at 100° (Patera, *l.c.*).

Sodium uranate Na_2UO_4 may be obtained by fusing the green oxide with sodium chloride and sodium carbonate (Ditte, *l.c.*; Zimmermann, *l.c.*).

Sodium diuranate $Na_2U_2O_7$ is prepared commercially from pitchblende, which is powdered and roasted to remove the greater part of the sulphur, arsenic, and molybdenum. The ore is then heated in a reverberatory furnace with sodium carbonate and a little sodium nitrate. The product is washed with water, when soluble arsenate, molybdate, tungstate, and vanadate of sodium are removed; sodium uranate is insoluble in water. The insoluble residue is dissolved in dilute sulphuric acid, the solution evaporated to remove excess of acid, diluted and filtered from silica, lead sulphate, and basic sulphate and arsenate of bismuth, and an excess of sodium carbonate solution added. A solution of uranyl sodium carbonate is thus obtained, while the basic

carbonates of iron, aluminium, nickel, and cobalt are precipitated and removed. The uranium is then precipitated as sodium diuranate by adding sodium hydroxide, or by neutralising with sulphuric acid and boiling. The yellow precipitate is thoroughly washed, dried, and pulverised (Patera, J. pr. Chem. 1849, [i.] 46, 182; 1850, 51, 122; Gieseke, J. 1852, 779; Anthon, J. 1860, 698; Kessler, J. 1857, 199; Hofmann and Strauss, Ber. 1900, 33, 2316; cf. Metzger and Heidelberger, J. Amer. Chem. Soc. 1909, 31, 1040).

Sodium diuranate is found in commerce as the hexahydrate $Na_2U_2O_7 \cdot 6H_2O$. It is a fine yellow powder, known as *uranium yellow*, and is used in painting and staining glass and porcelain, and for making the fluorescent 'uranium glass.'

PERURANATES.

These salts are formed by the action of hydrogen peroxide and alkali hydroxides on uranyl salts, and are usually precipitated by means of alcohol as orange-yellow crystals. The sodium salt has the formula $Na_2UO_6 \cdot 8H_2O$. These compounds have been studied by Fairley (Chem. Soc. Trans. 1877, 31, 134) and Melikoff and Pissarjewsky (Ber. 1897, 30, 2092; Zeitsch. anorg. Chem. 1898, 18, 59; J. Russ. Phys. Chem. Soc. 1902, 24, 472).

A red potassium peruranate $K_2UO_6 \cdot 3H_2O$ is obtained when peruranic acid is added to hydrogen peroxide containing alcohol, and the solution treated with potassium hydroxide (Aloy, Bull. Soc. chim. 1903, [iii.] 29, 292). The formation of this substance may be employed as a delicate colorimetric test for the presence of uranium (Aloy, *ibid.* 1902, [iii.] 27, 734).

URANIUM COMPOUNDS.

Uranium tetrafluoride or *Uranous fluoride* UF_4 is the main product of the action of fluorine on uranium. It is prepared by adding hydrogen fluoride to a solution of uranous chloride, and forms a green powder, insoluble in water and dilute acids (Smithells, Chem. Soc. Trans. 1883, 43, 125; Bolton, J. 1886, 209). It leaves a residue of oxide when heated in air; and forms double fluorides with the alkali fluorides.

Uranium hexafluoride UF_6 is best obtained by the action of fluorine on the cooled pentachloride—



It forms colourless, monoclinic prisms, which sublime at ordinary temperatures under diminished pressure. It melts at 69.2° under a pressure of two atmospheres, and boils at 56.3° . The solid has a density of 4.68; the vapour gives a value 11.7 (air=1). It is very hygroscopic, and highly reactive (Ruff and Heinzelmann, Zeitsch. anorg. Chem. 1911, 72, 63; cf. Ber. 1909, 42, 492).

Uranium trichloride UCl_3 is obtained by heating the tetrachloride in hydrogen (Péligot, Ann. Chim. 1842, 5, 20), and is a reddish-brown substance, which easily dissolves in water, forming a red solution that slowly evolves hydrogen and becomes green.

Uranium tetrachloride or *Uranous chloride*

UCl_4 is produced when uranium is heated in chlorine, and is prepared by passing chlorine over heated uranium carbide or a mixture of any oxide of uranium with carbon (Péligot, *Annalen*, 1842, 43, 258; Zimmermann, *ibid.* 1882, 213, 320; 1883, 216, 8; Roscoe, *Chem. Soc. Trans.* 1874, [ii.] 12, 933; Aloy, *Bull. Soc. chim.* 1899, [iii.] 21, 264; Roderburg, *Zeitsch. anorg. Chem.* 1913, 81, 122). It forms dark-green octahedra, is volatile at a red heat, and the vapour has a density (air=1) of 13.33 (Zimmermann). In molten bismuth chloride as solvent the molecular weight is 373 (theory=380.3) (Rüchcimer and Gonder, *Annalen*, 1908, 364, 45). It is extremely deliquescent, fumes in the air, and readily dissolves in water with evolution of heat; the solution is a powerful reducing agent. The solution reacts acid, and on evaporation, leaves an oxychloride. Boiling water completely hydrolyses the chloride.

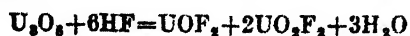
It forms double chlorides with the chlorides of the alkali and alkaline earth metals (Moissan, *Compt. rend.* 1896, 122, 1088; Aloy, *Bull. Soc. chim.* 1899, [ii.] 21, 264).

Uranium pentachloride UCl_5 is obtained by the direct union of the tetrachloride and chlorine. It exists in two forms: (i.) long, dark needles which are green by reflection, and ruby-red by transmission, light, and (ii.) a light-brown, mobile powder. It is very hygroscopic, and is decomposed by water. It cannot be volatilised without decomposition; in an atmosphere of carbon dioxide, dissociation into the tetrachloride and chlorine is complete at 235° (Roscoe, *Chem. Soc. Trans.* 1874, 12, 933).

Uranium tetrabromide or Uranous bromide UBr_4 is obtained by heating the green oxide of uranium with excess of sugar charcoal, and passing bromine vapour over the heated mixture of uranous oxide and carbon thus produced (Zimmermann, *Annalen*, 1883, 216, 2; Alibegoff, *ibid.* 1886, 232, 132; Richards and Merigold, *Zeitsch. anorg. Chem.* 1902, 31, 250). It forms lustrous, dark-brown tablets of sp.gr. 4.838 at $21^\circ/4^\circ$. At a red heat it is volatile; the vapour density (air=1) is 19.46 (Zimmermann). It closely resembles the tetrachloride in properties.

Uranium tetraiodide or Uranous iodide UI_4 is prepared by passing the vapour of iodine over powdered uranium heated to 500° in the absence of air (Guichard, *Compt. rend.* 1907, 145, 921). It forms black, crystalline needles, which melt at about 500° , and have a sp.gr. of 5.6. The aqueous solution is dark green and closely resembles the chloride in properties.

Uranous oxyfluoride UOF_2 is obtained by the action of hydrofluoric acid on uranoauranic oxide—



It is a fine green powder, insoluble in water (Giollitti and Agamennone, *Atti R. Acad. Lincei*, 1905, 14, i. 114).

Uranyl fluoride UO_2F_2 is formed in the preceding reaction, and is a yellow soluble mass. It also exists, according to Smithells (*Chem. Soc. Trans.* 1883, 43, 125) in a white crystalline form, which can be sublimed; this modification is prepared by carefully heating the tetrafluoride in air. It is hygroscopic and forms a yellow solution in water. Both forms unite with

potassium fluoride forming a lemon-yellow crystalline double salt $\text{UO}_2\text{F}_2 \cdot 3\text{KF}$, which can also be obtained from uranyl acetate and an excess of potassium fluoride. This salt is trimorphous (Baker, *ibid.* 1879, 35, 763). The corresponding double salts of other metals are also known, and are converted into deep yellow-coloured peroxyfluorides by hydrogen peroxide (Lordkipanidzé, *J. Russ. Phys. Chem. Soc.* 1900, 32, 283).

Uranyl chloride UO_2Cl_2 is obtained by heating uranous oxide to redness in a stream of chlorine. It is a yellow crystalline mass, stable in dry air; it is reduced by hydrogen at a red heat to the dioxide. Uranous chloride is soluble in water, alcohol, and ether, and its aqueous solution yields the monohydrate $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ on evaporation. A solution of uranyl chloride may be prepared by oxidising uranous chloride with nitric acid or by dissolving uranium trioxide in concentrated hydrochloric acid (Mylus and Dietz, *Ber.* 1901, 34, 2774; de Coninck, *Compt. rend.* 1909, 148, 1769; *Bull. Acad. roy. Belg.* 1909, 836). For a table of specific gravities of its aqueous solutions, v. de Coninck, *Ann. Chim.* 1904, [viii.] 3, 500.

Uranyl bromide UO_2Br_2 may be obtained in an impure state by heating uranous oxide in bromine vapour. It is obtained in aqueous solution by acting on uranous oxide with bromine water, or by dissolving uranic oxide in hydrobromic acid. Yellow needles of the hydrated compound separate on concentrating the solution; they decompose when heated (de Coninck, *Bull. Acad. roy. Belg.* 1902, 12, 1025).

Uranyl iodide UO_2I_2 is obtained by adding barium iodide in slight excess to an ethereal solution of uranyl nitrate. It separates from ether in red deliquescent crystals, and is not very stable (Aloy, *Ann. Chim.* 1901, [vii.] 24, 412).

Uranium monosulphide US is a black, amorphous powder formed by heating the sesquisulphide in hydrogen (Alibegoff, *Annalen*, 1886, 233, 131, 135).

Uranium sesquisulphide U_2S_3 is a greyish-black substance formed by heating the tribromide of uranium in hydrogen sulphide (Alibegoff, *l.c.*).

Uranium disulphide US_2 is formed by the direct union of its elements at 500° (Moissan); at a higher temperature uranium burns vividly in sulphur vapour. The sulphide is best prepared by heating the double chloride of uranium and sodium in a current of hydrogen laden with the vapour of sulphur; or the double chloride may be fused with sulphide of sodium, aluminium, magnesium, antimony or tin (Colani, *Compt. rend.* 1903, 137, 382; *Ann. Chim.* 1907, [viii.] 12, 59). It forms large, slender, pearly crystals; the amorphous powder, obtained by heating uranous chloride in hydrogen sulphide, is greyish-black in colour. It oxidises in the air to uranyl sulphide, and with nitric acid is rapidly converted into uranyl sulphate.

A black, hydrated disulphide is obtained by precipitating a uranous salt with ammonium sulphide; it rapidly oxidises in the air to uranyl sulphide.

Uranyl sulphide UO_2S is obtained by adding ammonium sulphide to an alcoholic solution of uranyl nitrate, washing the precipitate with alcohol and drying *in vacuo*. By precipitating in aqueous solution a brown hydrated form is obtained (Remelé, *Compt. rend.* 1864, 58, 716). It rapidly decomposes by heating to 180° ; warm water converts it into hydrated uranous oxide and sulphur. It dissolves in dilute acids and in ammonium carbonate. When digested for 48 hours with cold ammonium sulphide exposed to air, a deep-red solid is obtained, soluble in acids with the evolution of hydrogen sulphide and deposition of sulphur. This substance is called *uranium-red* (Patera, *J. pr. Chem.* 1850, [i.] 51, 122; Remelé, *Pogg. Ann.* 1865, 124, 158; Hermann, *J.* 1861, 14; Zimmermann, *Annalen*, 1880, 204, 204). A complicated substance of the formula $5\text{UO}_2 \cdot 2\text{K}_2\text{O} \cdot \text{KHS}_2 \cdot x\text{H}_2\text{O}$ is obtained by precipitating uranyl nitrate with potassium sulphide and treating the precipitate with potassium carbonate (Kohlschütter, *Annalen*, 1900, 314, 311). This is also called *uranium-red*; acids decompose it, liberating sulphur and hydrogen sulphide.

Uranyl sulphide is formed in black, tetragonal needles by heating uranosouranic oxide with sulphur and potassium thiocyanate (Milbauer, *Zeitsch. anorg. Chem.* 1904, 42, 448).

The *oxysulphide* $2\text{US}_2 \cdot \text{UO}_2$ has been described by Hermann (*J.* 1861, 260).

Uranium selenides USe_2 and U_2Se_3 are obtained in the crystalline state by heating the double chloride of uranium and sodium in a current of hydrogen containing the vapour of selenium (Colani, *Compt. rend.* 1903, 137, 382; *Ann. Chim.* 1907, [viii.] 12, 59).

Uranyl selenide is produced by heating uranosouranic oxide with selenium and potassium cyanide (Milbauer, *Zeitsch. anorg. Chem.* 1904, 42, 450).

Uranium telluride U_2Te_3 is prepared by fusing the double chloride of sodium and uranium with sodium telluride in an atmosphere of hydrogen (Colani, *l.c.*).

Uranium nitride U_2N_3 is a stable, greyish-black powder, prepared by heating uranous chloride in ammonia, and igniting the product mixed with ammonium chloride, once more in a stream of ammonia (Kohlschütter, *Annalen*, 1901, 317, 158). Uranium unites directly with nitrogen at 1000° , a yellow nitride being produced, the composition of which is not known (Moissan, *Compt. rend.* 1896, 122, 274).

Uranium phosphide U_2P_3 is obtained by fusing sodium uranous chloride with aluminium phosphide in a stream of hydrogen (Colani, *l.c.*). The *arsenide* U_2As_3 and *antimonide* U_2Sb_3 are similarly prepared. All three compounds are obtained as black crystalline powders; they are easily oxidised by nitric acid.

Uranium boride UB_2 is obtained by submitting a mixture of the finely powdered constituents to hydraulic pressure and using the mass as an electrode in the vacuum electrical furnace.

Uranium carbide U_2C_3 is prepared by strongly heating a mixture of 500 parts of uranosouranic oxide and 60 parts of carbon in the electric furnace. It is a lustrous, crystalline solid of

ρ 11.28 at 18° , and is harder than quartz, though not so hard as corundum. It is decomposed by fluorine when gently warmed; chlorine readily attacks it at 350° , whilst it reacts with oxygen at 370° . Uranium carbide is decomposed by water, a very complex change occurring. About one-third of the carbon is evolved in combination with hydrogen, mainly as methane, propane, butane, but mixed with a little ethylene and traces of acetylene; the gaseous mixture contains about 15 p.c. of free hydrogen. The remainder of the carbon is converted into a mixture of solid and liquid hydrocarbons (Moissan, *Compt. rend.* 1896, 122, 274; Lebeau and Damiens, *Compt. rend.* 1913, 156, 1987). A shower of brilliant sparks is produced when two pieces of the carbide are rubbed together.

Uranium silicide USi_2 is obtained from a mixture of silica and uranosouranic oxide by the aluminothermic process (*v.* THERMIT PROCESS). It crystallises in the cubic system, and has a density of 8.0. At 500° it reacts with chlorine giving a mixture of uranous and silicon chlorides (Defacqz, *ibid.* 1908, 147, 1050).

SALTS OF URANIUM.

Saturated aqueous solutions of uranyl formate, acetate, benzoate, and citrate are unstable even in the dark. The propionate, butyrate, oxalate, tartrate, and salicylate are stable in the dark. The benzoate and salicylate are not reduced even in sunlight (Courtois, *Bull. Soc. chim.* 1923, 33 [iv.] 1773; *Chem. Soc. Abstr.* 1924, 126, i. 285).

Uranyl formate $\text{UO}_2(\text{HCO}_2)_2 \cdot \text{H}_2\text{O}$, greenish-yellow crystals, readily soluble in methyl alcohol or water. Formed by adding hydrogen peroxide to a slightly acid solution of uranyl nitrate and treating the washed precipitate with excess of formic acid and evaporating the solution *in vacuo*.

Uranyl acetate $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ is prepared by dissolving in warm acetic acid the yellowish-red mass produced by heating uranyl nitrate until evolution of oxygen commences. It crystallises in yellow, monoclinic needles, and is used in photography and also for the volumetric estimation of phosphates.

For other uranium salts of the monocarboxylic acids of the fatty series, see Courtois, *Compt. rend.* 1914, 158, 1511, 1688.

Uranous arsenate $\text{UH}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Aloy, *Bull. Soc. chim.* 1899, [iii.] 21, 613; Rammelsberg, *Pogg. Ann.* 1842, 55, 318, 66, 125).

Uranyl arsenate $\text{UO}_2(\text{H}_2\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$, a yellow powder, insoluble in water and acetic acid, is obtained by double decomposition (Werther, *Annalen*, 1848, 68, 313). Several arsenates occur as minerals, *e.g.* *trögerite* $(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 12\text{H}_2\text{O}$; *walpurkite*, a basic bismuth uranyl arsenate; and *uranospinite*, a calcium uranium arsenate.

Uranyl benzoate $\text{UO}_2(\text{C}_6\text{H}_5\text{O}_2)_2$ (Courtois, *Bull. Soc. chim.* 1923, 33 [iv.] 1761; *Chem. Soc. Abstr.* 1924, i. 285).

Uranyl bromate $\text{UO}_2(\text{BrO}_3)_2 \cdot x\text{H}_2\text{O}$, *v.* Rammelsberg, *Pogg. Ann.* 1842, 55, 77.

Uranous carbonate and uranyl carbonate are not known (Parkman, *Amer. J. Sci.* 1862, [ii.] 34).

326). Numerous double carbonates exist. *Potassium uranyl carbonate* $\text{UO}_2(\text{CO}_3)_2 \cdot 2\text{K}_2\text{CO}_3$ is obtained by dissolving potassium uranate in potassium bicarbonate and evaporating the solution at a moderate temperature; the corresponding ammonium and sodium salts are prepared in a similar manner (Ebelmen, Ann. Chim. 1842, [iii] 5, 189; Anthon, J. 1860, 698; de Coninck, Bull. Acad. roy. Belg. 1904, 363, 448). They form yellow, rhombic prisms, which are not very soluble in water, but much more soluble in alkali carbonate solutions. The ammonium salt loses ammonia on keeping. Another ammonium compound $2\text{UO}_2 \cdot \text{CO}_3 \cdot 3(\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ has been obtained by mixing uranyl nitrate and ammonium carbonate (Giollitti and Vecchiarelli, Gazz. chim. ital. 1905, 35, ii. 170). *Uranyl calcium carbonate* $\text{UO}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 10\text{H}_2\text{O}$ occurs as the mineral *liebigite* in apple-green warty masses.

Uranyl chlorate $\text{UO}_2(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$ is a very soluble substance, which readily decomposes when heated (Rammelsberg, l.c.).

Uranyl chromate $\text{UO}_2 \cdot \text{CrO}_4$ is obtained by adding uranic oxide to boiling chromic acid solution; it crystallises, on cooling the solution in yellow needles, containing $5\frac{1}{2}\text{H}_2\text{O}$ (Formánek Annalen, 1890, 257, 108), or $3\text{H}_2\text{O}$ (Orloff, Chem. Zeit. 1907, 31, 375). The double salt



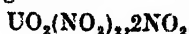
is obtained as yellow monoclinic crystals by treating potassium uranate with chromic acid. The ammonium salt is isomorphous with the preceding salt; the sodium salt contains $10\text{H}_2\text{O}$ (Formánek, l.c.).

Uranyl cyanate $\text{UO}_2(\text{CNO})_2$, a golden-yellow precipitate obtained by mixing dilute solutions of potassium uranyl cyanate and uranyl nitrate (Pascal, Bull. Soc. chim. 1914, [iv.] 15, 11).

Uranyl iodate $\text{UO}_2(\text{IO}_3)_2$ is precipitated on mixing boiling solutions of uranyl nitrate and sodium iodate in dilute nitric acid; it forms yellow prisms, slightly soluble in water. A hydrate $\text{UO}_2(\text{IO}_3)_2 \cdot 5\text{H}_2\text{O}$ is also known (Ditte, Thèse de doctorat ès Sc. Paris, 1870).

Uranous nitrate has not yet been prepared in the solid form (Isambert, Compt. rend. 1875, 80, 1087).

Uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ is a yellow amorphous compound obtained by heating the tri- and tetra-hydrates in a current of nitric anhydride at a temperature of 170° – 180° . It reacts violently with ether and dissolves readily in water with development of heat. It combines with nitrogen dioxide to form



The trihydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ crystallises in yellow, monoclinic forms, and melts at 121.5° ; the dihydrate is rhombic and melts at 179.3° (Vasilieff, J. Russ. Phys. Chem. Soc. 1910, 42, 570). The commercial salt is the hexahydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It is formed when any of the oxides of uranium are dissolved in nitric acid, and is prepared commercially by heating ammonium uranate and dissolving the residue in nitric acid (Janda, Oester. Zeit. Berg-Hütt, 1901, 49, 325). For methods of preparation from pitchblende, v. Péligot, Ann. Chim. 1844, [iii.] 12, 557; Ebelmen, *ibid.* 1842, [iii.] 5, 186.

The hexahydrate forms lemon-yellow, fluorescent, rhombic prisms, which melt at 60.2° and deliquesce in the air (Vasilieff, l.c.; de Coninck, Compt. rend. 1900, 131, 1219, 1303; 1901, 133, 90, 204; Bull. Acad. roy. Belg. 1901, 222; 1909, 743). Water at 18° dissolves twice its weight of the salt. It is very soluble in alcohol and ether, and is best purified by crystallisation from the latter solvent. The aqueous solution is slightly hydrolysed, and has an acid reaction. An *icositetrahydrate* $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ forms spontaneously at -35° and exists only below -20° (Germann, J. Amer. Chem. Soc. 1922, 44, 1466; Ley, Zeitsch. physikal. Chem. 1899, 30, 193; Ber. 1900, 33, 2658; Dittich, Zeitsch. physikal. Chem. 1899, 29, 449).

Uranium nitrate is triboluminescent, the crystals occasionally exploding with a bright flash in contact with water (Iwanow; Andrews, Chem. Zeit. 1912, 1463; Eichhorn, *ibid.* 1914, 38, 139). According to Müller (Chem. Zeit. 1916, 40, 38) this is not a property of the salt itself, but is due to the formation of an unstable compound of a lower oxide of nitrogen with a uranium-ether addition compound (Lebeau). The phenomenon only appears when the original aqueous solution contained free nitric acid.

Double nitrates of the type $\text{RUO}_2(\text{NO}_3)_2$, where R may be potassium, ammonium, thallium, rubidium, or caesium, but not sodium or lithium, are obtained by crystallising solutions of the mixed salts in nitric acid. Water decomposes them into their components (Meyer and Wendel, Ber. 1903, 36, 4055; Rimbach, *ibid.* 1904, 37, 461). For other double nitrates, see Lancein, Chem. Zentr. 1912, i. 208.

Uranyl nitrate is used in photography, and also for the volumetric estimation of phosphates and arsenates.

Uranous phosphate $\text{UH}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranyl phosphate $\text{UO}_2 \cdot \text{HPO}_4$. This is precipitated in an amorphous form by adding a soluble phosphate to uranyl nitrate solution. When this precipitate is continuously boiled with dilute hydrochloric acid for a long time, it is converted into $\text{UO}_2 \cdot \text{HPO}_4 \cdot 4\text{H}_2\text{O}$, which crystallises in tetragonal plates (Bourgeois, *ibid.* 1897, [iii.] 19, 733). The *dihydrogen phosphate* $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ is obtained by heating uranic oxide with dilute phosphoric acid, and concentrating the solution. It separates in small yellow crystals (Werther, J. pr. Chem. 1848, [i.] 43, 321). *Uranyl ammonium phosphate* $\text{UO}_2(\text{NH}_4)\text{PO}_4 \cdot x\text{H}_2\text{O}$ is a greenish-yellow precipitate formed by the addition of a soluble phosphate to a mixture of a uranyl and an ammonium salt. It is obtained in the volumetric estimation of phosphates. The precipitate is insoluble in acetic acid. Upon ignition it leaves a yellow residue of *uranyl pyrophosphate* $\text{UO}_2)_2\text{P}_2\text{O}_7$.

Various phosphates occur in nature, e.g. *halcolite* or *torberite* $(\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O})$ and *autunite* or *uranite* $(\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$.

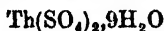
Complex uranyl hypophosphites have been described by Rosenheim and Trewendt (Ber. 1922, 55, [B] 1937). *Uranyl hypophosphite*



is a microcrystalline yellow powder, prepared by agitating solutions of one molecular proportion of uranyl nitrate with four molecular proportions of sodium hypophosphite; almost insoluble in water, but readily soluble in an excess of sodium hypophosphite or uranyl nitrate solution.

Uranyl salicylate $\text{UO}_2(\text{C}_6\text{H}_5\text{O}_2)_2$ forms orange-yellow crystals (Courtois, Bull. Soc. chim. 1923, 33, [iv.] 1761).

Uranous sulphate $\text{U}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is prepared by dissolving the green oxide in dilute sulphuric acid, adding alcohol and allowing the solution to crystallise. The mother liquor contains uranyl sulphate; on exposure to light it is reduced to uranous sulphate, and another crop of crystals is obtained. A large number of other hydrates are known, e.g. di-, tri-, tetra-, penta-, hexa-, hepta-, and nonohydrates (Orloff, J. Russ. Phys. Chem. Soc. 1902, 34, 381; de Coninck, Bull. Acad. roy. Belg. 1901, 483; Kohlschütter, Ber. 1901, 34, 3628; Giolitti and Bucci, Gazz. chim. ital. 1905, 35, ii. 151, 162; Giolitti and Liberi, *ibid.* 1906, 36, ii. 443). The tetrahydrate is a stable substance, and the nonohydrate $\text{U}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ crystallises from aqueous solution in green monoclinic prisms that frequently exhibit twinning and are isomorphous with thorium sulphate



(Rammelsberg, Zeitsch. Krystall. 1889, 15, 640). Uranous sulphate forms double salts with sulphates of the alkali metals, e.g.



(Kohlschütter, Ber. 1901, 34, 3619). Aqueous solutions of uranous sulphate are readily hydrolysed, basic sulphates being precipitated.

A sulphate of the composition $\text{UH}(\text{SO}_4)_2$, which is supposed to contain trivalent uranium, has been described (Rosenheim and Loebel, Zeitsch. anorg. Chem. 1908, 57, 234).

Uranyl sulphate $\text{UO}_2 \cdot \text{SO}_4$ is obtained by dissolving the hydroxide of uranium trioxide in concentrated sulphuric acid and crystallising the solution (Schultz-Sellack, Ber. 1871, 4, 13); or by drying either of its hydrates at 300° . It forms yellow fluorescent crystals. The hydrate $\text{UO}_2 \cdot \text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ is obtained by concentrating a solution of uranic hydroxide in dilute sulphuric acid; the solution does not crystallise readily. Another method is to dissolve uranosouranic oxide in concentrated sulphuric acid, dilute, and boil with nitric acid to oxidise the uranous sulphate present. The hydrate forms citron yellow prisms, which effloresce in air, losing water and leaving the trihydrate $\text{UO}_2 \cdot \text{SO}_4 \cdot 3\text{H}_2\text{O}$. This dissolves in twenty times its weight of water at ordinary temperatures (de Coninck, Bull. Acad. roy. Belg. 1901, 222, 349; 1902, 94, 161). Dried *in vacuo* or at 100° it retains 1 molecule of water. When dissolved in moderately concentrated sulphuric acid, a beautiful yellow, fluorescent, crystalline acid sulphate



crystallises out. The pyrosulphate $(\text{UO}_2)_2\text{S}_2\text{O}_7$ crystallises from a solution of the anhydrous sulphate in pyrosulphuric acid (Schultz-Sellack, Ber. 1871, 4, 13).

Uranyl sulphate forms a double sulphate with

hydroxylamine sulphate (Rimbach, Ber. 1904, 37, 461); a salt $\text{Ti}_2\text{SO}_4 \cdot \text{UO}_2 \cdot \text{SO}_4 \cdot 3\text{H}_2\text{O}$ with thalious sulphate (Kohn, Zeitsch. anorg. Chem. 1908, 59, 111); and combines with equimolecular quantities of the sulphates of ammonium, potassium, lithium, caesium, and magnesium, forming double salts which crystallise with from 2 to 5 molecules of water (de Coninck, Bull. Acad. roy. Belg. 1904, 1171; 1905, 50, 74, 151, 182; de Coninck and Chauvenet, *ibid.* 1908, 50).

A number of *basic sulphates* occur naturally, e.g. *zippéite* $(\text{UO}_2 \cdot \text{SO}_4 \cdot \text{UO}_3)$ and *uraconite* $(\text{UO}_2 \cdot \text{SO}_4 \cdot 2\text{UO}_3 \cdot 14\text{H}_2\text{O})$, which are alteration-products of pitchblende.

Uranyl sulphite. The crystalline precipitate obtained by evaporating a solution of uranic oxide in aqueous sulphurous acid, or by passing sulphur dioxide into an aqueous solution of uranyl acetate, has the empirical composition $\text{UO}_2 \cdot \text{SO}_2 \cdot 4\text{H}_2\text{O}$ (Girard, Compt. rend. 1852, 34, 22). According to Kohlschütter (Annalen, 1901, 314, 311) it is really uranyl sulphurous acid $\text{SO}_3\text{H} \cdot \text{UO}_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$ (cf. Ley, Ber. 1900, 33, 2659).

Uranyl thiocyanate $\text{UO}_2(\text{CNS})_2 \cdot 8\text{H}_2\text{O}$, orange-yellow needles obtained by the action of barium thiocyanate on uranyl sulphate. Highly deliquescent and very soluble in water, alcohol, acetone, ether or amyl alcohol. Forms double salts with the alkali and alkaline earth metals (Pascal, Compt. rend. 1914, 158, 1672).

Tungstates, v. Rammelsberg, Pogg. Ann. 1843, 59, 31; Lefort, Compt. rend. 1878, 87, 748.

Detection and estimation.—In qualitative analysis uranium is obtained together with iron. All the uranyl salts of weak acids, e.g. carbonate, sulphide, phosphate, &c., are soluble in ammonium carbonate and the other alkali carbonates. The ferrocyanide, a brown precipitate, insoluble in dilute acids, is characteristic; alkalis turn it yellow. Uranium is usually weighed as uranosouranic oxide, or else as uranyl pyrophosphate; uranous salts may be titrated with permanganate. V. ANALYSIS; and Finn, J. Amer. Chem. Soc. 1906, 28, 1443; McCoy and Bunzel, *ibid.* 1909, 31, 367; Giolitti, Gazz. chim. ital. 1904, 34, ii. 166; Mazzucchelli, Atti R. Accad. Lincei, 1906, [v.] 15, ii. 429, 494; Campbell and Griffin, J. Ind. Engin. Chem. 1909, 1, 661; Ibbotson and Clark, Chem. News, 1911, 103, 146; Schwarz, Helv. chim. Acta, 1920, 3, 330; Auger, Compt. rend. 1920, 170, 995; Holladay and Cunningham, Trans. Amer. Electrochem. Soc. 1923, 43, 329; Jander and Reeh, Zeitsch. anorg. Chem. 1923, 129, 293; Moser, Monatsch. 1923, 44, 90.

URANIUM DISINTEGRATION PRODUCTS.

The disintegration of uranium proceeds in all probability in the following manner: Uranium I, of atomic weight 238, expels an α -particle and changes into uranium X_1 , an isotope of thorium. The half-period of this first change is 5000 million years. Uranium X_1 is short-lived, and changes with a half-period of 24.6 days into uranium X_2 , or brevium, in the Vth family, expelling a very soft β -radiation. Uranium X_2 has a half-period of only 1.15 minutes, and expels a penetrating β -radiation. It produces uranium II, which after two further α -ray changes gives, first, ionium, and then radium. Uranium II is an isotope of uranium I.

with atomic weight four units less. Its half-period is estimated to be about two million years. All uranium must thus consist of a mixture of two isotopes differing by four units in atomic weight, the proportion between the heavier and the lighter being 2500 to 1. No separation, or even partial separation, has as yet been effected. Independent evidence of the existence of uranium II is afforded by the fact that uranium gives two α -particles of different ranges per atom disintegrating.

See also A. S. Russell (Phil. Mag. 1923, 46, 642); Soddy and Hitchins (Phil. Mag. 1924, 47, 1148).

Uranium X. Estimated at.wt. 234. A radioactive element produced by the disintegration of uranium. It emits two kinds of β -rays, and also γ -rays, and its presence in ordinary uranium salts is responsible for the penetrative rays they emit. Uranium salts, when freed from uranium X, only emit α -rays. In course of a few months the β -radiation is regenerated, whilst that of uranium X decays.

Uranium X may be separated in a number of ways. When a concentrated solution of uranyl nitrate (sp.gr. of solution 2.05) is allowed to cool, the mother liquor left after removing the crystals formed contains about 85 p.c. of the uranium X present (Soddy and Russell, Phil. Mag. 1909, [vi.] 18, 620). If crystals of hydrated uranyl nitrate are shaken with ether, two layers are formed; the aqueous (lower) layer retains the uranium X. In the purification of a uranyl solution from iron, aluminium, &c., by pouring into excess of ammonium carbonate, the precipitated impurities contain all the uranium X. If this precipitate is dissolved in concentrated hydrochloric acid, and the solution extracted with ether, saturated with hydrogen chloride, the ferric chloride is removed, but not the uranium X, which remains in the aqueous layer (Lloyd, J. Phys. Chem. 1910, 14, 509; Soddy, Phil. Mag. 1909, [vi.] 18, 861). It has been recommended to add a thorium salt to a uranyl salt, and then precipitate the thorium in acid solution as fluoride; the precipitate contains the uranium X (Keetman, Jahr. Radioaktivität, 1909, 6, 269; Ritzel, Zeitsch. physikal. Chem. 1909, 67, 725). Thorium fluoride is, however, quite soluble in uranium solutions when these are concentrated. By using a lanthanum salt containing a very little thorium, converting the precipitated fluorides into sulphates and then precipitating by boiling with sodium thiosulphate, a precipitate is obtained, consisting mainly of sulphur, which on ignition leaves a very slight residue containing all the uranium X originally present (cf. Antonoff, Phil. Mag. 1911, [v.] 22, 431).

The most practical way of obtaining a continuous supply of uranium X as required is to keep a strong ethereal solution of uranyl nitrate and to shake this with a few drops of water, pour the aqueous extract into excess of N/2 ammonium carbonate and filter off the insoluble precipitate which contains the uranium X.

Chemically, uranium X is an isotope of thorium; for its radioactive properties, v. RADIOLOGY.

On the influence of substances on the adsorp-

tion of uranium X, v. Ritzel (Zeitsch. physikal. Chem. 1909, 67, 724); Freundlich and Neumann (Zeitsch. physikal. Chem. 1914, 15, 537); Brown (Chem. Soc. Trans. 1922, 1736).

On the γ -radiation from uranium X, v. Richardson (Phil. Mag. 1914, [vi.] 27, 252).

On the electro-chemical separation of uranium X and uranium, v. Rossi (Nuovo Cim. 1913, [vi.] 5, i. 5).

On the magnetic spectrum of the β -rays of uranium X, v. von Baeyer, Hahn and Meitner (Zeitsch. physikal. Chem. 1914, 15, 649).

Uranium X₁. v. Fajans and Göhring (Zeitsch. physikal. Chem. 1913, 14, 877); Fleck (Phil. Mag. 1913, [vi.] 26, 528); Hahn and Meitner (Zeitsch. physikal. Chem. 1913, 14, 758).

On the γ -rays of Uranium X₁ and their relations to Uranium X₁ and Uranium X₂, see Otto Hahn and Lise Meitner (Zeitsch. Physik. 1923, 7, 157-167; J. Chem. Soc. Abstr. 1923, 124, ii. 676).

Uranium X₁ is completely adsorbed by charcoal from a solution of uranium salt, but if a small quantity of a thorium salt is added the uranium X₁ is not adsorbed at all. If the thorium nitrate used is previously shaken with charcoal, it loses to a great extent its power of preventing the adsorption of uranium X₁. This is shown to be due to the fact that thorium nitrate contains colloidal particles, and these are responsible for the displacement of the equilibrium in the adsorption of uranium X₁ (H. Freundlich and M. Wreschner, Zeitsch. physikal. Chem. 1923, 106, 366-377; J. Soc. Chem. Ind. 1923, 42, 1220 A).

Uranium Y, v. Soddy (Phil. Mag. 1914, 215).

Uranium V, v. O. Hahn (Zeitsch. physikal. Chem. 1923, 103, 461); cf. also A. Piccard and E. Stahel (Physikal. Z. 1922, 23, 1; 24, 80).

Uranium Z (symbol U-Z), the existence of which has been announced by Hahn (Ber. 1921, 54 (B), 1131), has been further investigated by Guy and Russel (Chem. Soc. Trans. 1923, 123, 2618) (*q.v.*).

URANIUM MICA v. AUTUNITE; TORBERNITE; URANITE.

URANIUM YELLOW v. URANIUM.

URAO. A native form of sodium sesquicarbonate $\text{Na}_4\text{H}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$, found in South America, Africa, and other places. According to Chatard (Bulletin No. 60, U.S. Geol. Surv. 1887-1880), the formula of urao is



URAPURGOL (*helmitol*). Trade name for hexamethylenetetramineanhydromethylene citrate.

URARI v. CURARA.

p-URAZINE v. HYDRAZINES.

UREABROMIN. A molecular combination of carbamide and calcium bromide



prepared by mixing the two components in solution. It is readily soluble in alcohol or water, insoluble in ether, light petroleum or benzene, and melts at 186°. It gives all the ordinary reactions of its components when

dissolved in water. Used in medicine as a substitute for alkali bromides (Biltz, Pharm. Zentr. 1912, 53, 245).

UREA, carbamide, aminoformamide, $\text{CO} < \text{NH}_2$

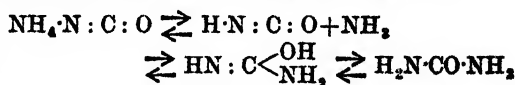
occurs in human urine to the extent of 1.5 p.c. to 2 p.c.; in the urine of other mammalia, especially the carnivora; in small quantities in the blood, bile, milk, perspiration, the aqueous humour of the eye, and other animal fluids (Wurtz, Compt. rend. 1859, 49, 52; Popp, Annalen, 1869, 151, 88; Argutinsky, Pflüger's Archiv. 1891, 46, 594; North, Proc. Roy. Soc. 1886, 39, 443; Pautz, Zeitsch. biol. 1894, 31, 212); in the liver, muscle and blood of the dog-fish, the blood containing 2.78 p.c. (v. Shroeder, Zeitsch. physiol. Chem. 1890, 14, 576; Baglioni, Beitr. chem. Physiol. Path. 1906, 9, 50); in the bile and blood of other fish (Hammarsten, Zeitsch. physiol. Chem. 1898, 24, 322; Baglioni, l.c.). According to Marshall and Davis (J. Biol. Chem. 1914, 18, 53) urea is present in all tissues and organs of normal animals; v. also Karr and Lewis (J. Amer. Chem. Soc. 1916, 38, 1615), and v. Cullen and Ellis (J. Biol. Chem. 1915, 20, 571). In the vegetable kingdom urea has been found in *Lycoperdon bovista*, *Psolliota campestris* and other higher fungi to the extent of 4.3 p.c. of the dry weight, and is present in minute quantities in the juice from the washed leaves of a number of plants and also in seedlings of wheat, barley, maize, peas, clover, and beans (Bamberger and Landseidl, Monatsh. 1903, 24, 218; Gaze, Arch. Pharm. 1905, 243, 78; Goris and Mascré, Compt. rend. 1908, 147, 1488; Fosse, *ibid.* 1912, 155, 851; 1913, 156, 567, and 1938; Ann. Chim. 1916, 6, 13; Compt. rend. 1919, 168, 1164).

As much as 13 p.c. of urea has been found in dried mushrooms that have been cultivated in manure (Ivanov, Biochem. Zeitsch. 1923, 143, 62; Chem. Soc. Abstr. 1924, 126, 353).

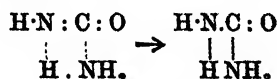
A. niger and *P. glaucum* both produce urea in the presence of ammonia and carbohydrates (Fosse, Compt. rend. 1912, 156, 263). For the formation of urea by higher plants, see Fosse (Ann. Chim. Phys. [ix.] 1916, 6, 567). A number of plants hydrolyse urea in presence of chloroform (Fosse, Ann. Inst. Pasteur, 1916, 30, 642).

Urea was first obtained synthetically by Wöhler in 1828 from ammonium cyanate, which undergoes a spontaneous transformation into its isomeride urea when an aqueous solution is

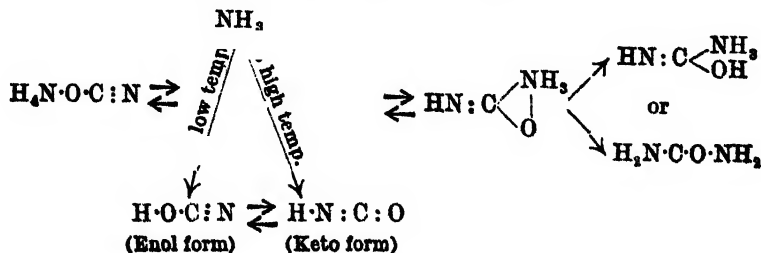
evaporated at the temperature of boiling water. The mechanism of the reaction has been studied by Walker and others (Chem. Soc. Trans. 1895, 67, 746; 1896, 79, 193; 1897, 71, 489; 1900, 77, 30), who have shown: (1) that the reaction is a reversible one, equilibrium being reached in a decinormal solution when there is about 95 p.c. of urea and 5 p.c. of ammonium cyanate present (cf. Lewis and Burrows, J. Amer. Chem. Soc. 1912, 34, 1515); (2) that the reaction is a bimolecular one; (3) that the velocity of the reaction is thirty times as great in 90 p.c. ethyl alcoholic as in aqueous solutions; and (4) that pure dry ammonium cyanate passes rapidly into urea when heated at about 80°. These authors suggest that the active molecules in the reaction are ammonium ions and cyanic acid ions, $\text{NH}_4^+ + \text{CNO}^- = \text{CO}(\text{NH}_2)_2$; and that the increased velocity of the reaction in alcoholic solution is due to the effect of the alcohol in increasing the rate at which the dissociated ions interact, and this more than counterbalances the diminution in the velocity due to the diminished degree of electrolytic dissociation of the cyanate (cf. Burrows and Fawsitt, Chem. Soc. Trans. 1914, 105, 609). Another explanation of the reaction offered by Chattaway (Chem. Soc. Trans. 1912, 101, 170) is that ammonium cyanate dissociates into ammonia and cyanic acid, that these interact to form isourea, which rapidly undergoes molecular rearrangement



Wheeler and others (J. Amer. Chem. Soc. 1912, 34, 1269) offer a somewhat simpler explanation of the interaction between the cyanic acid and ammonia by introducing the idea of partial valency



Werner has shown that cyanic acid is capable of existing in equilibrium in the two forms, *normal* and *iso*-, or, as he prefers to call them, *enol* and *keto*, the relative proportions being a function of the temperature. Being a weak acid in the enolic form, cyanic acid would naturally yield a very unstable ammonium salt, easily dissociated by heat, both in the dry state and in solution, and transformable into urea according to the following scheme:



(Chem. Soc. Trans. 1913, 103), see also Werner and Fearon (*ibid.* 1920, 1356).

Urea can be obtained from lead cyanate by direct hydrolysis with boiling water (Cumming,

Chem. Soc. Trans. 1903, 83, 1391); by heating ammonium sesquicarbonate or ammonium carbamate at 130°–135° under pressure (Bourgeois, Bull. Soc. chim. 1897, [iii.] 17, 474; Fichter and

Becker, Ber. 1911, 44, 3473; J. Soc. Chem. Ind. 1915, 34, 924; Eng. Pats. 23939, 24117, 24042, 1914; Matignon and Fréjaques, Compt. rend. 1920, 171, 1003; Badische Anilin and Soda-Fabrik, D. R. PP. 332679, 301279; Eng. Pat. 145060; Krass and Gaddy, J. Ind. Eng. Chem. 1922, 14, 611; by the electrolysis of a solution of ammonium carbonate (Fichter, Steiger and Stanisch, Verh. Schweiz. Nat. ges. 1916, 28, ii, 66; Fichter, Zeitsch. Elektrochem. 1918, 24, 41); by passing a mixture of ammonia and carbon dioxide through a red hot tube (Mixer, Amer. Chem. J. 1882, 4, 34). For the explanation of the mechanism of these reactions, see Werner (Chem. Soc. Trans. 1920, 1046). Bailey (Compt. rend. 1922, 175, 279). Urea is also formed by the action of carbonyl chloride on ammonia (Natanson, Annalen, 1856, 98, 287; Bouchardat, Compt. rend. 1869, 69, 961; Fenton, Chem. Soc. Trans. 1879, 35, 793; Hantzsch and Stuer, Ber. 1905, 38, 1041; Werner, Chem. Soc. Trans. 1918, 694); by passing a stream of air charged with ammonia and benzene vapour or acetylene over a heated platinum spiral (Herroun, Chem. Soc. Trans. 1881, 39, 471); by heating a solution of carbon monoxide in ammonium cuprous chloride at 105° under pressure (Jouve, Compt. rend. 1899, 128, 114); by the decomposition of copper or ammonium fulminate with sulphuretted hydrogen (Gladstone, Quart. J. Chem. Soc. 1849, 1, 228); by the decomposition of an aqueous solution of prussic acid (Campani, Gazz. chim. ital. 1871, 1, 472), or by the oxidation of potassium cyanide with potassium permanganate or sodium hypochlorite (Volhard, Annalen, 1890, 259, 377; Reychler, Bull. Soc. chim. 1893, [iii.] 9, 327). (For industrial conversion of ammonia into urea, see Matignon and Fréjaques, Chem. Ind. 1922, 7, 1057. In abstract, J. Soc. Chem. Ind. Aug. 31, 1922, p. 646 A. See also under Patents, p. 647 A., Bad. Anil. u. Soda Fabrik, Eng. Pat. 182331). Urea is also obtained by the hydrolysis of guanidine (Flemming, Chem. Zeit. 1900, 24, 56), arginine (Schulze and Likiernik, Ber. 1891, 24, 2701) or lysatine (Drechsel, *ibid.* 1890, 23, 3096) with barium hydroxide solution; and is a constant product of oxidation with acid potassium permanganate of a large number of organic compounds containing nitrogen: for example, acid amides and amino acids (Hofmeister, Chem. Zentr. 1896, ii, 389; Jolles, Ber. 1900, 33, 2834; J. pr. Chem. 1901, [ii.] 63, 516), and proteins (Ritter, Compt. rend. 1872, 73, 1219; Hofmeister, *l.c.*; Hugouneq, Compt. rend. 1901, 132, 1240; Jolles, Ber. 1901, 34, 1447; Fosse, Compt. rend. 1912, 154, 1187, 1819; 1919, 168, 1164; 1921, 172, 684, 1240; 173, 318). Urea is found abundantly when *d*-glucose, levulose, sucrose, dextrin or cellulose is oxidised in presence of ammonia; and much higher yields of urea are obtained by oxidising under the same experimental conditions formaldehyde or urotropine (Fosse, Ann. Inst. Pasteur, 1916, 30, 642; Compt. rend. 1919, 168, 1164; 1921, 172, 684, 1240; 173, 318).

Cyanamide is slowly converted into urea by the action of water (Schmidt, Arch. Pharm. 1917, 255, 351), by the action of dilute mineral acids in the presence of ferrosulphuric oxide (Farbwerke vorm. Meister, Lucius and Brüning,

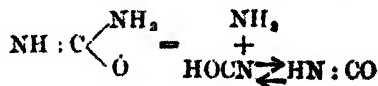
D.R.P. 301278, from Chem. Zentr. 1922, ii, 1135).

Urea is usually obtained from urine by treating the concentrated filtered liquid with a hot saturated solution of oxalic acid and decomposing the sparingly soluble urea oxalate thus obtained with powdered chalk; the filtrate is decolorised with animal charcoal and evaporated until the urea crystallises out on cooling. Another method consists in extracting the urea with alcohol from the syrup obtained by evaporating the urine, precipitating the urea as the sparingly soluble nitrate by the addition of concentrated nitric acid, and decomposing the salt by boiling with barium carbonate and alcohol; the urea is obtained by crystallisation from the filtrate. It can be purified and decolorised by boiling it in aqueous solution with hydrogen peroxide (Kunz-Krause, Kolloid Zeitsch. 1919, 25, 240).

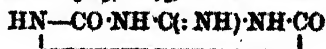
Urea can be prepared on a large scale by passing dry ammonia into fused phenyl carbonate until the odour of ammonia is persistent. The product is poured into hot water, when it separates into two layers consisting respectively of phenol and a solution of urea; 5 kilos. of phenyl carbonate yield 1 kilo. of urea and the whole of the phenol is recovered. The phenyl carbonate is obtained in an almost theoretical yield by passing dry carbonyl chloride into a solution of phenol in its equivalent quantity of dilute caustic soda (Hentschel, Ber. 1884, 17, 1286). By a similar reaction, guaiacol carbonate is rapidly converted into urea and guaiacol when an alcoholic solution is saturated with ammonia (Cazeneuve, Compt. rend. 1896, 122, 999).

Urea crystallises in needles, or in four-sided rhombic anhydrous prisms; it is readily soluble in water, 1 grm. of water dissolving 0.779 grm. of urea at 5.5°, 1.00 grm. at 17.1°, and 1.094 grm. at 20.92° (Krummacker, Zeitsch. biol. 1905, 46, 302). It dissolves in five parts of cold alcohol, is soluble in methyl and in amyl alcohol, and is insoluble in ether, ethyl acetate or chloroform. The heat of combustion is 2.532 cal., and the heat of solution 3.57 cal. (Krummacker, *l.c.*). For the entropy changes at low temperature, see Gibson, Latimer and Parks (J. Amer. Chem. Soc. 1920, 42, 1533).

Urea melts at 130°–132°, and sublimes readily when heated under reduced pressure at 120°–130° (Bourgeois, Bull. Soc. chim. 1892, [iii.] 7, 45). When pure dry urea is heated slightly above its melting-point it undergoes rapid dissociation into ammonia and cyanic acid



Cyanuric acid is produced as a result of the polymerisation of a portion of the cyanic acid originally present in the keto-form, whilst biuret is simultaneously formed by the action of cyanic acid on unchanged urea. Biuret $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, when heated at 195° decomposes into ammonia and cyanic acid, cyanuric acid $\text{C}_3\text{N}_3(\text{OH})_3$, and ammelide



(Werner, Chem. Soc. Trans. 1913, 103, 2275; Chem. Soc. Proc. 1914, 262). When urea is sublimed in a vacuum at 160°–190°, the sublimate consists of ammonium cyanate (Escalles, Chem. Zeit. 1911, 35, 595). When an aqueous solution of urea is boiled, it is partially converted into ammonium cyanate. The reaction is a reversible one, equilibrium being reached in a N/10 solution, when there is about 5 p.c. ammonium cyanate present (Walker and Hambly, Chem. Soc. Trans. 1895, 67, 746; Fawsitt, Zeitsch. physikal. Chem. 1902, 41, 602). When heated with water in a sealed tube at 180°, urea undergoes complete hydrolysis, forming ammonium carbonate. For the decomposition of urea by acids and alkalis, see Werner (Chem. Soc. Trans. 1918, 84; 1920, 1078). Urea is decomposed by the action of nitrous acid, yielding nitrogen and carbon dioxide (Claus, Ber. 1871, 4, 140); compare, however, Werner (Chem. Soc. Trans. 1914, 863). Urea is decomposed when heated with dilute hydrochloric, sulphuric, or nitric acid, yielding carbon dioxide and the ammonium salt of the acid (Fawsitt, Zeitsch. physikal. Chem. 1902, 41, 601; Werner, Chem. Soc. Trans. 1918, 113, 84; Price, *ibid.* 1919, 115, 1354; Burrows, J. Roy. Soc., New South Wales, 1919, 53, 125). It is oxidised by a hot acid solution of potassium permanganate, yielding two vols. CO₂ and 1 vol. N (Wanklyn and Gamgee, Chem. Soc. Trans. 1868, 21, 25). By the action of sodium hypochlorite or hypobromite, urea is converted into carbon dioxide, nitrogen, and water; together with a small quantity of carbon monoxide (Hurtley, Bio-Chem. J. 1921, 15, 11). For an explanation of the course of this reaction, compare Sohestakow (J. Russ. Phys. Chem. Soc. 1905, 37, 1); Dehn (J. Amer. Chem. Soc. 1910, 31, 1220); Werner (Chem. Soc. Trans. 1922, 2318). Urea is decomposed by bromine, yielding cyanuric acid, ammonium bromide, and nitrogen; chlorine has a similar reaction on fused urea (Smolka, Monatsh. 1887, 8, 64). Urea is converted into cyanamide NC-NH₂ by the action of sodium (Fenton, Chem. Soc. Trans. 1882, 41, 262) or of sulphuryl chloride (Moureu, Bull. Soc. chim. 1894, [iii.] 11, 1068). Compare Werner (Chem. Soc. Trans. 1915, 107, 715) for the relationship of cyanamide to urea, and (*ibid.* 1913, 106, 923) for the constitution of carbamides and isocarbamides.

Urea readily undergoes bacterial fermentation with production of ammonium carbonate (Miguel, Compt. rend. 1890, 111, 397; Frankland, Chem. Soc. Trans. 1885, 47, 175; Hatton, *ibid.* 1881, 39, 256; Jacoby, Biochem. Zeitsch. 1916, 74, 109); a ferment present in urine is particularly active in causing this decomposition, and if this ferment is collected on paper by filtration, washed and dried at 35°–40°, its activity revives when brought into contact with water; and such papers, when previously coloured with turmeric, form a convenient test for urea, becoming deep brown when dipped into a solution containing even $\frac{1}{1000}$ part of urea (Musculus, Compt. rend. 1874, 78, 132). For the decomposition of urea by moulds, v. Kossovitz (Amer. Chem. Abs. 1913, 807).

Detection.—Urea can be detected by the formation of its sparingly soluble nitrate or oxalate. In the case of the latter salt, the

precipitation is facilitated by using an amyl alcoholic solution of the urea and of the oxalic acid (Brücke, Monatsh. 1881, 3, 195). The *biuret* test is the commonest test for urea. It consists in heating gently the urea until it ceases to evolve ammonia freely, dissolving the residue in a little water and adding a few drops of very dilute copper sulphate solution, on the subsequent addition of a drop of concentrated potassium hydroxide, a beautiful violet colour is developed. If the urea is in solution, it may be detected by evaporating to dryness with hydrochloric acid, heating the residue until it ceases to evolve thick white fumes and then dissolving in ammonia; on adding barium chloride solution and stirring, crystals of barium cyanurate separate on the lines of friction made by the rod; or copper sulphate may be added to the ammoniacal solution of the residue, when violet crystals of cuprammonium cyanurate separate out (Bloxam, Chem. News, 1883, 47, 285; v. Werner, Chem. Soc. Proc. 1914, 30, 262, for proof that biuret is formed by the interaction of urea and its dissociation product cyanic acid). Other colour reactions that can be used for the detection of urea are (1) the formation of a fine purple violet colour, when a solution of urea is treated with a concentrated solution of furfural and a few drops of concentrated hydrochloric acid (Schiff, Ber. 1877, 10, 773; Ganassini, Arch. Farm. sperim. sci. app. 1918, 26, 238; from Chem. Zentr. 1919, ii, 473); (2) the development of an intense blue colour when minute quantities of urea (or other compounds containing the $\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ group) and methylfural ($\text{C}_4\text{H}_3\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_4\text{H}_3\text{O}\cdot\text{CH}_3$) are mixed on a filter paper and treated with a drop of fuming hydrochloric acid (Fenton, Chem. Soc. Trans. 1903, 83, 187; Proc. Camb. Phil. Soc. 1911, 16, 64); (3) the development of the characteristic red colour of the sodium violurate when the urea (or its mono- or sym. di-substituted derivatives) is condensed with malonic acid by cautiously heating the mixture moistened with phosphoryl chloride, the resulting barbituric acid dissolved in water, neutralised with solid sodium carbonate, and then treated with a crystal of sodium nitrite and a drop of acetic acid (Whiteley, *private communication*); (4) urea condenses with *o*-nitrobenzaldehyde when heated in alcoholic solution, the *o*-nitrobenzodiuireide $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, thus obtained melts at 200°, and if present in very small amount may be readily detected by decomposing it with dilute hydrochloric acid and testing for *o*-nitrobenzaldehyde by the red colour it gives with phenylhydrazine (Lüdy, Monatsh. 1889, 10, 295); see also Arreguine and Garcia (Anal. Asoc. Quim. Argentina, 1921, 9, 183). According to Fosse (Compt. rend. 1913, 157, 948) it is possible to precipitate urea by means of its xanthhydrol derivative at a dilution of 1 in 1,000,000, to identify it by analysis at a dilution of 5 parts in 100,000, and to identify it microscopically at a dilution of 1 in 100,000; see also Werner and Fearon (Chem. Soc. Trans. 1920, 1360); and Bonnet and Haushalten (Compt. rend. Soc. Biol. 1922, 86, 395); Stübel (Anat. Anz. 1921, 54, 236).

Estimation.—The determination of the amount of urea present in urine, blood serum or other animal liquids, is a problem of great

physiological importance. Of the large number of methods that have been described for the estimation of urea, only those are now in use that involve the conversion of urea into ammonia, under such conditions that other nitrogenous substances that may be present in the specimen are not simultaneously hydrolysed. The most important methods are those of Folin and of Benedict, Möerner and Sjöquist, and of Pfüger and Bleibtreu. For estimation by the hypobromite method, see Philibert (J. Pharm. Chim. 1919 [vii.] 19, 335, 386, 434); Golse (*ibid.* 1919, [vii.] 19, 20). For estimation by the xanthhydrol method, v. Fosse (Compt. rend. 1914, 158, 1076, 1588; 1914, 159, 253, 367); Maestro (Chem. Zentr. 1915, 11, 984, from Arch. Farmacol. Sperim. 19, 572); Frenkel (Ann. Chim. anal. 1920, [ii.] 2, 234); Carra (Biochem. therapia. sper. 1921, 8, 225), who has examined the various methods for the estimation of urea, states that this method is very accurate. For a microchemical method based on this reaction, see Nicloux and Welter (Compt. rend. 1921, 173, 1490).

I. Folin's method is based on the fact that urea is quantitatively converted into ammonia and carbon dioxide when heated with fused magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In using this method for the estimation of urea in urine, 3 c.c. of the sample are boiled for half an hour with 20 grms. of hydrated magnesium chloride (phosphoric acid or potassium acetate, v. Folin, J. Biol. Chem. 1912, 11, 507) and 2 c.c. concentrated hydrochloric acid in a small reflux apparatus supplied with a special 3-bulb safety tube. After careful dilution, 7 c.c. of 20 p.c. sodium hydroxide are added to liberate magnesium hydroxide and the ammonia distilled over into a known volume of N/10 acid, the distillation being prolonged until the contents of the flask are almost dry. Allowance must be made for the ammonia present in the magnesium chloride (Folin, Zeitsch. physiol. Chem. 1901, 32, 504; 1902, 36, 333; Folin and Farmer, J. Biol. Chem. 1912, 11, 493, 507, 523; cf. Bock, *ibid.* 1913, 14, 295). In this method creatinine yields traces of ammonia and allantoin yields all its nitrogen as ammonia. Benedict (J. Biol. Chem. 1910, 8, 405) modifies the method by adding to the urine potassium hydrogen sulphate, zinc sulphate, a little powdered pumice, and a piece of paraffin to prevent frothing; the mixture is boiled to dryness, the residue heated at 162° – 165° for an hour, then mixed with sodium hydroxide and the liberated ammonia distilled into standard acid. For the conversion of urea to ammonia by means of urease, which does not decompose allantoin, v. Marshall, J. Biol. Chem. 1913, 14, 283; Van Slyke and Cullen, *ibid.* 1914, 19, 211; 1916, 24, 117; Plimauer and Skelton, Bio-Chem. J. 1914, 8, 70; 1916, 24, 117; Fiske, J. Biol. Chem. 1915, 23, 455; Halen, Chem. Zentr. 1916, 1, 997, from Deut. med. Woch. 1916, 42, 414; Yamazaki, J. Tokyo Chem. Soc. 1918, 39, 125. This method, according to Carra (*l.c.*), gives excellent results. Folin and Denis (*ibid.* 1916, 26, 501) give directions for the estimation of the nitrogen by direct Nesslerisation after hydrolysing the urea by urease and removing the latter with phosphoric acid.

When crude soya-bean meal is used for the estimation of urea, the addition of sodium

carbonate in sufficient amount to liberate the ammonia formed in the free state is without deleterious effect upon the activity of the urease. This observation is made use of in the following method: Three large test tubes are constricted by drawing them out in a blowpipe flame in such a manner that the capacity below the constriction is about three times that of the liquid to be contained. These tubes are fitted with corks and connecting tubes as wash-bottles, the upper end of the first inlet tube being provided with a three-way piece and stopcock. Into the first tube 20 c.c. of water, 5 c.c. of urine, and 3 to 5 grms. of soya-bean meal are placed, and the central narrow tube is inserted and surrounded by a few glass beads above the constriction. The remaining tubes contain known volumes of 0.1 N sulphuric acid for absorption of the ammonia liberated. The tube containing the mixture is immersed in a water-bath at 40°C ., and a current of ammonia-free air is drawn through the apparatus at a rate exceeding $5\frac{1}{2}$ litres per minute. Two c.c. of saturated sodium carbonate solution are introduced by means of the stopcock into the tube containing the mixture, and aeration is continued for 40 minutes, after which the urea is calculated from the titration of the standard acid. Results obtained with known amounts of urea show a maximum error of 0.88 p.c. (G. M. Wishart, Bio-Chem. J. 1923, 17, 403–405; Analyst, 1923, 48, 501).

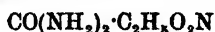
Urea in urine or in milk may be estimated by means of urease obtained from the seeds of *Canavalia ensiformis* by extracting the powder with glycerol and water, then, after about 3 hours, acidifying with hydrochloric acid and filtering. In the case of urine, the estimation is carried out by diluting about 5 c.c. with 50 c.c. of water and adding 3 c.c. of the solution of urease and 1 c.c. of 3 p.c. solution of calcium caseinate to serve as indicator; after about 3 hours, 40 c.c. of 0.1 N hydrochloric acid are added, and the excess of acid titrated back with sodium hydroxide solution, the precipitation of the casein indicating the end-point. In the case of milk, 10 c.c. are diluted with 40 c.c. of water, 3 c.c. of urease solution are added, and the estimation continued as above. Cow's milk usually contains 0.25 to 0.30 gm. of urea per litre, and, for the first few weeks after calving, 0.75 gm. per litre. Goat's milk is richer in urea than that of the cow, the average being 0.80 gm. per litre (G. Morimoto, Bio-Chem. J. Japan, 1922, 69; Ann. Chim. anal. 1923, 5, 153; Analyst, 1923, 48, 394).

II. In the Möerner-Sjöquist method of estimating urea in urine, uric acid, purine bases, tyrosine, allantoin, &c., are removed by precipitation with barium chloride and hydroxide in a mixture of alcohol and ether. The filtrate and washings are evaporated at 55° to about 25 c.c., a little water and magnesia added and the distillation continued until the steam has no longer an alkaline reaction. The volume is then concentrated to 10–15 c.c. and the nitrogen present estimated by the Kjeldahl method (Chem. Soc. Abstr. 1901, 758; compare Braunstein, Zeitsch. physiol. Chem. 1900, 31, 381).

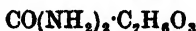
III. In the Pfüger-Bleibtreu method for the estimation of urea in urine, the nitrogenous compounds other than urea are precipitated by

means of a mixture of hydrochloric and phosphotungstic acids; the urea decomposed in the neutralised filtrate by heating it with phosphoric acid, and the ammonia estimated. For working details of this and the other methods, see Abderhalden's *Handbuch der Biochemischen Arbeitsmethoden*, vol. iii. part 2, 776-782.

Derivatives. Salts.—Urea forms salts with metals; *silver urea* $\text{CO}(\text{NHAg})_2$ (Mulder, Ber. 1873, 6, 1019); *monopotassium urea* $\text{CON}_2\text{H}_2\text{K}$, colourless needles; *dipotassium urea* $\text{CON}_2\text{H}_2\text{K}_2$, gelatinous mass (Franklin and Stafford, Amer. Chem. J. 1902, 28, 83). It also forms salts with acids, some of which combine with metallic salts to form stable crystalline double salts. The *nitrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ forms sparingly soluble monoclinic crystals that decompose at 140° (Gaubert, Compt. rend. 1907, 145, 378; v. Barker, Min. Mag. 16, 207, for crystallographic constants); it is precipitated quantitatively when concentrated solutions of cyanamide and nitric acid are mixed at below 20° (D. R. P. 285259, from J. Soc. Chem. Ind. 1915, 34, 1166); the *hydrochloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$ dissociates in aqueous solution (Datta, Chem. Soc. Trans. 1912, 101, 166); see also du Toit (Proc. K. Akad. Wetensch. Amsterdam, 1913, 16, 555); the *phosphate* $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, large rhombic crystals, readily soluble in alcohol or water; the *phosphotungstate* crystallises in rhombic prisms (Drummond, Bio-Chem. J. 1918, 12, 5); *acetate* $\text{CO}(\text{NH}_2)_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, large deliquescent crystals (Matignon, Compt. rend. 1891, 112, 1367); *glycine urea*



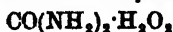
large crystals (Matignon, Bull. Soc. chim. 1894, [iii.] 11, 576); the *salicylate (ursal)*



has m.p. 122° ; the *acid salt* $\text{CO}(\text{NH}_2)_2 \cdot 2\text{C}_7\text{H}_5\text{O}_3$ has m.p. 115° ; the *guinate (urol, urocol)*



m.p. 107° ; the *picrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ decomposes at 142° (Smolka, Monatsh. 1885, 6, 915); the *oxalate* $[\text{CO}(\text{NH}_2)]_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ forms rhombic plates or prisms, sparingly soluble in water (1:23), less so in alcohol (1:62), amyl alcohol, and insoluble in ether. With hydrogen peroxide urea forms the compound



in large transparent crystals (Tanatar, J. Russ. Phys. Chem. Soc. 1908, 40, 376). Urea forms crystalline compounds with *sodium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$ rhombic plates or prisms, m.p. 60° - 70° ; with *ammonium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$ quadric plates or needles that readily dissociate; with *calcium nitrate* $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, the compound is crystalline, readily soluble in water and not deliquescent (Boech, U.S. Pat. 1369383); with *calcium chloride* $\text{CaCl}_2 \cdot 4\text{CO}(\text{NH}_2)_2$, m.p. 158° - 160° , stable in air, said to be useful for subcutaneous injection in hay fever and asthma (Knoll & Co., D.R.P. 306804, from Chem. Zentr. 1918, ii. 420; Okuda and Fujiwaka, J. Tokyo Chem. Soc. 1919, 40, 404); with *calcium bromide (ureabromin)* $4\text{CO}(\text{NH}_2)_2 \cdot \text{CaBr}_2$, m.p. 186° , which has therapeutic properties resembling those of the alkali bromides (Biltz, Pharm.

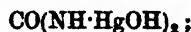
Zentr. 1912, 53, 245); $\text{CaBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$, hexagonal plates, m.p. 146° (Okuda and Fujiwaka, l.c.); with *calcium iodide* $\text{CaI}_2 \cdot 6\text{CO}(\text{NH}_2)_2$, hexagonal plates, m.p. 168° - 169° (Okuda and Fujiwaka, l.c.); $\text{CaI}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, large transparent plates, m.p. 167° (Spitz, D. R. P. 318343, from Chem. Zentr. 1920, ii. 601); with *mercuric chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{HgCl}_2$; with *zinc chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{ZnCl}_2$; with *cadmium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{CdCl}_2$; with *silver nitrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{AgNO}_3$; with *palladium chloride* $\text{PdCl}_2 \cdot 2\text{CO}(\text{NH}_2)_2$; and with *magnesium bromide* $\text{MgBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$, m.p. 167° - 170° , with decomposition, and $\text{MgBr}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ decomposes at 165° - 170° (Menschutkin, Petersburger polytechn. Inst. 1906, 6, 101). Among the double salts formed by urea are the *platinichlorides* $[\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}]_2 \cdot \text{PtCl}_4 \cdot 2\text{H}_2\text{O}$, hygroscopic yellow prisms (Heintz, Annalen, 1879, 198, 91) and $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{PtCl}_6$, m.p. 119° - 120° , red prismatic crystals (Pickard and Kenyon, Chem. Soc. Trans. 1907, 91, 902); the *aurichlorides* $2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot \text{AuCl}_3$ and $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot \text{AuCl}_3 \cdot \text{H}_2\text{O}$; the *quinine hydrochloride* $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{HCl} \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot 5\text{H}_2\text{O}$, and similar compounds containing quinidine and cinchonidine (Drygin, Chem. Zentr. 1881, 245); the double hydrobromide



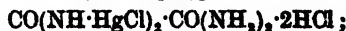
m.p. 70° - 75° , decomposes at 130° - 140° ; the corresponding double hydrochloride is employed as a local anæsthetic (Golubev, J. Russ. Phys. Chem. Soc. 1914, 46, 189); *cotarnine carbamide*, m.p. 180° , possesses therapeutic properties (Knoll & Co., D. R. P. 232785). The compounds with *mercuric nitrate* $2\text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 3\text{HgO}$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO}$ and



are obtained by precipitation between urea and mercuric nitrate under different conditions of concentration. Urea also combines with mercuric salts to form salts of the divalent radicle $\text{CO}(\text{NHHg})_2$, 'mercuroidcarbamide'; the *hydroxide*



the *chloride* $\text{CO}(\text{NH} \cdot \text{HgCl})_2$, and



the *nitrate*



and the *acetate* $\text{CO}(\text{NH} \cdot \text{HgOAc})_2$ (Ruspaggiari, Gazz. chim. ital. 1897, 27, i. 1). Salts containing chromium complexes and urea have been described by Sell (Proc. Roy. Soc. 1882, 33, 267; 1889, 45, 321).

Acyl derivatives of urea, v. UREIMIDES.

Chloro and nitro derivatives.—*Chlorourea*



decomposes at 71° , dissolves in five parts of water at ordinary temperature, giving a neutral solution that loses nitrogen and forms biuret. It reacts slowly in aqueous solution with aliphatic ketones, yielding the monochloroketone (Béhal and Detoef, Compt. rend. 1911, 153, 681 1229); and with ethylenic hydrocarbons, giving the corresponding chlorohydrin (Detoef, Bull. Soc. chim. 1922, [iv.] 31, 102). *Dichlorourea* $\text{CO}(\text{NHCl})_2$, prepared by passing a rapid stream of chlorine into a well-cooled solution

of urea in water, forms colourless plates that melt with decomposition at 82° when cautiously heated and detonate when rapidly heated, forming nitrogen chloride; on decomposition with ammonia in strong aqueous solution *p*-urazine $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{CO}$ is formed (Chattaway, Proc. Roy. Soc. 1908, A. 81, 381; Chem. Soc. Trans. 1909, 95, 236; compare Datta, *ibid.* 1912, 101, 166; Dowell, J. Amer. Chem. Soc. 1919, 41, 124).

Nitrourea $\text{NO}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, prepared by the action of concentrated sulphuric acid on urea nitrate, forms sparingly soluble crystals that decompose on melting; it is a strong acid, liberating acetic acid from its salts. The potassium, sodium and mercury salts have been prepared. On reduction with zinc dust and sodium hydroxide, it forms *nitrosourea* $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NO}$, and this develops a purple colour with ferrous sulphate (Thiele and Lachmann, Annalen, 1895, 288, 281). On further reduction it yields semicarbazide



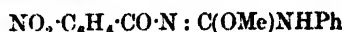
See Backer (Rec. trav. chim. 1912, 31, 1) for the electrolytic reduction of nitrourea. *Carbaminoazoisimide* $\text{NH}_2 \cdot \text{CO} \cdot \text{N}_2$, from sodium nitrite and semicarbazide has m.p. 92°–93° (Thiele and Stange, Annalen, 1894, 283, 1); *cyanocarbamide* $\text{CN} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ (Mauguin and Simon, Compt. rend. 1920, 170, 998).

The *alkyl* and *aryl* derivatives of urea are prepared by Wöhler's method from the corresponding mono- or di-substituted ammonium cyanate; by the action of ammonia on the *isocyanic* ester, and by the action of carbonyl chloride on the amine. For a description of these derivatives, see Michler, Ber. 1875, 8, 1664; Schiff, Annalen, 1877, 189, 157; Michler and Escherich, Ber. 1879, 12, 1162; Hemmelmayr, Monatsh. 1891, 12, 89; Chancel, Compt. rend. 1892, 115, 242; Schneegans, Arch. Pharm. 1894, 231, 675; A. E. Dixon, Chem. Soc. Trans. 1895, 47, 559; Diels and Golimann, Ber. 1911, 44, 3158; Cannizzaro, Gazz. chim. ital. 1871, 1, 41; Letts, Chem. Soc. Trans. 1872, 25, 448; Paternó and Spica, Gazz. chim. ital. 1875, 5, 388; Michler, Ber. 1876, 9, 396, 710; Claus, *ibid.* 693; Weith, *ibid.* 821; Pagliani, Gazz. chim. ital. 1879, 9, 28; Cosack, Ber. 1879, 12, 1449; 1880, 13, 1088; Michler and Zimmermann, *ibid.* 1881, 14, 2177; Michler and Keller, *ibid.* 2181; Traube, *ibid.* 1882, 15, 2122; Kym, *ibid.* 1890, 23, 424; Kühn and Landau, *ibid.* 811; Manuelli and Comanducci, Gazz. chim. ital. 1899, 29, ii. 136; Davis, Roberts, Brewster, J. Amer. Chem. Soc. 1916, 38, 731). For a summary of the alkyl substituted ureas, see Abderhalden's Biochemisches Handlexikon, 1911, vol. i. part 2, pp. 772, 773. For ureas of the naphthalene series, v. Bayer & Co., D. R. PP. 278122, 284938, 289107, 289163, and for the di-*aryl*-urea chlorides v. D. R. P. 285134.

Urea forms condensation derivatives with *formaldehyde* (Goldschmidt, Ber. 1896, 29, 2438; Chem. Zeit. 1897, 21, 460; Di Palma, Boll. Chim. Farm. 1912, 51, 78; Einfeld and Hamburger, Ber. 1908, 41, 24; Dixon, Chem. Soc. Trans. 1918, 113, 238; Van Laer, Bull. Soc. chim. Belg. 1919, 28, 381); with β -*diketones* (Evans, J. pr. Chem. 1892, [ii.] 45, 499); with

maleic anhydride (Dunlap and Phelps, Amer. Chem. J. 1897, 19, 492); with *acetone* (Weinschenk, Ber. 1901, 34, 2185); with *ethyl oxalacetate* (Müller, J. pr. Chem. 1897, [ii.] 55, 505); with *hydrazine* (Curtius and Heidenreich, Ber. 1894, 27, 55) with *phenylhydrazine* (Edeleanu, Chem. Zentr. 1892, i. 628); with *chloral hydrate* (Coppin and Titherley, Chem. Soc. Trans. 1914, 105, 32); and with *alloxan* (Biltz, Annalen, 1921, 423, 282). For the condensation derivatives of ureas with acid esters, v. Roeder, Ber. 1913, 46, 2560.

*iso*Ureas, ψ -*carbamides*. The tautomeric form of urea $\text{HN} : \text{C}(\text{OH})\text{NH}_2$ is not known in the free state, but certain of its ethers have been prepared by the action of hydrogen chloride on cyanamide and the corresponding alcohol at 60°–70°. *Methyl-isourea* $\text{HN} : \text{C}(\text{OMe})\text{NH}_2$ has m.p. 44°–45°, b.p. 82°/9 mm.; the *hydrochloride* melts at 130°; *ethylisourea* $\text{HN} : \text{C}(\text{OEt})\text{NH}_2$ has m.p. 42°, b.p. 95°–96°/15 mm.; asym. *phenylmethylethylisourea* $\text{HN} : \text{C}(\text{OEt})\text{NMePh}$ has b.p. 137°/21 mm., the isomeric asym. *phenylethylmethylethylisourea* $\text{HN} : \text{C}(\text{OMe})\text{NEtPh}$ has b.p. 126°/15 mm. (Stieglitz and McKee, Ber. 1900, 33, 807); *propylisourea hydrochloride* melts at 64° and decomposes at 121° (Stieglitz and Noble, *ibid.* 1905, 38, 2243); sym. *m-nitrobenzoylphenylisourea methyl ether*



has m.p. 124° (Bruce, J. Amer. Chem. Soc. 1904, 26, 419).

Thiourea. Isomerism amongst the derivatives of the sulphur analogue of urea is much more general than is the case with the derivatives of urea, and the convention has been adopted of limiting the term *thiocarbamides* to derivatives of the true thiocarbamide



derivatives of the isomeric form $\text{HN} : \text{C}(\text{SH})\text{NH}_2$, being called *thioureas*¹ (Reynolds, Chem. Soc. Trans. 1891, 59, 395).

Thiourea is prepared by heating ammonium thiocyanate at 160°–170°, the reaction is a balanced one; equilibrium is reached in about an hour, when the mixture contains about 25 p.c. of thiourea (Reynolds, Annalen, 1869, 150, 224; Reynolds and Werner, Chem. Soc. Trans. 1903, 83, 1; Findlay, *ibid.* 1904, 85, 403). Thiourea can also be obtained by the action of hydrogen sulphide on cyanamide



(Baumann, Ber. 1875, 8, 26).

Thiourea crystallises in needles that melt at about 172° if rapidly heated; the true melting-point cannot be determined, owing to tautomeric change; it is probably above 177° (Findlay, *l.c.*).

Derivatives. The *nitrate* $\text{OSN}_2\text{H}_4 \cdot \text{HNO}_3$, the *hydrochloride* $\text{CSN}_2\text{H}_4 \cdot \text{HCl}$, and the *silver*

¹ To distinguish between the three isomeric forms of substituted derivatives of thiourea, Dixon (Chem. Soc. Trans. 1895, 67, 564) proposes to designate the NH and NH_2 attachments as α and ν , whilst if the sulphur attachment is occupied by the substituent the compound is designated a *pseudothiourea*. Thus, for example, the systematic names of $\text{EtN} : \text{C}(\text{SH})\text{NMe}_2$, $\text{NH} : \text{C}(\text{SMe})\text{NH}_2$, and $\text{EtN} : \text{C}(\text{SMe})\text{NHMe}$ would be, respectively, α -ethyl- ν -dimethylthiourea, methyl- ν -thiourea, and methyl- α - ν -diethylthiourea.

nitrate derivative $\text{CSN}_2\text{H}_4\cdot\text{AgNO}_3$ are crystalline (Stevens, Chem. Soc. Proc. 1902, 17, 210; Kurnakow, Ber. 1891, 24, 3956). Dithiocarbamide dichloride $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$ can be crystallised from concentrated hydrochloric acid, and forms the dinitrate $(\text{CSN}_2\text{H}_4)_2(\text{NO}_3)_2$ by the action of dilute nitric acid; the dibromide



and di-iodide $(\text{CSN}_2\text{H}_4)_2\text{I}_2$ are colourless and decompose on warming or by the action of solvents (Claus, Annalen, 1875, 179, 135; McGowan, Chem. Soc. Trans. 1886, 49, 190). The potassium compound $\text{CSN}_2\text{H}_4\cdot\text{K}(\text{CSN}_2\text{H}_4)_2$ forms needles, m.p. 145° (Werner, Chem. Soc. Trans. 1916, 109, 1120); acetylthiocarbamide, m.p. 165° ; diacetylthiocarbamide, m.p. 151° – 152° (Hohmam, J. Amer. Chem. Soc. 1915, 37, 2130; Werner, l.c.).

For the alkyl and aryl substituted derivatives of thiourea and thiocarbamide, see Arzruni, Ber. 1871, 4, 406; Miguel, Bull. Soc. chim. 1877, [ii.] 28, 104; de Clermont, Compt. rend. 1876, 82, 512; Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358; A. E. Dixon, Chem. Soc. Trans. 1891, 59, 562; 1892, 61, 536; 1893, 63, 318, 538; 1895, 67, 556; 1899, 75, 373; 1906, 89, 892; 1907, 91, 912; 1908, 93, 18; Werner, Chem. Soc. Trans. 1919, 115, 1168. M. W. A.

UREASE v. FERMENTATION.

Urease is produced more profusely by pure cultures of *Bacterium radicum* than by the nodules, particularly by *viciae*, *trifolii*, and *pisiformis*. Urease is also, in certain cases, a product of normal papilionaceous plants (M. W. Beijerinck, Chem. Soc. Abstr. 1923, 124, i. 1157).

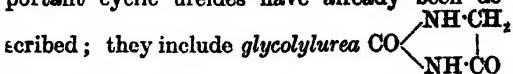
From dried cultures of *Bacillus proteus* a soluble urease has been extracted by the use of various phosphate solutions (Tetsugora Takahata, Chem. Soc. Abstr. 1923, 124, i. 1157).

The presence of two constituents in urease has been confirmed by N. Katô (Biochem. Zeitsch. 1923, 139, 352–365). The urease system consists of a thermo-labile constituent which possesses fermentative properties, and a thermo-stable constituent with no fermentative action which N. Katô calls 'stable component X.' This last, at urea concentrations above the 'equivalent urea concentration' (l.c.), increases the activity of the urease, but has no influence at substrate concentrations below this value; its action resembles that of glycine. The action of 'stable component X' is not due to alteration of the hydrogen ion concentration nor to the presence of mineral salts (J. Chem. Soc. Ind. 1923, 42, 993 A).

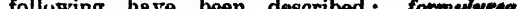
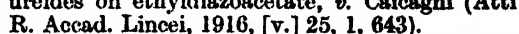
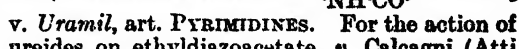
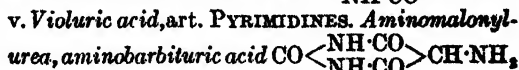
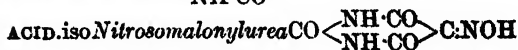
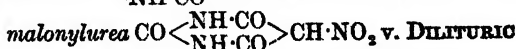
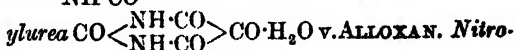
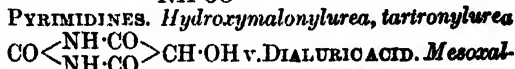
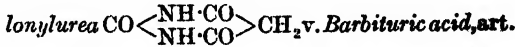
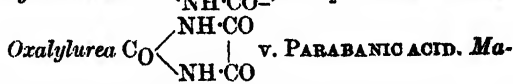
Urease effects complete conversions of urea into ammonium carbonate. The sample of urea, in aqueous solution, is brought to exact neutrality, a neutral urease solution (freshly extracted from jack-bean flower by means of water, the mixture being exactly neutralised with hydrochloric acid) added, and the mixture kept at room temperature for one hour. A known excess of N/10 hydrochloric acid is then added and the carbon dioxide removed by aeration. The excess of acid is titrated with N/10 sodium hydroxide; each c.c. of N/10 acid consumed is equivalent to 3 mg. of urea originally present. The results are accurate to within a few hundredths of 1 p.c. The method can be used for determining urea in cyanamide and in

phosphate mixtures (after precipitating the phosphate with baryta), and appears to be of quite general application. Most salts have a depressant effect on the action of urease, and barium and calcium chlorides must be removed prior to its addition (E. J. Fox and W. J. Geldard, Ind. Eng. Chem. 1923, 15, 743–745; J. Soc. Chem. Ind. 1923, 42, 901 A).

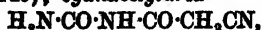
UREIDES or acyl derivatives of urea are formed by condensation between urea and the acid with the elimination of water; in the case of a monocarboxylic acid the product may be a monoureide $\text{RCONH}\cdot\text{CO}\cdot\text{NH}_2$ or a diureide $\text{CO}(\text{NH}\cdot\text{COR})_2$, according as one or two molecules of the acid condense with one molecule of urea. Similar products may be obtained in the cases of the hydroxy acids and the di-carboxylic acids, but usually condensation occurs between one molecule of the acid and one of urea with the elimination of two molecules of a water and the formation of a cyclic ureide. The more important cyclic ureides have already been described; they include glycolylurea



v. HYDANTOIN. β -Lactylurea, hydracrylurea, hydrouaril $\text{CO} \begin{array}{l} \text{NH}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{array} \text{CH}_2$ v. PYRIMIDINES.



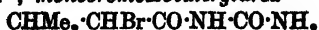
tribromacetylurea, m.p. 158° (Baeyer, Annalen, 1864, 130, 149); *cyanacetylurea*



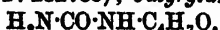
m.p. 200°–210°; *isovalerylurea*



m.p. 191°; *monobromoisovalerylurea*

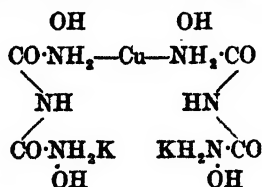


(*bromoura*), m.p. 149°, is a narcotic (van der Eekhout, Arch. exp. Path. Pharm. 1907, 57, 338); it yields two *cotarnine* derivatives, m.p. 125°–127° and 105°–110° respectively, and these have therapeutic values (Knoll & Co., D. R. P. 232785); *butyrylurea*



m.p. 176°; *succinylurea* $\text{C}_4\text{H}_5\text{O}_2(\text{NH}\cdot\text{CO}\cdot\text{NH})_{1/2}$; *benzoylurea* $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{COPh}$, m.p. 200°; *adibenzoylurea* $\text{CO}(\text{NH}\cdot\text{COPh})_2$, m.p. 210°; *aa-dibenzoylurea* $\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{COPh})_2$, m.p. 197°; *p-nitrobenzoylurea*, m.p. 243°–245° (evolution of gas); *o-chloroacetylaminobenzoylurea*, m.p. 222°–223° (effervesces); the *meta*-derivative melts at 252°–253° (decomp.) (Jacobs and Heidelberger, J. Amer. Chem. Soc. 1917, 39, 2418).

Carbonyldiurea $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ decomposes on heating (Schmidt, J. pr. Chem. 1872, [ii.] 5, 39); *carboxylurea*, *allophanic acid* $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{COOH}$ does not exist in the free state; the *esters* can be obtained by the action of phosphoric oxide on the corresponding urethane (Billmann and Bjerrum, Ber. 1917, 50, 503); the *methyl ester* has m.p. 208° (Ephraim, Ber. 1893, 26, 2172), the *ethyl ester*, m.p. 191° (Liebig and Wöhler, Annalen, 20, 396; 59, 291); the *amide* $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CONH}_2\cdot\text{H}_2\text{O}$ is *biuret*, m.p. 190°; it gives a purplish-violet colour with copper sulphate and potassium hydroxide, due to the formation of the double salt



A similar reaction is given by proteids which contain two amino groups in the molecule, these groups being joined directly together or through a single atom of nitrogen or carbon. The amino groups must be either two $\cdot\text{CONH}_2$ groups or one $\cdot\text{CONH}_2$ group and one $\cdot\text{CSNH}_2$, $\text{Q}(\text{NH})\text{NH}_2$, or $\cdot\text{CH}_2\text{NH}_2$ group. Substances that are non-proteid in character but which contain the necessary groups will also give the biuret reaction, for example, *oxamide* and *malonamide*.

The *ureides of substituted aminonaphthol sulphonic acids* form dyes when coupled with diazotised aniline or similar compounds, and may be employed as therapeutic agents for destroying blood parasites. They form metallic salts, which also possess therapeutic properties (Heymann, Dresel, Kothe, Ossenbeck, U.S. Pat. 1308071).

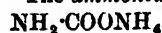
Carbonyldiurethane, m.p. 108°, is produced by the action of urethane on carbonyl chloride; for the action of ammonia and amines on this compound, see Dains, Greder and Kidwell (J. Amer. Chem. Soc. 1919, 41, 1004); Dains and Werthein (*ibid.* 1920, 42, 2303).

Ureides of Sugar. The term *ureide* is also

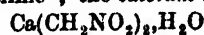
applied to certain condensation products of urea with aldehydes; these are of the type $\text{RCH}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ and the most important are those derived from the aldoses. *Glucoseureide* $\text{CH}_2\text{OH}[\text{CH}\cdot\text{OH}]_4\text{CH}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, thick rhombic crystals, m.p. 207° (decomp.), $[\alpha]_D^{15} = -23.5^\circ$ in 10 p.c. aqueous solution; the *penta-acetyl derivative* $\text{C}_7\text{H}_5\text{O}_5\text{N}_2(\text{CH}_2\text{CO})_5$ has m.p. 200°, and the *tetrabenzoyl* m.p. 117°. *Galactoseureide* is a white amorphous powder $[\alpha]_D + 15^\circ$; *mannoseureide*, m.p. 188°, $[\alpha]_D^{20} = -45.8^\circ$; *lactoseureide* ($\text{C}_{12}\text{H}_{22}\text{O}_{10}\text{N}_2$) $\text{N}\cdot\text{CO}\cdot\text{NH}_2$ decomposes at 240°, $[\alpha]_D^{20} + 2.1^\circ$ (Schoorl, Rec. trav. chim. 1903, 22, 31; Mayer, Biochem. Zeitsch. 1909, 17, 1345). M. A. W.

URETHANE v. SYNTHETIC DRUGS.

URETHANES are the esters of *carbamic acid* (*aminoformic acid*) $\text{H}_2\text{N}\cdot\text{COOH}$; the free acid is not known, but it is said to occur in blood-serum (Drechsel, J. pr. Chem. 1875, [ii.] 12, 417; cp. Hofmeister, Archiv. Physiol. 1876, 12, 337), and in urine (Abel and Drechsel, Chem. Zentr. 1891, ii. 713; Hahn and Nencki, Arch. Sc. biol. Petersb. 1892, 1, 467; Abel and Muirhead, Arch. exp. Path. Pharm. 1893, 31, 15; 32, 467). The *ammonium salt*

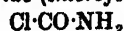


is produced by the direct action of carbon dioxide on ammonia in cooled absolute alcohol. It is a white crystalline powder. The *sodium* $\text{NaCH}_2\text{NO}_2\cdot\text{H}_2\text{O}$ and *potassium* KCH_2NO_2 salts are also crystalline; the *calcium salt*



is insoluble in alcohol and crystallises from concentrated ammonia solution in four-sided prisms.

Carbamyl chloride (chloroformamide)



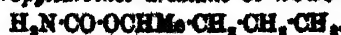
prepared by passing hydrogen chloride over heated metallic cyanates, or carbonyl chloride over heated ammonium chloride, forms long, broad needles, m.p. 50°, b.p. 61°–62° (Gattermann and Schmidt, Ber. 1887, 20, 858).

Urethane, *ethyl carbamate* $\text{NH}_2\cdot\text{COOEt}$, prepared by the action of ammonia on ethyl carbonate or ethyl chlorocarbonate; by heating urea nitrate with alcohol; or by the action of alcohol on carbamyl chloride, crystallises in large pliable plates or prisms that break with a fibrous fracture, sublime readily, melt at 50° and boil at 184°. The system urethane-benzene forms a eutectic containing 97 mols. p.c. at 4.2°, and solid solutions in the interval from 97 to 100 mols. p.c. of benzene (Puschin and Mazarovitch, J. Russ. Phys. Chem. Soc. 1914, 46, 1366). For the use of urethane as a cryoscopic solvent, see Bruni (Atti R. Accad. Lincei, 1918, [v.] 27, i. 321). When heated with water or ammonia, urethane yields a small quantity of urea; for the explanation of this reaction, see Werner (Chem. Soc. Trans. 1918, 113, 622).

Urethane has therapeutic properties, being employed as a hypnotic. Certain of its substituted derivatives have similar properties; for example, *phenylurethane* or *euphorine*



methylpropylcarbinol urethane or *hedonal*



and *cotarnine-urethane*, m.p. 110° (Knoll & Co., D. R. P. 232785).

Urethanes when heated with calcium or strontium bromide yield double compounds of the urethane and the metallic bromide;



is a powerful hypnotic (v. J. Soc. Chem. Ind. 1915, 34, 1166; and Gebe & Co., D. R. P. 284734).

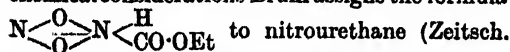
p-Benzylphenyl carbamate, m.p. 144°, *p*-isomylphenyl carbamate, m.p. 73°–74°, *p*-butylphenyl carbamate, m.p. 123°–124°, *p*-isopropylphenyl carbamate, m.p. 93°–95°, *p*-butylphenyl *N*-dimethylcarbamate, m.p. 92°, *o*-allylphenyl carbamate, m.p. 122°–123°, are white powders, sparingly soluble in water, and possess anthelmintic properties (Synthetic Patents Co., U.S. Pat. 1252452, and Farbenfabriken vorm. Friedr. Bayer & Co., D. R. P. 296889, from Chem. Zentr. 1917, i. 714).

4-Hydroxy-3-urethano-phenylarsine



is a white powder, (Farbwerke vorm. Meister, Lucius and Brüning, D. R. P. 275216, addition to D. R. P. 268220).

Nitrourethane $\text{NO}_2 \cdot \text{NH} \cdot \text{COOEt}$ melts at 64°, is readily soluble in water and alcohol and forms metallic salts, the *potassium*, *mercury*, and *silver* salts having been prepared (Thiele and Lachmann, Annalen, 1895, 288, 304). From spectrochemical considerations Brühl assigns the formula



physikal. Chem. 1898, 26, 47; 25, 577). *Nitroso-urethane* $\text{NO} \cdot \text{NH} \cdot \text{COOEt}$ melts and decomposes at 51°–52° and does not develop a purple colour with ferrous sulphate and potassium hydroxide: the *silver*, *potassium* and *ammonium* derivatives are yellow (Thiele and Lachmann, l.c.). From index of refraction values, Brühl regards nitro-

sourethane as diazourethane $\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{NH} \cdot \text{COOEt}$

(Ber. 1902, 35, 1148), whilst Hantzsch formulates it as an *antidiazohydrate* $\text{HO} \cdot \text{N} : \text{N} \cdot \text{COOEt}$ (*ibid.* 1899, 32, 575). *Dibromourethane* $\text{NBr}_2 \cdot \text{COOEt}$ has b.p. 100°–104°/10–11 mm. (Diels and Ochs, Ber. 1907, 40, 4571). *Ethylchlorocarbamate* $\text{NHCl} \cdot \text{CO}_2\text{Et}$ is obtained by the action of chlorine on ethyl carbamate if the solution is kept well cooled; it is a pale yellow viscous oil, b.p. near 99° (decomp.) (Datta and Gupta, J. Amer. Chem. Soc. 1914, 36, 386); it is slowly hydrolysed by water, yielding ethyl 4-chloromethylcyclomethylenhydrazineimide 1:3-dicarboxylate $\text{CH}_2\text{Cl} \cdot \text{CH} \begin{array}{c} \text{N}(\text{CO}_2\text{Et}) \\ \diagdown \text{N}(\text{CO}_2\text{Et}) \end{array} \text{NH}$, colourless needles, m.p. 143°, which forms a crystalline *acetyl* derivative, m.p. 117°–118°, and *imide chloride*, m.p. 75°–76° (Datta and Chatterjee, *ibid.* 1922, 44, 1538).

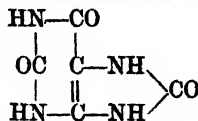
Urethane forms condensation products with aldehydes and keto acids. *Chloralurethane* $\text{OCl} \cdot \text{CH}(\text{OH})\text{NH} \cdot \text{COOEt}$ has m.p. 103°; *bromalurethane* $\text{CBr}_2 \cdot \text{CH}(\text{OH})\text{NH} \cdot \text{COOEt}$ has m.p. 132° (Bischoff, Ber. 1874, 7, 628, 1078; Conrad and Hoek, *ibid.* 1903, 36, 2306; Simon, Compt. rend. 1901, 133, 536; Simon and Chavanne, *ibid.* 1904, 143, 51).

Thiourethane, a mixture of the isomeric thiourethanes, is obtained by acting on an alcoholic solution of potassium thiocyanate with concentrated hydrochloric acid; these correspond with two of the isomeric forms of the hypothetical thiocarbamic acid, *ethyl xanthamide* $\text{NH}_2 \cdot \text{CS} \cdot \text{OEt}$, m.p. 38°, and *carbonylthioethylamine* $\text{NH}_2 \cdot \text{CO} \cdot \text{SEt}$ (Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358).

M. A. W.

URGINEA. v. SQUILL.

URIC ACID, 2:6:8-trioxypurine



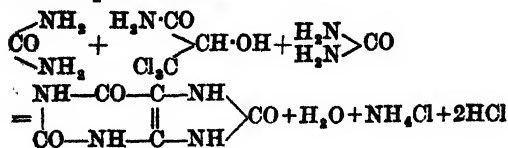
was discovered in human urine by Scheele in 1776 (Opuscula, 1776, 2, 73), independently by Bergmann in urinary calculi (*ibid.* 1776, 4, 232), and in 'chalk-stones' by Pearson in 1798 (Trans. Roy. Soc. 1798, 15).

Uric acid occurs in the urine of all animals, though only to a small extent in the case of herbivorous animals; the average daily excretion in normal man being 0.597 grm. (Hanzlik and Hawk, J. Biol. Chem. 1908, 5, 355). It occurs in the excrement of birds, reptiles, scaly amphibians, snails and insects; the wing scales of the group of butterflies known as the white *Pieridae* contain uric acid, those of the yellow *Pieridae* contain, as their pigment, a yellow derivative of uric acid, which can be obtained synthetically by heating uric acid with water in sealed tubes at a high temperature (Hopkins, Proc. Roy. Soc. 1894, 57, 5). Uric acid is a normal constituent of the organs and blood of birds, but only occurs in human blood under certain pathological conditions. For its occurrence in blood, v. Bass (Amer. Chem. Abs. 1914, 1602).

Preparation.—Uric acid can be isolated from serpent's excrement, bird's excrement or guano by boiling the material with dilute alkali hydroxide or milk of lime, filtering the hot liquid and precipitating the uric acid by adding excess of hydrochloric acid to the filtrate. Uric acid can also be obtained from the yellow acid urates deposited from urine; this is boiled with sodium hydroxide until it ceases to evolve ammonia, the liquid is filtered and the acid sodium urate precipitated from the filtrate by means of carbon dioxide; this is redissolved in sodium hydroxide and the solution decomposed by acetic acid, or the hot solution of the alkali salt may be purified by boiling with a little potassium permanganate or dichromate and the filtrate decomposed by hydrochloric acid.

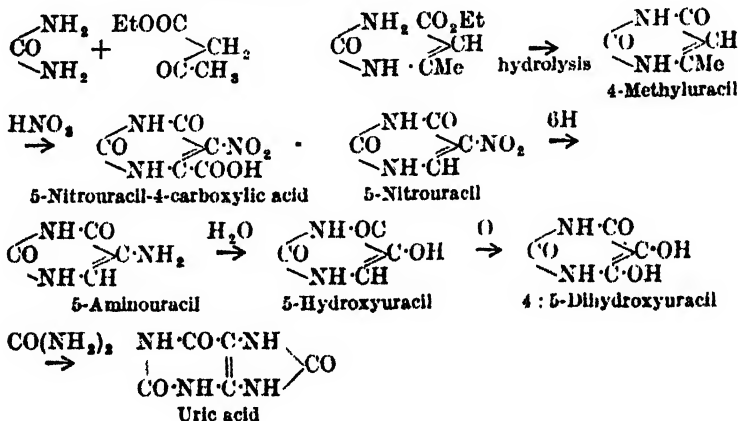
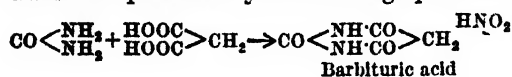
Synthesis.—Uric acid was first synthesised by Horbaczewski by carefully fusing glycine with 10 to 15 times its weight of urea in small quantities at a time, until a considerable quantity of precipitate had formed in the molten mass; the uric acid was precipitated in the form of its sparingly soluble silver magnesium salt, which on treatment firstly with potassium sulphide and subsequently with hydrochloric acid, yielded pure uric acid (Monatsh. 1882, 3, 796; 1885, 6, 366). Compare, however, Behrend (Annalen, 1925, 441, 2159; Chem. Soc. Abstr. 1925, i. 441). Further syntheses were effected by Horbaczewski

(*ibid.* 1887, 8, 201) by fusing trichlorolactamide with 10 parts of urea

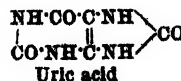
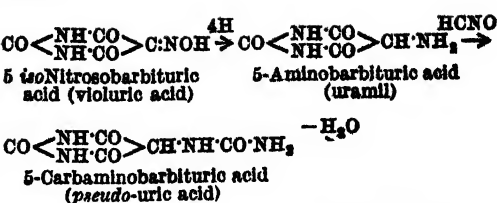


and by fusing trichlorolactic acid with urea (*ibid.* 1887, 8, 584).

In 1863, Baeyer (Annalen, 1863, 127, 3, 234) synthesised *pseudouric acid*, starting with malonic acid and urea; but it was not until 1895 that Fischer and Ach (Ber. 1895, 28, 2473) showed that uric acid could be readily obtained from pseudouric acid by fusion with oxalic acid, or by boiling with hot dilute mineral acids (Fischer, *ibid.* 1897, 30, 559); a complete synthesis of uric acid from malonic acid and urea is therefore represented by the following equations:

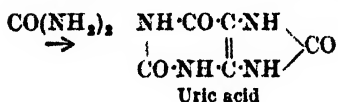
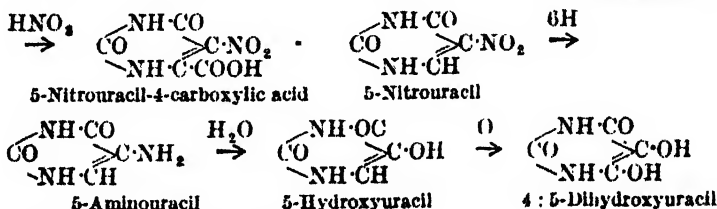
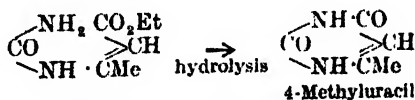


Traube's synthesis of uric acid, starting with cyanacetic acid and urea, is also important, and by substituting alkyl ureas for urea, the method can be extended to the preparation of substituted uric acids. Cyanacetylurea, prepared by the condensation of urea with cyanacetic acid, is converted by the action of alkali into 4-amino-

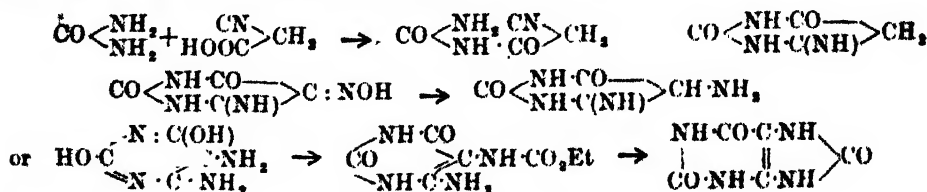


This is the most important synthetic method of preparing uric acid, and by replacing urea by its alkyl or aryl substituted derivatives, it is possible to prepare the corresponding alkyl or aryl substituted uric acids.

The synthesis of uric acid effected by Behrend and Roosen (Annalen, 1888, 251, 235), starting with ethyl acetoacetate and urea, is represented in the following series of equations:



2:6-dioxypyrimidine, from which 4:5-diamino-2:6-dioxypyrimidine is obtained by reducing its isonitroso derivative; this diamine condenses with ethyl chloroformate to form a urethane derivative, from the sodium derivative of which uric acid is produced by heating at 180°-190° (Ber. 1900, 33, 1375, 3035).



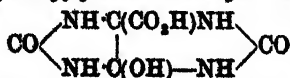
Properties. Pure uric acid forms a colourless microcrystalline powder consisting of rhombic transparent plates or prisms; as precipitated from urine or guano extracts, the crystals are yellowish red or brown. These exhibit, under the microscope, characteristic irregularities in form, due to the rounding of the obtuse angles of the rhombic prisms, and the interpenetration of the crystals, and present the form of dumb-bells, whetstones, rosettes of

prismatic crystals, six-sided irregular plates or rectangular plates with partly jagged sides.

Uric acid is odourless and tasteless; it is sparingly soluble in water, one part dissolving in 39,480 parts at 18° (His and Paul, Zeitsch. physiol. Chem. 1900, 31, 41), or 15,505 parts at 37° (Gudzent, *ibid.* 1909, 60, 27). When shaken with water, uric acid decomposes so that the solubility tends to increase with the time; the increase is only noticeable at the end of 24 hours

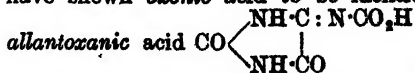
and then rises rapidly until at the end of 10 days the solubility is 11 times as great as at the end of a few hours, and in the same time the electrical conductivity has increased 55 times (Gudzent, *l.c.*; cf. Biltz and Herrmann, *Annalen*, 1923, 104). The supersaturation which occurs when a warm aqueous solution of uric acid is allowed to cool to a room temperature in contact with solid uric acid is probably the cause of the high values for the solubility found by Bensch (*Annalen*, 1845, 54, 190); Behrend and Roosen (*Annalen*, 1889, 251, 250). The molecular electrical conductivity of a saturated solution of uric acid is 32.24 at 18° (His and Paul, *l.c.*) or 33.92 at 37° (Gudzent, *l.c.*); the dissociation constant $k=0.000151$ at 18° or 0.000233 at 37°. See also Kanitz (*Zeitsch. physiol. Chem.* 1921, 116, 96). Uric acid has the power of adsorbing precipitated colloids from their solutions. If a trace of dye is added to a hot saturated solution of uric acid, coloured crystals of the latter are deposited from the cold solution (Benoit, *Compt. rend. soc. biol.* 1919, 82, 1051, 1052). Uric acid is fairly readily soluble in lactic acid, acetic acid (see Rossi, *Biochem. Zeitsch.* 1913, 54, 297) or warm concentrated sulphuric acid. For the influence of hydrogen-ion concentration on its solubility, see Jung (*Helv. Chim. Acta*, 1922, 5, 688). It dissolves in glycerol, but is insoluble in alcohol or ether; it dissolves readily in aqueous solutions of alkali hydroxides, of lithium carbonate, and of certain bases such as ethylamine, propylamine, piperazine, but is only sparingly soluble in solutions of *urotropine* (hexamethylenetetramine), *lycetol* (piperazine tartrate) or ammonia (Stevens and May, *J. Amer. Chem. Soc.* 1911, 33, 434; v. also Hanzlik, *Amer. Chem. Abs.* 1916, 1226). The solubility of uric acid in a 1 p.c. solution of sodium salicylate is twice as great, and in a 0.1 p.c. solution of sodium 2-phenylquinoline 4-carboxylate three times as great as in water (Stern, *Biochem. Zeitsch.* 1924, 151, 268; 1925, 159, 192).

Uric acid is not volatile: on being strongly heated it breaks up into urea, hydrocyanic acid, cyanuric acid and ammonia (Wöhler, *Pogg. Ann.* 1839, 15, 529, 619). When oxidised by strong nitric acid or potassium chlorate and hydrochloric acid, or by chlorine or bromine water in the cold, uric acid is broken down into alloxan (mesoxalylurea (*q.v.*) and urea. For cyanuric acid as oxidation product of uric acid, v. Venable and Moore (*J. Amer. Chem. Soc.* 1917, 39, 7750). Warm dilute nitric acid produces parabanic acid (oxalylurea) (*q.v.*). By the action of such oxidising agents as potassium permanganate, or ferricyanide, lead peroxide, mercuric oxide or ozone in neutral or alkaline media, uric acid yields carbon dioxide and allantoin (glyoxyldiureide) (*q.v.*). According to Behrend (*Annalen*, 1904, 333, 141) and Behrend and Schultz (*ibid.* 1909, 365, 21), the first product of oxidation of uric acid in alkaline media is *hydroxyglycoluril carboxylic acid*



which on treating (a) with an excess of alkali hydroxide takes up the elements of water, forming *urosonic acid* (dicarbaminomalonic acid)

(COOH), $\text{C}(\text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$ (*q.v.*; see also Behrend and Zieger, *Annalen*, 1915, 410, 337; Biltz and Max, *Ber.* 1920, 53, 1964; Biltz and Robl, *ibid.* 1967); (b) with acetic acid yields potassium hydrogen *oxonate* (Strecker, *Chem. Soc. Trans.* 1875, 555); Biltz and Robl (*Ber.* 1920, 53, 1967), have shown *oxonic acid* to be identical with



When oxidised by hydrogen peroxide in alkaline solution, uric acid yields *tetracarbonimide* $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{CO} \cdot \text{NH} \end{array} \text{CO}$ (Scholtz, *Ber.* 1901, 34, 4130), *carbonyldiurea* $\text{CO}(\text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$, and *urea* (Schittenhelm and Wiener, *Zeitsch. physiol. Chem.* 1909, 62, 100; cf. Venable and Moore, *l.c.*; Venable, *ibid.* 1918, 40, 1099; Moore and Thomas, *ibid.* 1120; see also Ohta, *Biochem. Zeitsch.* 1913, 54, 439).

Uric acid is decomposed when fused with potassium hydroxide, yielding the potassium salts of prussic, cyanic, carbonic and oxalic acids. When heated under pressure at 160°–170° with concentrated hydrochloric or hydriodic acid, it yields carbon dioxide, ammonia and glycocholl; it is oxidised by a solution of copper oxide in ammonia (Schweizer's reagent) in the presence of potassium hydroxide to urea and oxalic acid, and a similar oxidation is effected by boiling with ferric chloride. It is decomposed by certain moulds (Kossowicz, *Bied. Zentr.* 1912, 41, 791; *Chem. Zentr.* 1912, ii, 1300, 1482; 1913, i, 640).

For the physiological properties of uric acid, its origin, and the rôle it plays in the animal economy, see Article URINE; also *Biochemisches Handlexikon von Abderhalden*, vol. iv. 1095–1106; and *Oxidations and Reductions in the Animal Body*, by H. D. Dakin, 92. For the influence of drugs on the elimination of uric acid from the blood, v. Abl (*Arch. Expt. Path. Pharm.* 1913, 74, 119); Denis (*J. Pharmacol.* 1915, 7, 255, 601); Folin and Lyman (*J. Pharmacol. Expt. Ther.* 1913, 4, 539); Impens (*Chem. Zentr.* 1914, 563).

Detection.—Uric acid is readily identified by the appearance of the crystals under the microscope. The most characteristic and delicate test for uric acid is the 'murexide test,' which is applied as follows: a few drops of strong nitric acid is added to the uric acid or urate and the solution evaporated to dryness on the water bath, preferably in a porcelain basin; a yellowish-red residue of alloxantin is obtained which acquires the rich purple colour of ammonium purpurate (*murexide*, *q.v.*) on moistening with ammonia, the colour changing to blue on the addition of sodium hydroxide. The nitric acid employed in the test may be replaced by chlorine or bromine water, or by a few drops of concentrated hydrochloric acid and a small crystal of potassium chlorate. Other colour reactions of uric acid are described by (1) Denigès (*J. Pharm. Chim.* 1888, [v.] 18, 161), the uric acid is oxidised to alloxan by evaporating a solution in dilute nitric acid; on adding successively to the residue a few drops of concentrated sulphuric acid and of benzene containing thiophen, a bluish coloration is obtained; (2) Ganaassini (*Boll. chim. farm.* 1908, 47, 714), the uric acid or urate is suspended in water and

dissolved in 10 p.c. sodium hydroxide; subsequent saturation of the solution with potassium persulphate and the gradual addition of 10 p.c. zinc sulphate solution, until the precipitate formed no longer redissolves, causes the precipitate to assume a bluish-green colour. This test is not disturbed by the presence of proteins, other purines or pyrimidines, and may be applied for the detection of uric acid in urine or in blood. According to Vitali (*ibid.* 1911, 50, 799), sodium peroxide is the only oxidising agent that can replace the potassium persulphate in the above test, and no other metallic salt can be used instead of the zinc salt. (3) Folin and Denis (J. Biol. Chem. 1912, 12, 239), a blue coloration is developed when a solution containing 1 mg. of uric acid is mixed with 2 c.c. of a solution prepared by boiling for two hours a mixture of 100 grms. sodium tungstate, 80 c.c. of 85 p.c. phosphoric acid, and 750 grms. of water, cooling and diluting to a litre (compare Leturc, Ann. Chim. anal. 1907, 12, 194; Bass and Wiechowski, Chem. Zentr. 1913, i. 331 Obermayer, Popper and Zak, *ibid.* 658). Tests based upon the reducing properties of uric acid are the formation of a yellow, brown, or black stain of silver, when filter paper previously moistened with silver carbonate is treated with a drop of a solution of uric acid in sodium carbonate; and the reduction of Fehling solution on boiling an alkaline solution of uric acid with excess of the reagent. For the detection of uric acid in blood, Weber (Pharm. Zeit. 1912, 57, 252) recommends the following method: the blood is treated with sodium chloride and potassium phosphate to remove the proteins, the filtrate evaporated to a small bulk and saturated with ammonium chloride, the uric acid is thus precipitated as ammonium urate, which is collected and treated with a few drops of hydrochloric acid and the crystals of uric acid identified under the microscope or by the murexide test.

Estimation.—The methods of estimating uric acid in urine are based upon the precipitation of the uric acid in the form of the sparingly soluble ammonium or the double silver magnesium salt, and the subsequent determination of the uric acid in the carefully washed precipitate. Hopkins' method (Proc. Roy. Soc. 1892, 52, 93; J. Path. and Bacteriology, 1893, 1, 451), 30 grms. of ammonium chloride are added to 150 c.c. of the filtered urine previously warmed to 40° to 45°, after about an hour the precipitate of ammonium urate is collected on a small filter, washed with a 10 p.c. solution of ammonium sulphate until free from chlorine, and transferred to a beaker by means of a jet of hot water, the solution cooled and diluted with water to 100 c.c., 20 c.c. of pure concentrated sulphuric acid are added, and N/20 potassium permanganate run into the acid liquid at 60° until it acquires a pink tint permanent for some seconds and not changed by stirring. Each c.c. of N/20 permanganate solution decolorised represents 0.00375 gm. of uric acid. See Herles (Eighth Inter. Cong. App. Chem. 1912, 19, 141); Telle (Bull. Sci. Pharmacol. 1918, 25, 208).

Wörner (Zeitsch. physiol. Chem. 1900, 29, 70) recommends decomposing the washed ammonium urate with 1-2 p.c. sodium hydroxide solution, heating the solution on the water-bath

until it ceases to evolve ammonia and then determining the nitrogen in the residue by the Kjeldahl method: 1 c.c. N/10 sulphuric acid corresponds with 0.0042 gm. uric acid; Kowarsky (Berlin, Klin. Woch. 1917, 54, 987) recommends the estimation of the ammonia in the ammonium urate by the formalin method.

Folin and Shaffer's modification of Hopkins' method (Zeitsch. physiol. Chem. 1901, 32, 552) is as follows: A solution containing 500 grms. of ammonium sulphate, 5 grms. uranium acetate, and 10 p.c. acetic acid, 60 c.c. per litre is prepared, and 75 c.c. of this solution are mixed with 300 c.c. of the urine, kept for five minutes, passed through a double filter and two quantities of 125 c.c. each collected. Five c.c. of concentrated ammonia are added to each and after about 12 hours the precipitates of ammonium urate are collected and washed and the uric acid in each estimated by the permanganate method. The addition of uranium acetate is made in order to precipitate a small quantity of protein material which is otherwise thrown down on the addition of the ammonia, and which reduces permanganate. Ganassini (Boll. Chim. Farm. 1914, 53, 257) uses a modification of this method for precipitating the uric acid, which is then estimated by means of standard iodine solution, the uric acid being oxidised to alloxan, see Curtman and Lehmann (J. Biol. Chem. 1918, 26, 187).

Salkowski's method modified by Ludwig (Chem. Zentr. 1891, 390) consists in precipitating the uric acid in the urine (100 to 200 c.c.) with a mixture of ammoniacal silver solution and magnesia mixture (cf. Salkowski, Zeitsch. physiol. Chem. 1913, 83, 152); the precipitate containing all the uric and phosphoric acids is filtered and washed with very dilute ammonia. It is then decomposed by a warm dilute solution of potassium sulphide forming potassium urate which passes into solution, the filtrate is acidified with hydrochloric acid, evaporated to a small bulk, and the uric acid that separates on cooling is collected on a tared filter, washed with water, alcohol, ether, carbon disulphide, and again with ether, dried at 110° and weighed, see Salkowski (Zeitsch. physiol. Chem. 1913, 83, 152); Kretschmer (Biochem. Zeitsch. 1913, 50, 223); Graves and Kober (J. Biol. Chem. 1915, 20, xx.); (v. Bernard (Chem. Zentr. 1913, 1, 1364; from Bull. Sci. Pharmacol. 1913, 20, 65, for a comparative investigation of different methods; he maintains Salkowski's method gives the best results).

Folin and Shaffer (Zeitsch. physiol. Chem. 1901, 32, 552) recommend the following modification of the method in order to facilitate the removal of the silver from the silver magnesium urate; the double salt is decomposed by sulphuretted hydrogen in an acid solution containing 5 to 10 c.c. of 1 p.c. copper sulphate solution and the liquid boiled for a few minutes before filtering (cf. Schneller, Chem. Zentr. 1913, 1234).

Folin and Macallum recommend a colorimetric method for estimating uric acid in dilute solution based upon the blue colour produced when phosphotungstic acid and an alkali are added to uric acid (J. Biol. Chem. 1912, 11, 305; Folin and Denis, *ibid.* 1912, 14, 95; Brughsh and Kristeller, Chem. Zentr. 1915, i. 1090;

Benedict and Hitchcock, *J. Biol. Chem.* 1915, 20, 619, 629). The replacement of phosphotungstic by arsenotungstic or arseno-phosphotungstic acid gives a greater depth of colour (Morris and Macleod, *J. Biol. Chem.* 1922, 50, 55; Benedict, *ibid.* 1922, 51, 187; 52, 387). It is claimed that the method as modified by Benedict and Hitchcock (*ibid.* 1915, 20, 624) gives as accurate results as the titration method of Folin and Shaffer (*v. Morris, ibid.* 1916, 25, 205; *Proc. Amer. Soc. Biol.* 1916, xiii.; 1917, 29), who recommends precipitating the uric acid with zinc acetate in alkaline solution as a preliminary to the application of Benedict's method. See Salkowski (*Zeitsch. physiol. Chem.* 1913, 85, 346); Kaschiwabara, (*ibid.* 1913, 84, 223); Hüst (*Zeitsch. physiol. Chem.* 1915, 95, 88); Bogert (*J. Biol. Chem.* 1917, 31, 165); Morris (*Proc. Amer. Soc. Biol. Chem.* 1917, xxi.; *J. Biol. Chem.* 1918, 33; 1919, 37, 231); Cohen Tervaert (*Arch. Néerland. physiol.* 1918, 2, 337); Zaleski and Sachnovska (Russ. *Physiol. J.* 1919, 2, 14); Folin and Wu (*J. Biol. Chem.* 1919, 38, 81, 459); *cf.* Brown and Raiziss (*J. Lab. Clin. Med.* 1922, 8, 129); and Rogers (*J. Biol. Chem.* 1923, 55, 325); Guillaumin (*J. Pharm. Chim.* 1922, [vii.] 25, 5); Thiéry (*ibid.* 87); Jackson and Palmer (*J. Biol. Chem.* 1922, 50, 89; 53, 373).

For the rapid estimation of uric acid in urine, Vaillant (*Ann. Chim. Anal.* 1922, [ii.] 4, 178) titrates the liquid with a standard iodine solution made by dissolving 3·78 grms. of iodine and 15 grms. of potassium iodide in 1 litre of water. Two c.c. of this solution oxidise 0·005 gm. of uric acid to alloxan and urea. The analysis is carried out by measuring into a small tube 2 c.c. of iodine solution and 1 c.c. of carbon disulphide, and allowing the urine to fall a drop at a time from a burette, shaking the tube after each addition, until the carbon disulphide becomes first pale rose and then colourless. The uric acid content per litre of urine is calculated by dividing the number of c.c. used into 5. Sugar and small amounts of albumin do not interfere; larger amounts should be removed by heating to coagulate and then filtering. If the urine is alkaline a few drops of acetic acid are added (*Chem. Soc. Abstr.* 1922, ii. 668).

For the separation of and estimation of uric acid and xanthine bases by means of potassium-zinc ferrocyanide, *see* Thiéry (J. Pharm. Chim. 1921, 23, 494).

A colorimetric method, based on the action of uric acid on iodic acid, whereby iodine is liberated, is recommended by Autenrieth and Funk (Chem. Zentr. 1915, 1, 1918 from Münch. med. Wchschr. 1914, 61, 457); Maase and Zondek (Chem. Zentr. 1915, ii. 858). For a critical review of methods for estimating uric acid and xantho-uric substances, v. Sauzéat (J. Pharm. Chem. 5, 164, 445, 485).

Derivatives. *Salts.*—All four hydrogen atoms of uric acid are acidic and can be replaced by metals, as is shown by the formation of salts from each of the four trimethyl uric acids; the hydrogen atom 3 is the most acidic, then hydrogen 9, the hydrogen atoms 1 and 7 are much weaker in their acidity; hence uric acid behaves as a feeble dibasic acid (Biltz and Herrmann, Ber. 1921, 54, 1676), and forms three

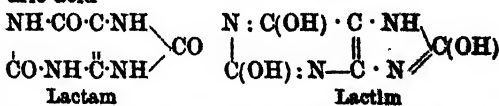
series of salts, the *normal* urates of the type $\text{Na}_2\text{C}_4\text{H}_3\text{O}_6\text{N}_4$ are readily soluble in water and are never found in the animal system; the *acid* or *diurates* $\text{NaC}_4\text{H}_2\text{O}_6\text{N}_4$ are sparingly soluble and occur pathologically in gouty concretions; and the *quadr- or hemi-urates*



are more readily soluble than the diurates and are the common form in which uric acid occurs physiologically.

Normal urates may be obtained by dissolving uric acid in the theoretical quantity of alkali. They are alkaline in reaction and are decomposed by carbon dioxide, forming the acid salt. The *potassium* salt $K_2C_5H_2O_3N_4$ is crystalline; it dissolves with partial decomposition into the acid salt in about 36 parts of cold water; the *sodium* salt $Na_2C_5H_2O_3N_4 \cdot H_2O$ is less soluble than the potassium salt, and is stated to be rendered more soluble by radium D (Gudzent, Zeitsch. f. klin. Med. 71, 3-6), and to be decomposed by the α -rays from radium emanation (Mesernitzky, Compt. rend. 1912, 154, 770); according to Knaff-Lenz and Wiechowski (Zeitsch. physiol. Chem. 1912, 77, 303), and to Kerb and Lazarus (Biochem. Zeitsch. 1912, 42 82), radium has no action on the salt under sterile conditions, but accelerates the degradation of the compound in the presence of enzymes or moulds; the *calcium* $CaC_5H_2O_3N_4$, *strontium* $SrC_5H_2O_3N_4 \cdot 2H_2O$, *barium* $BaC_5H_2O_3N_4 \cdot H_2O$, and *lead* $PbC_5H_2O_3N_4$ salts are sparingly soluble. The *mercury* salt $HgC_5H_2O_3N_4$ is a white amorphous precipitate; it does not give mercuric oxide with sodium hydroxide solution and is therefore probably a lactam salt (Auld, Chem. Soc. Trans. 1907, 1046). *Zinc*, *nickel*, and *copper* salts are described by Curtman and Hart (J. Biol. Chem. 1921, 46, 599).

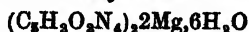
Acid or di-urates.—According to Gudzent (Zeitsch. physiol. Chem. 1909, 60, 38), uric acid forms two series of primary metallic salts (mono-sodium, potassium and ammonium urates), which differ as regards solubility. The salts of the *a*-series cannot be obtained pure, as at the moment of formation in water they tend to pass into the salts of the *b*-series. The probable cause of the change is an intramolecular rearrangement, so that the two series correspond with the two tautomeric forms of uric acid



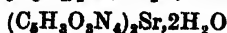
The unstable α -salts are probably the *lactam* urates, and the stable δ -salts the *lactim* urates. The α -salts have solubilities and specific conductivities that at 18° are some 33-4 p.c., or at 37° some 33-9 p.c. greater than the corresponding values for the more stable δ -salts.

The sodium salt $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{N}_2 \cdot 11\text{H}_2\text{O}$ forms a crystalline powder soluble in 1200 parts of cold or 120 parts of boiling water, forming a neutral solution. The solubility of freshly percolated sodium urate at 18° is 2.03 grms. or 9.8×10^{-3} grms. molecules per litre. On keeping, or more particularly on stirring in contact with the solution, the solubility decreases and approaches that of the crystalline form. The potassium salt $\text{KC}_2\text{H}_3\text{O}_2 \cdot \text{N}_2$ is amorphous.

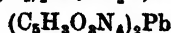
and dissolves in 800 parts of cold or 70–80 parts of boiling water; *lithium* salt $\text{LiC}_5\text{H}_3\text{O}_2\text{N}_4$ forms crystalline grains and is soluble in 370 parts of cold or 39 parts of boiling water; the *ammonium* salt $\text{NH}_4\text{C}_5\text{H}_3\text{O}_2\text{N}_4$ is soluble in 1500 parts of cold water and quite insoluble in saturated solutions of ammonium chloride or sulphate; and the *magnesium*



calcium $(\text{C}_5\text{H}_3\text{O}_2\text{N}_4)_2 \cdot \text{Ca} \cdot 2\text{H}_2\text{O}$, *strontium*



barium $(\text{C}_5\text{H}_3\text{O}_2\text{N}_4)_2 \cdot \text{Ba} \cdot 3\text{H}_2\text{O}$, and *lead*

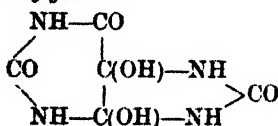


salts are described. For the formation of *colloidal uric acid* in the presence of alkalis, see Schade and Boden (Zeitsch. physiol. Chem. 1913, 83, 347); compare, however, Lichtwitz (*ibid.* 1913, 84, 416); Schade and Boden (*ibid.* 1913, 86, 238); Gudzent (*ibid.* 1914, 89, 352); Haskins (J. Biol. Chem. 1916, 26, 205); Kohler (Z. Klin. Med. 1919, 88, 14); Schade (*ibid.* 1922, 23, 1).

The *quadri-urates* are difficult to obtain pure as they readily break down into diurates and uric acid; according to Rosenheim (Lancet, 1900; Zeitsch. physiol. Chem. 1911, 71, 272) and Kohler (*ibid.* 70, 360) the quadri-urates are only mixtures, in molecular proportions, of primary urates and uric acid; they are stated to exist normally in the urine and constitute the whole of the urinary excretion of birds and reptiles (v. URINE).

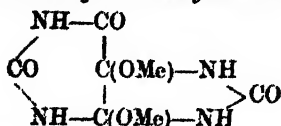
Adrenaline urate $\text{C}_9\text{H}_{13}\text{O}_3\text{N} \cdot \text{C}_5\text{H}_3\text{O}_2\text{N}_4$ forms small pointed plates (Pauly, Ber. 1904, 37, 1388). *Piperazine urate* $\text{C}_4\text{H}_{10}\text{N}_2 \cdot \text{C}_5\text{H}_3\text{O}_2\text{N}_4$ is soluble in 50 parts of water at 17°. The *phosphotungstate* of uric acid forms reddish-brown cubical plates (Drummond, Bio-Chem. J. 1918, 12, 5).

Uric acid glycol



crystallises with half a molecule of water of crystallisation; it reddens at 150° and melts 165°–168° (effervesces) (Biltz and Heyn, Ber. 1912, 45, 1677; *ibid.* 1914, 47, 459; Ann. 1916, 413, 7).

4 : 5-Di-methoxy-4 : 5-dihydrouric acid



crystallizes in slender needles, m.p. 202°–203° (decomp.); it is reduced by sodium amalgam to uric acid and by hydriodic acid (D 1.96) on the water bath to ψ -uric acid (Biltz, Annalen 1916, 413, 1; Ber. 1921, 54, 2477).

p-Nitrobenzyl urate $\text{C}_5\text{H}_3\text{O}_2\text{N}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ melts above 350° (Lyons and Reid, J. Amer. Chem. Soc. 1917, 39, 1727).

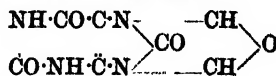
Uric acid forms the following condensation products with formaldehyde:—

Diformaldehyde-uric acid $\text{C}_6\text{H}_4\text{O}_2\text{N}_4 \cdot 2\text{CH}_2\text{O}$ is a crystalline, sparingly soluble compound,

monobasic towards N/3 sodium hydroxide and forms a *barium* and a *calcium* salt (Weber, Pott and Pollens, Ber. 1897, 30, 2514; Annalen, 1898, 299, 340). *Formaldehyde uric acid*



crystallises in needles or prisms, decomposes at 37°, and forms crystalline alkali salts; and *anhydroformaldehyde-uric acid*



formed by dissolving diformaldehyde-uric acid in concentrated sulphuric acid and pouring the solution into ice water (Nicolaier, Chem. Zentr. 1907, i. 949). For other derivatives of uric acid, v. Biltz (*l.c.*). M. A. W.

ψ -URIC ACID v. PYRIMIDINES.

URIDINE v. PYRIMIDINES.

URINE. The kidneys are compound tubular glands, and possess the power of excreting from the blood certain waste products which in aqueous solution constitute the urine. Its most important constituents are the result of the breakdown of nitrogenous materials in the body, but these substances, urea, uric acid, &c., are not actually formed in the kidneys themselves. The liver is the most important organ for their actual formation; the kidney is merely the situation where they find an exit from the body.

The characters of the urine differ greatly in different parts of the animal kingdom, according to the character of the food ingested, and the different metabolic habits of animals. The most striking difference is seen when one compares the liquid urine of mammals (in which urea is the main substance in solution) and the semi-solid urine of birds and snakes, in which urates form the preponderant constituents. In the following account attention will be in the main directed to the urine which is most familiar, namely that of man and other mammals.

A man of average weight and height, taking a normal mixed diet, passes from 1400 to 1600 c.c. (about 50 oz.) daily, and this contains about 50 grms. (1½ oz.) of solids. Its yellow colour varies considerably with the concentration of the urine, and is due to the presence of a number of pigments, of which *urochrome* (an amorphous nitrogenous substance of doubtful composition, originally so named by Thudichum) is the most abundant. Another named *urobilin*, a derivative of the bile pigment, is present in health in small quantities, but may be considerably increased in certain diseases.

The reaction of urine is acid; this is partly due to free acid, but mainly to acid salts, of which acid sodium phosphate is the most abundant. During digestion, however, there is a formation of free hydrochloric acid in the stomach, and a corresponding liberation of bases in the blood causes the urine to be less acid, or even alkaline. Alkaline urine is also seen in herbivorous animals and vegetarians; here the food contains excess of alkaline salts of acids such as tartaric, citric, malic, &c. These acids in the body are oxidised into carbonates which, passing into the urine, give it an alkaline reaction.

The specific gravity varies inversely as the quantity of urine passed; the quantity depends on the amount of water ingested, and also on

the amount of water that leaves the body by other channels, such as the skin. It varies normally from 1.015 to 1.025. A sp.gr. below 1.010 should excite suspicion of hydruria; one over 1.030 of a febrile condition, or of diabetes, in which disease it may rise to 1.050. The sp.gr. has, however, been known to sink as low as 1.002 (after large potations, *urina potus*), or to rise as high as 1.035 (after great sweating) in perfectly healthy people.

When a normal urine is distilled, an unknown, or imperfectly known, substance begins to volatilise at 60°–70°C., but does not completely leave the urine until the boiling-point is reached. The distillation is carried out on the urine which has been acidified with phosphoric acid: at least one-quarter of the urine should distil over. This distillate is a limpid colourless liquid of intense urinous odour, and is neutral to all reagents. It is not precipitated by alkalis or acids, nor with the bicarbonate and sublimate mixture; it does not react with Fehling's solution, nor give the diazo reaction in neutral or acid media; no apparent change takes place with salts of silver, cadmium, iron, lead, mercury, or zinc. With Nessler's reagent it gives a greenish-yellow precipitate similar to that given with many other substances, such as alkaloids, amides, all amines, organic ammonias, aldehyde and methylene derivatives. It is concluded that there is a volatile body in normal urine resembling ketone, but different from ordinary acetone, precipitated by Nessler's reagent, and that it is to this substance that the characteristic odour of the urine is due (E. Pittarelli, *La Riforma Med.* May 14th, 1923, through *Lancet*, June 9th, 1923, 1172).

The following table gives the average amounts of the urinary constituents passed by a man taking an ordinary diet containing about 100 grms. of protein in the 24 hours—

Total quantity of urine	1500	grms.
Water	1400	
Solids	60	
Urea	35	
Creatinine	0.9	
Uric acid	0.75	
Hippuric acid	1.0	
Ammonia	0.65	
Sodium chloride	16.5	
Phosphoric acid	3.5	
Sulphuric acid	2.0	
Chlorine	11.0	
Potassium	2.5	
Sodium	5.5	
Calcium	0.26	
Magnesium	0.21	

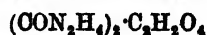
The most abundant constituents are, therefore, water, urea, and sodium chloride. We will take the most important individual constituents one by one.

Urea. The time-honoured formula of urea as carbamide $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ must be replaced

according to Werner by the cyclic formula $\text{H} \cdot \text{N} : \text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \diagdown \\ \diagdown \diagup \end{smallmatrix}$. This offers a satisfactory explanation for the behaviour of urea during hydrolysis. It was first prepared synthetically

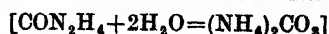
by Wöhler (1828) from its isomeride ammonium cyanate.

It crystallises in the dimetric system, and is readily soluble in water and in alcohol; it has a faint saltish taste, and is neutral to litmus. When treated with nitric acid, octahedra, or lozenge-shaped tablets are formed of urea nitrate ($\text{CON}_2\text{H}_4 \cdot \text{HNO}_3$); when treated with oxalic acid prismatic crystals of urea oxalate



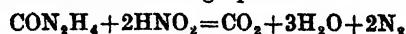
are formed.

Under the influence of certain micro-organisms which grow readily in stale urine, it is converted into ammonium carbonate

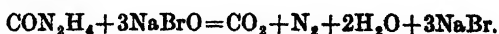


Hence the ammoniacal odour of putrid urine. In the soil the urinary ammonia is converted into nitrates by nitrifying organisms (*see SOILS*).

By means of nitrous acid, urea is broken up, as shown in the following equation:



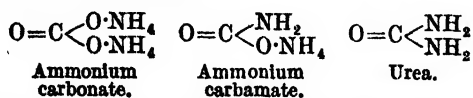
Sodium hypobromite decomposes urea as follows:



A critical examination of this reaction shows that there is always a deficit in the quantity of urea found, whether it is calculated from the volume of the nitrogen liberated, the carbon dioxide formed, or the hypobromite used. Side reactions of a complex nature also occur under usual conditions, giving rise to a small amount of CO. Moreover, other urinary constituents (uric acid, creatinine, &c.) also yield nitrogen under the conditions of the experiment. Hence the method which was formerly much used for the estimation of urea is now abandoned when accuracy is required. The methods at present in use are those in which the urea is decomposed into ammonia and carbon dioxide; the ammonia formed is estimated, but as the urine contains a small amount of preformed ammonia this has to be previously estimated and deducted from the total. The methods of Möerner and Sjöquist, Folin and others (*v. UREA*) are examples of this type of estimation, but the enzymatic method depending on the action of the enzyme urease contained in soy-beans promises to replace all other methods. It was introduced by Marshall. Urease is a specific enzyme, which rapidly and quantitatively decomposes urea at 35°–40°C. into ammonia and carbon dioxide. The ammonia formed is driven off in a suitable apparatus by a current of air, absorbed with standard acid, and estimated by titration, alizarin-red or methyl-orange being used as indicator.

The quantity of urea is practically uninfluenced by muscular work, but depends mainly on the amount of protein ingested. The amino acid fragments formed by the digestion of protein are utilised in two ways. A small portion is used by the tissue cells to repair their waste. In time this will be catabolised and the waste products discharged as urea, ammonia, creatinine, &c. The amount of such *endogenous* metabolism is constant. The other and larger part of the cleavage products of the food proteins are deaminised and converted into urea by the liver, the non-nitrogenous fatty residue being

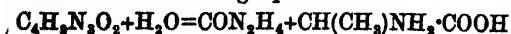
burnt, and so utilised as a source of heat and other forms of energy. This part of metabolism is termed *exogenous*. Urea excretion is usually at a maximum about 3 hours after a meal. The conversion of amino acids into urea is, in part at any rate, due to enzymic action; e.g. arginase is an enzyme which converts arginine (one of the more complex amino acids resulting from protein disintegration) quantitatively into urea and ornithine (di-amino-valeric acid). There is also no doubt that ammonia is an important intermediate between such amino acids as glycine (amino-acetic acid), leucine (amino caproic acid), &c., and the final product urea. Ammonia so liberated unites with the carbon dioxide of the blood, and ammonium carbonate and carbamate are thus formed. The close relationship of these two salts to urea is apparent from their formulae—



This view, though simple, must be modified if Werner's conception of the structure of urea is accepted.

A small quantity of ammonia always slips through into the urine, because a small quantity of the ammonia-containing blood passes through the kidney before reaching the organ (the liver), which is capable of converting it into urea. Acids are very toxic to the body, and the defence of the body against acids (administered as such, or produced in pathological metabolism, e.g. fatty acids in diabetes) is an increase of ammonia formation, or to put it more correctly, less of the ammonia formed is converted into urea.

Creatine and creatinine.—Creatine is an abundant constituent of muscular tissue; *in vitro* by boiling it with baryta it takes up water and splits up into urea and methyl-glycine, as shown in the following equation—



Creatine, however, is absent from normal urine, and only occurs in starvation and in other conditions, in which there is a rapid loss of muscular tissue. Its normal fate in the body is unknown, since creatine injected into the circulation leaves the body in the urine unchanged, and leads to no increase of urea.

It also is not converted into creatinine, which was formerly held to be its fate. Here, again, we have an instance of reactions, which occur *in vitro*, but not *in vivo*. Creatinine is a crystalline, strongly basic substance, which chemically is creatine *minus* a molecule of water. It is always present in the urine, and next to urea, is its most abundant nitrogenous constituent. Mellanby believes that certain products of protein catabolism, the nature of which is uncertain, are carried to the liver, and from these the liver forms creatinine; this is transported to the muscles, and there stored as creatine, excess being then eliminated in the urine. The small amount of creatinine excreted in liver disease favours the view that the liver is the great agent in its production, as it is in that of urea and uric acid. In health the amount of creatinine is very constant, and is not influenced by diet or muscular exercise.

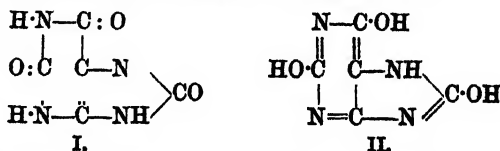
Uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_6$) is excreted as urates in mammals in small quantities only, but in birds and serpents is the principal nitrogenous constituent of their urine. It can be readily prepared from the latter urine, in which it is mainly present as the acid ammonium urate, by dissolving it in sodium hydroxide and precipitating with hydrochloric acid. It crystallises in rectangular plates and prisms. Uric acid dissolves in pure water in the proportion 1 : 15,000 (Gudzent), and at 18° in the proportion 1 : 39,500 (His and Paul). On oxidation it yields urea and oxalic acid, alloxan ($\text{C}_4\text{H}_2\text{N}_4\text{O}_4$) or allantoin ($\text{C}_4\text{H}_6\text{N}_4\text{O}_3$), being intermediate products, according to the oxidising agent employed. It can be best identified by the *murexide* reaction, which consists in evaporating to dryness with nitric acid; the yellowish-red residue gives, on the addition of ammonia, the violet ammonium purpurate.

Uric acid does not contain the COOH group which is typical of organic acids, and in aqueous solution its reaction is neutral. Nevertheless one of its hydrogen atoms is replaceable by a metallic radicle, and it acts therefore as a monobasic acid, and forms *primary* salts (mono- or acid urates). In the presence of strong bases it forms *secondary* salts (di-urates); these only exist in the solid condition or in the presence of strong alkali. By water they are at once decomposed forming primary salt and alkali. A third series of salts (quadri-urates) was formerly assumed to exist, but these are merely mixtures of uric acid and primary urate.

In water, urine and blood, we have therefore only to deal with primary urates. It has been shown that the primary sodium urate



occurs in two modifications, the α - and the β -forms. The unstable α salt is gradually transformed in aqueous solution into the stable β salt, owing to an intramolecular change. These two salts correspond to two tautomeric modifications of uric acid, the lactam form (formula I) giving rise to the unstable, and the lactim form (formula II) to the stable salt.



These facts have a bearing on gouty conditions; normally the small amount of urate in the blood is held in solution. In gout the amount is increased, and the excess is probably in the unstable α -form. The conversion of this into the β -form gives rise to the deposition of urates in the tissues which occurs during the course of the attack.

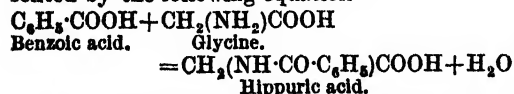
The quantity of uric acid excreted by an adult varies from 0.5 to 0.75 gm. daily. The method used for estimation is based on Hopkins' discovery, that when the urine is saturated with an ammonium salt (chloride or sulphate), all the uric acid is precipitated as ammonium urate; this is collected and the uric acid in it determined. The Folin-Shaffer method is founded on this reaction. Folin has also introduced a colorimetric method, which depends on the

blue colour uric acid strikes with phosphotungstic acid (v. URIC ACID).

In birds uric acid originates from the combination of ammonia and lactic acid. In mammals it mainly arises from the purine bases of the food, which are cleavage products of nucleic acid, the main constituent of the nuclei of the body cells. In this process several tissue enzymes come into play; first nuclease liberates adenine (amino-purine $C_5H_7N_5NH_2$) and guanine (amino-oxypurine $C_5H_7N_5O.NH_2$) from nucleic acid; then 'deaminising' enzymes convert adenine into hypoxanthine (monoxypurine $C_5H_7N_4O$) and guanine into xanthine (dioxypurine $C_5H_7N_4O_2$); oxidases step in next and convert hypoxanthine into xanthine, and xanthine into uric acid (trioxypurine $C_5H_4N_4O_6$). The liver is the principal seat of these transformations, and in some animals some of the uric acid so formed is destroyed in the same organ, and appears as allantoin and urea. So far as tissue extracts can give a true picture of metabolism *in vivo* the human tissues are destitute of the uricolytic (uric acid destroying) enzyme)

Small quantities of purine bases are found in the urine in addition to uric acid.

Hippuric acid ($C_9H_9NO_3$) in the form of hippurates is present in small quantities in the urine of man, but is specially characteristic of herbivorous urine. This is due to the food of herbivora containing substances of the benzoic acid group. The condensation of benzoic acid with glycine to form hippuric acid appears to occur in the kidney itself, and may be represented by the following equation—



For the estimation of hippuric acid in urine, see Snapper and Laquer, Archives Néerlandaises de Physiologie, 1921, 6, 48, which contains further references to the literature of the subject.

Kynurenic and urocanic acids are present in small quantities in dog's urine. Kynurenic acid $C_{10}H_9NO_3$ is hydroxyquinoline carboxylic acid ($HO \cdot C_6H_4 \cdot N \cdot COOH$) and originates from one of the decomposition products of protein called tryptophan (indole-amino-propionic acid). Urocanic acid ($C_{11}H_{12}N_4O_4$) is a rarer constituent, and its origin in the body is not clear.

Inorganic constituents of urine. The principal salt is *sodium chloride*, and its amount varies with that in the food. The *sulphates* present are principally those of sodium and potassium. They are derived from the metabolism of protein, and their excretion, although it occurs earlier than that of urea, runs parallel with it. About one-tenth of the total sulphates are etheral sulphates, such as potassium phenyl sulphate and potassium indoxyl sulphate (urinary indican); the organic radicles originate from protein putrefaction in the alimentary canal, and abnormally great putrefactive processes there lead to an increase in the excretion of such sulphates. Sulphur is also present in the form of less highly oxidised organic compounds, usually spoken of as 'neutral sulphur,' a term which includes thiocyanic acid and its salts, taurine, cystine, methyl mercaptan.

Carbonates are only present in alkaline urine. Alkaline and earthy *phosphates* are also present and small quantities of organic phosphates, for instance, glycerophosphates. They arise partly from the food, but chiefly from the metabolism of organic phosphorised constituents of the body, such as nucleic acid, lecithin, and other phosphorised fats (phosphatides).

According to Amberg and Mayer (Amer. J. Physiol. 1922, 60, 564) minute quantities of citric acid occur in normal human urine.

Abnormal constituents of urine. The most commonly occurring of these are albumin (in Bright's disease) and other proteins, dextrose, acetone, aceto-acetic acid, and β -hydroxybutyric acid in diabetes, lactose in nursing mothers, bile in jaundice, blood when hæmorrhage occurs in any part of the urinary tract, hæmoglobin, and certain derivatives of hæmoglobin in black water fever and other pathological states, and pus as the result of suppuration in any part of the urinary tract.

Urinary deposits. Normal urine is clear except for a faint cloud of mucus. Formed or anatomical elements such as blood corpuscles, pus corpuscles, bacteria, entozoa, &c., may be present in various pathological conditions, and are identified by microscopic examination. A special chemical interest attaches, however, to crystalline deposits, and without entering into any discussion of the medical reasons that lead to their appearance, these may be briefly enumerated as follows:—

A. In acid urine may be found—

1. Uric acid, as whetstone, dumb-bell, or sheaf-like aggregations of crystals deeply tinged with urinary pigment, looking like cayenne pepper.

2. Urates. These are generally amorphous. The acid urate of sodium and ammonium may sometimes occur in star-shaped clusters of needles or spheroidal clumps with projecting spines. The deposit has the appearance of brick-dust, as it is coloured by one of the urinary pigments (uroerythrin). This deposit dissolves on warming the urine.

3. Calcium oxalate in the form of octahedral crystals insoluble in acid.

4. Cystine (diamino-dithio-lactic acid $C_6H_{12}N_2S_2O_4$)

in colourless hexagons; a rare condition often hereditary.

5. Calcium phosphate $CaHPO_4 \cdot 2H_2O$, rare.

6. Leucine (*amino-caproic acid*) and tyrosine β -p-hydroxyphenyl- α -aminopropionic acid, rare.

B. In alkaline urine we may find—

1. Phosphates; calcium phosphate $Ca_3(PO_4)_2$

which is amorphous; triple phosphate $MgNH_4PO_4 \cdot 6H_2O$

in 'coffin lid' crystals or feathery stars; calcium hydrogen phosphate $CaHPO_4$ in rosettes, spherules, or dumb-bells; magnesium phosphate $Mg_3(PO_4)_2$ in long plates. All are soluble in acetic acid without effervescence.

2. Calcium carbonate $CaCO_3$, biscuit-shaped crystals, common in herbivorous urine, soluble in acetic acid with effervescence.

3. Ammonium urate $C_6H_5(NH_4)_2N^+O_2$ 'thorn apple' spherules.

4. Leucine and tyrosine, very rare.

Of these deposits, urates in acid urine, and phosphates in alkaline urine are the commonest; these are not necessarily pathological; thus urates may form in the urine when it cools, especially if that secretion is concentrated, e.g. after sweating profusely. Urine, when it becomes alkaline, always deposits phosphates, and the alkaline urine of herbivora is always thick for that reason.

Urinary calculi. Concretions called sand, gravel, and stones, according to their size, may form in the kidney, the ureter, or in the bladder. They result from the conglomeration of urinary deposits, the deposition occurring in concentric layers. The substances deposited in acid urine are most frequently uric acid, urates or calcium oxalate, or a mixture of these materials; in alkaline urine, phosphates. If the reaction of the urine changes during the formation of the calculus alternate layers of these two sets of materials will be found. The uric acid calculus is generally regarded as the commonest form of stone in the bladder, but in renal calculi, as B. Moore has shown, the most abundant constituent is calcium oxalate, frequently mixed with calcium phosphate, the second constituent in frequency and abundance. Calcium is practically the only base associated with oxalic acid, phosphoric acid, and in less amount with uric acid. All these acids form highly insoluble salts with calcium. Oxalic and uric acids are associated products in metabolism, and occur in cases of incomplete oxidation.

The physical properties of a calculus—colour, hardness, smoothness, or roughness, &c.—give little or no clue to its chemical nature. A chemical analysis is always necessary, and this gives valuable indications for after treatment; for instance, in renal calculi, consisting of calcium oxalate, the treatment should be designed to diminish alkalinity, to avoid calcium-rich foods, and to induce the taking of exercise to promote oxidation in the body.

There are, in addition to these common forms of stone, others of a rarer kind, and a list of the different varieties of calculus is as follows—

1. Those composed of uric acid or urates with little or no admixture with phosphates.

2. Mixed calculi, like the preceding, but containing often in alternate layers a large quantity of phosphate.

3. Calcium oxalate calculi, often containing small quantities of phosphates and urates.

4. Phosphate calculi: a stone composed of pure calcium phosphate is rare; a nucleus of uric acid is generally present.

5. Calcium carbonate calculi are those generally found in the prostate.

6. Cystine calculi are mostly small, smooth, and have a yellow tinge, turning to green on exposure to air. These are rare.

7. Xanthine calculi are still rarer.

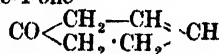
8. Fibrinous calculi composed of fibrin or inspissated albumin, have a glassy appearance on fracture; blood calculi have been described in cases of renal hamaturia; 'urostealith' calculi have been described, and consist of fatty acid with more or less cholesterol. One case of 'isidig' calculus has been described.

No attempt has been made in the foregoing outline sketch of the chemical properties of the

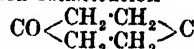
urine in health and disease to give complete bibliographical references. The literature of urine is enormous, and those interested in it should consult standard works on physiology, physiological chemistry, pathology, and medicine. One of the most trustworthy handbooks on the urine only, and containing abundant references to literature, is Neubauer and Vogel's *Analyse des Harns*, edited by Huppert, Wiesbaden, C. W. Kreidel.

W. D. H.

URINOD C_6H_8O , a pale yellow oil, obtained from urine, slightly heavier than water, b.p. $108^\circ/28$ mm.; possessing a very penetrating, persistent and disagreeable odour and to which the characteristic smell of urine is due. Is readily volatile with steam, reduces potassium permanganate and ammoniacal silver nitrate in the cold, and reacts with Millon's reagent, but not with Barreswil's (Fehling's) solution, or solution of alkali picrate. The dinitro-derivative, m.p. 78° forms golden needles. Urinod acts with ser carbazide with production of a compound m.p. 254° , which crystallises in thin, hexagonal leaflets. When urinod is treated with bromine, two compounds are produced; one of these has m.p. about 110° , whilst the other is not melted at 250° . The compound probably has the structure of cyclohexene-4-one



or the quinonoid constitution



Urinod does not occur in the free state in urine, but exists in a conjugated form, and is liberated by fermentation, or by the action of dilute sulphuric acid. It is very toxic, and may have some connection with uramia (Dehn and Hartman, J. Amer. Chem. Soc. 1914, 36, 2136).

URISOL. Syn. for hexamethylenetetramine.

URITONE (hexamine). Syn. for hexamethylenetetramine.

UROCITRAL, UROPHENIN, v. SYNTHETIC DRUGS.

URODONAL. Trade name for a preparation of hexamethylenetetramine, piperazine quinate and methylglyoxalidine.

UROGENIN. Trade name for an addition product of theobromine and lithium hippurate.

UROL. Trade name for urea quinate.

UROPHERIN v. SALICYLIC ACID.

UROPURGOL (helmitol, neurotine, formamol). The hexamethylenetetramine salt of anhydromethylene-citric acid.

UROSIN. Trade name for lithium quinate.

UROTROPIN. Hexamethylenetetramine, v. SYNTHETIC DRUGS.

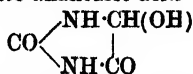
UROXANIC ACID, dicarbaminomalonic acid $(CO_2H)_2C(NH-CO-NH)_2$, is prepared by the gradual oxidation of uric acid in alkaline solution by the oxygen of the air (Städeler, Annalen, 1851, 78, 286; Strecker, *ibid.* 1870, 155, 177; Biltz and Robl, Ber. 1920, 53, 1950); by oxidising an alkaline solution of uric acid with 5 p.c. potassium permanganate solution (1 atom of oxygen to 1 mol. of uric acid) (Behrend, *ibid.* 1904, 333, 152; Sundvik, Zeitsch. physiol. Chem. 1904, 41, 343; Behrend and Schultz, *ibid.* 1909, 365, 21; Biltz and Robl, *l.c.*).

For the mechanism of the formation of uroxanic acid from uric acid, see Biltz and

VALERIAN.

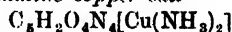
Max (Ber. 1920, 53, 1964). The two carbamido groups in uroxanic acid can be quantitatively eliminated by sodium nitrite with the formation of mesoxalic acid (Biltz and Robl, l.c.).

Uroxanic acid crystallises in indistinct tetrahedra (decomp. 162°); it is sparingly soluble in cold water and insoluble in alcohol; it is a strong dibasic acid and its normal alkali salts are neutral towards litmus and phenolphthalein. It readily loses CO_2 and yields allantonic acid when shaken for several days with cold 95 p.c. methyl alcohol. When heated with water it breaks down into allanturic acid



mesoxalic acid and urea. The aniline and hydroxylamine salts are sparingly soluble; the latter, melts at 155° ; the normal phenylhydrazine salt, $\text{C}_6\text{H}_5\text{O}_4\text{N}_4 \cdot 2(\text{C}_6\text{H}_5\text{N}_2)$, crystallises in colourless plates, m.p. 130° – 132° (decomp.), when boiled with water it is decomposed, yielding the phenylhydrazine salt of mesoxalic acid phenylhydrazone $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, this forms yellow needles that melt at 154° – 158° , solidify at 160° and then decompose at 183° . The normal silver, sodium, barium, and calcium salts of uroxanic acid are crystalline.

The potassium salt forms colourless crystals, $a:b:c=0.88576:1:1.2044$, and gives hydrates containing 3.5, 3, and probably 0.5, H_2O ; the ammonium salt decomposes at 182° . The methyl ester decomposes at 213° , and is converted by boiling water into spirodihydantoin, which yields the di-silver salt $\text{C}_6\text{H}_2\text{O}_4\text{N}_4\text{Ag}_2 \cdot 2\text{H}_2\text{O}$ and the diammine copper salt



(Biltz and Robl, l.c.).

For the physiological action of uroxanic acid, see Saiki (J. Biol. Chem. 1910, 7, 263).

M. A. W.

URSAL. Urea salicylate. A uric acid eliminant.

URSOL v. p- PHENYLENEDIAMINE.

URSOL P v. p- AMINOPHENOL.

URSONE. Urson. A white crystalline optically active substance $\text{C}_{22}\text{H}_{47}\text{O} \cdot \text{COOH} \cdot 2\text{H}_2\text{O}$, m.p. 273° , $[\alpha]_D^{15} = +58^{\circ}$, found in holly, maté, and other species of *Ilex*, and in many ericaceous plants. With sulphuric acid it gives an orange-yellow colour with green fluorescence; an acetic anhydride solution gives with sulphuric acid a red coloration passing to violet, green, and blue; a chloroform solution shaken with an equal volume of sulphuric acid colours the latter

yellow. Soluble in ethyl and methyl alcohols, chloroform, carbon disulphide, ether, and ethylene bromide. Yields a readily crystallisable methyl ester (Dodge, J. Amer. Chem. Soc. 40, 12; Nooyen, Pharm. Weekblad. 1920, 57, 1128). According to van Der Harr (Rec. trav. chim. 1924, 43, 367) urson has the formula $\text{C}_{21}\text{H}_{40}\text{O}_8$, m.p. 279° – 280° , and gives sesquiterpene and CO_2 on distillation with zinc dust. It forms an acetyl derivative, m.p. 201° , a methyl ester, m.p. 165° , and an acetyl derivative of the methyl ester, m.p. 245° . It thus appears to contain a hydroxyl and a carboxyl group.

URUSHIOL v. LACQUER; RESINS. Cf. Majima, Ber. 1922, 55 [B.] 172; Levin, J. Amer. Med. Assoc. 1924, 465; Pharm. J. 1924, 112, 236.

USNIC ACID $\text{C}_{18}\text{H}_{18}\text{O}_7$ (Stenhouse, Proc. Roy. Soc. 18, 222), $\text{C}_{18}\text{H}_{18}\text{O}_8$ (Paterno, Ber. 9, 345). An acid found in certain lichens (v. LICHENS).

UVANITE. Hydrated uranium vanadate $2\text{UO}_2 \cdot 3\text{V}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$, crystallised in the orthorhombic system. It occurs as a brownish-yellow powder disseminated in sandstone at Temple Rock in Emery Co., Utah. In appearance and mode of occurrence it thus resembles carnotite (q.v.), but it has not the clear yellow colour characteristic of carnotite. The mineral dissolves readily in a solution of ammonium carbonate. The name uvanite is a contraction of the words uranium and vanadium with the mineralogical termination *ite*. (F. L. Hess and W. T. Schaller, 1914.) L. J. S.

UVAROVITE v. GARNET.

UVITONIC ACID v. BONE OIL.

UZARA. The root of a species of *Gomphocarpus* (N.O. *Asclepiadaceae*) is used by medicine men in the region of the great African lakes against diarrhoea. The action of an extract was first described by Gürber (Muench. Med. Wochenschr. 1911, 58, 2100) and was found to be specific on the intestine, resembling that of opium, but without the undesirable after effects of the latter drug. A dried alcoholic extract has been placed on the market in Germany under the name uzaron. According to Hennig (Arch. Pharm. 1917, 255, 382) the active principle is the glucoside *uzarin* (5 p.c. of the root) $\text{C}_{25}\text{H}_{108}\text{O}_{30} + 9\text{H}_2\text{O}$, relatively well soluble in water and hydrolysed by acids into one molecule of propyl alcohol, three of dextrose and three of *uzaridin* $\text{C}_{18}\text{H}_{22}\text{O}_6$, which is strongly bitter. The glucoside is only slightly bitter. Cf. Kofler, Arch. Pharm. 1917, 255, 550; and Holmes, Pharm. J. 1920, 507. G. B.

V

VALAMIN. Trade name for the *isovaleric* ester of tertiary amyl alcohol.

VAL D'ARNO SUPERIORE RESIN v. RESINS.

VALEARIN. Trade name for valeryl trimethylammonium chloride.

VALENTINITE. Antimony trioxide Sb_2O_3 , crystallised in the orthorhombic system and dimorphous with senarmontite (q.v.). The small tabular or prismatic crystals are often arranged in fan-shaped groups. They have perfect cleavages in three plane directions (the unit prism and the brachypinacoid) parallel to the

vertical axis, and consequently broken surfaces present a fibrous aspect with pearly lustre. They are white or greyish, translucent, adamantine in lustre, very soft (H. 2), and readily distorted. Sp.gr. 5.76. The mineral occurs in the upper oxidised portions of lodes, having resulted by the alteration of stibnite and other antimony minerals. It is found at Bräunsdorf in Saxony, Příbram in Bohemia, Malaczka in Hungary, Algeria, Bolivia, &c. L. J. S.

VALERIAN. The root of *Valeriana officinalis* (Linn.) yields on distillation with water an essential oil of a pale yellow or greenish colour,

having a strong smell of valerian, an aromatic taste, and acid reaction; sp.gr. 0.90-0.93. Thickens at -15° , and begins to boil at about 200° . Consists of a mixture of valeric acid, a camphene, a stearoptene, and a resin (Pierlot, Ann. Chim. [iii.] 56, 291; Gerhardt, *ibid.* [iii.] 7, 275).

Valerian root contains two alkaloids: *chatinine* and *valerine*. One kilo of the fresh root yielded only 0.10 grm. of mixed alkaloids, chatinine predominating (Goris and Vischniac, Compt. rend. 1921, 172, 1059).

For the assay of Valerian Root, see Bullock, Pharm. J. 1924, 113, 109.

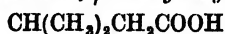
VALERIC or PENTOIC ACIDS C_4H_8COOH .

Four isomerides are known.

1. *n*-Valeric acid $CH_3[CH_2]_3COOH$, is found in pyroligneous acid, and occurs free and as esters in the animal and vegetable kingdoms, chiefly in the roots of *Valeriana officinalis* (Linn.) and of *Archangelica officinalis* (Hoffm.), from which it may be isolated by boiling with water or sodium hydroxide. It may be obtained by boiling *n*-butyl cyanide with potash (Lieben and Rossi, Annalen, 159, 58); by oxidation of α -hydroxycaproic acid (Erlenmeyer, Ber. 1876, 1840); by reduction of levulic acid (β -acetylpropionic acid) with phosphorus iodide or sodium amalgam (Kehrer and Tollens, Annalen, 206, 233; Fittig and Wolff, *ibid.* 208, 109); by heating propylmalonic acid (Juslin, Ber. 1885, 2504); by the fermentation of calcium lactate (Fitz, *ibid.* 1880, 1309); and by the action of CO_2 on magnesium *n*-butyl bromide (Gilman and Parker, J. Amer. Chem. Soc. 1924, 46, 2816; Chem. Soc. Abstr. 1925, 128, i, 228). A colourless oil having a disagreeable smell, b.p. 186° - 186.4° (Fürth, Monatsh. 9, 310); sp.gr. 0.9415 at $20^{\circ}/4^{\circ}$ (Lieben and Rossi); 1 vol. of acid dissolves in 27 vols. of water at 16° .

Methyl valerate boils at 127.3° , *ethyl valerate* at 144.6° (736.5 mm.), and *isobutyl valerate* at 167.0° - 168.5° ; sp.gr. 0.8544 $20^{\circ}/4^{\circ}$.

2. isoValeric acid, β -methylbutyric acid



Discovered in 1817 by Chevreul in dolphin oil from *Delphinus globiceps* and *D. phocaena*, and termed by him *phocenic acid* (cf. André, Compt. rend. 1924, 178, 1188; J. Soc. Chem. Ind. 1924, 43, 479). Found in other fish oils and in perspiration. In the roots of *Valeriana officinalis* (Linn.), *Archangelica officinalis* (Hoffm.), and in the berries of *Viburnum Opulus* (Linn.). Formed in the putrefaction of albuminoids; by the oxidation of glue, oleic acid, fats, and fusel oil (Lawkrow and Jazukowitsch. J. 1864, 337; Pierre and Pouchet, Ann. Chim. [iv.] 29, 229; Koizami and Ichinose, Japan. Pat. 41910; Chem. Soc. Abstr. 1924, 126, i, 259). Prepared by the action of alcoholic potash on isopropyl cyanide, and by long boiling of amyl alcohol with sodium methoxide (Guerbet, Compt. rend. 128, 512). Colourless oily liquid, smelling like valerian root and putrid cheese; b.p. 173.7° (Kahlbaum, Ber. 1883, 2480), sp.gr. 0.931 at 20° . Soluble in 23.6 parts of water at 20° . The valeric acid of pharmacy is prepared from valerian root or from amyl alcohol. The ammonium and zinc valerates are also used in medicine.

For quantitative estimation of isovaleric acid

in the presence of acetic acid, v. Chapman, Annalen, 1899, 114.

Methyl isovalerate boils at 116.7° , and *Ethyl isovalerate* at 134.3° .

isoAmyl isovalerate $C_8H_{17}O(C_2H_5)_2O$; b.p. 194° ; dissolved in spirits of wine is used in confectionery as *essence of apples*.

3. α -Methylbutyric acid $CH_3\cdot CH(C_2H_5)\cdot COOH$ is found in the oil of *Archangelica officinalis* (Hoffm.) (Ciamician and Silber, Ber. 1896, 1815), and may be obtained by heating methyl-crotonic acid (tiglic acid) with hydriodic acid (Schmidt and Berendes, Annalen, 191, 117); by the action of sodium amalgam on bromomethyl-ethylacetic acid in a sulphuric acid solution (Pagenstecher, *ibid.* 195, 109); and by heating methyl ethyl-malonic acid (Conrad and Bischoff, *ibid.* 204, 151). On oxidising optically active amyl alcohol, a mixture of isovaleric and α -methylbutyric acids is obtained which can be separated by converting them into their silver salts, silver isovalerate being six times less soluble in water than silver α -methylbutyrate (Erlenmeyer and Hell, Annalen, 160, 301; Conrad and Bischoff, *ibid.* 204, 157). A colourless somewhat mobile liquid; b.p. 173° - 174° , sp.gr. 0.938 at $20^{\circ}/20^{\circ}$ (Schütz and Marckwald, Ber. 1896, 26).

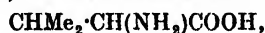
4. $\alpha\alpha$ -Dimethylpropionic acid $(CH_3)_2C\cdot COOH$. Obtained by heating trimethyl-acetonitrile with strong hydrochloric acid (Butlerow, Annalen, 170, 151; 173, 355); or by the oxidation of pinacolin (Butlerow, *l.c.*; Friedel and Silva, Ber. 6, 146, and 816). Crystallises in the regular system; m.p. 34° - 35° , b.p. 163° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 475), sp.gr. 0.905 at 50° ; soluble in 45 parts of water at 20° .

VALEROBROMINE $(CH_3)_2CH\cdot CHBr\cdot COONa$. Obtained by hydrolysing and neutralising the product formed by the action of bromine on valerianic acid. Used as a sedative.

VALEROPHEN. Methyl ester of phenolphthalein.

VALERYDIN, VALIDOL, VALISAN, VALYL, v. SYNTHETIC DRUGS.

VALINE, α -aminoisovaleric acid



was isolated first by Gorup-Besanez (Annalen, 1856, 98, 1) from the pancreas of the ox, and occurs in the young seedlings of *Lupinus luteus* (L.), *Lupinus albus* (L.), *Lupinus angustifolius* (L.), *Vicia sativa* (L.), the etiolated seedlings containing more than the green plants (Schulze and Barbieri, J. pr. Chem. 1883, [i.] 27, 337; Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 308; Schulze, *ibid.* 1894, 20, 306; 1896, 22, 423; Schulze and Castoro, *ibid.* 1903, 38, 199; Wassilieff, Landw. Versuchstat. 1901, 55, 45; Schulze, Zeitsch. physiol. Chem. 1893, 17, 193; Menozzi, Ber. 1888, 21, 619); in zein (Osborne and Clapp, Amer. J. Physiol. 1908, 20, 470); Dakin (J. Biol. Chem. 1924, 61, 137); in Emmenthaler cheese (Winterstein, Zeitsch. physiol. Chem. 1904, 41, 500). Valine is one of the products of hydrolysis of such proteins as horn, keratin, edestin, etc., and occurs together with leucine and proline in the fraction of esters, b.p. 60° - $90^{\circ}/10$ mm.; it is formed in the autolysis of the pancreas and liver, and in peptic and tryptic digestion (Fischer and Dörpinghaus, *ibid.* 1902, 36, 462; Abderhalden and Voitino-

vici, *ibid.* 1907, 52, 348; Levene and van Slyke, J. Biol. Chem. 1909, 6, 419; Levene, Zeitsch. physiol. Chem. 1904, 41, 393; Lawrow, *ibid.* 1901, 33, 312). The valine occurring naturally is the dextrorotatory form; the racemic form was prepared first synthetically by Fittig and Clark (Annalen, 1866, 139, 200) by the action of concentrated ammonia on α -bromoisovaleric acid at 100°; and later by Lipp (*ibid.* 1880, 205, 1) by hydrolysing the aminoisovaleronitrile obtained by the condensation of isobutyraldehyde with ammonia and hydrocyanic acid. It is prepared most conveniently, and the yield is 70 p.c. of the theoretical, by Slimmer's modification of Fittig and Clark's method (Ber. 1902, 35, 400); 500 grms. of α -bromoisovaleric acid with 1500 grms. of aqueous ammonia saturated at 15° and 500 grms. of powdered ammonium carbonate are heated in an autoclave at 100° for eight hours; the resulting brownish liquid is filtered and evaporated to one-third its bulk, when most of the amino acid crystallises out. The rest is obtained in the form of its hydrochloride by acidifying the mother liquor with hydrochloric acid, evaporating to dryness and extracting the residue with 80 p.c. alcohol.

Racemic valine can be resolved into its optically active isomerides by the fractional crystallisation of the brucine salt of the formyl derivative; the brucine salt of formyl-*L*-valine being less readily soluble in methyl alcohol than is the corresponding salt of formyl-*D*-valine: *D*-valine and *L*-valine are obtained by hydrolysing with hydrobromic acid the corresponding formyl derivatives (Fischer, Matsubara and Hilpert, Ber. 1906, 39, 2320).

dl-Valine. In addition to the synthetic methods already described for the preparation of *dl*-valine, it can be obtained by racemising the active acids by heating them with baryta water at 180° (Fischer, Zeitsch. physiol. Chem. 1911, 33, 162).

dl-Valine crystallises in colourless plates from alcohol, has a sweet taste, and melts in a closed tube at 298° (corr.) with decomposition; it is readily soluble in water, 1 part dissolving in 11.7 parts of water at 15°, is almost insoluble in cold alcohol or ether, sparingly so in boiling alcohol (Slimmer, *l.c.*); when oxidised by hydrogen peroxide it yields isobutyraldehyde, isobutyric acid (part of which is further oxidised to acetone and carbon dioxide), ammonia and carbon dioxide; with lead peroxide or sodium hypochlorite as the oxidising agent, isobutyraldehyde is the product (Dakin, J. Biol. Chem. 1908, 4, 63; Langheld, Ber. 1909, 42, 2360). When *dl*-valine undergoes putrefactive decomposition it yields isovaleric acid and a small quantity of butylamine; the residual aminovaleric acid is laevorotatory indicating an asymmetric attack by the bacteria (Neuberg and Karczag, Biochem. Zeitsch. 1908, 18, 435).

Salts and derivatives of dl-Valine.—The copper salt $(C_5H_{11}O_2N)_2Cu$, blue crystals soluble in 3644 parts of methyl alcohol at 20°, or in 9230 parts of 96 p.c. ethyl alcohol at 21°, and sparingly soluble in cold water (Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 399); the silver salt $C_5H_{11}NO_2Ag$ is crystalline and insoluble in cold water. The hydrochloride



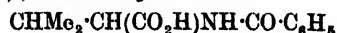
crystalline plates, readily soluble in water or in alcohol, insoluble in ether; the nitrate



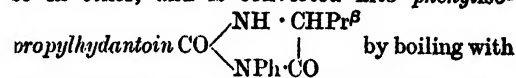
is a readily soluble crystalline compound. The ethyl ester $CHMe_2.CH(NH_2)CO_2Et$ has b.p. 33.5°/8 mm. or 174° with decomposition under atmospheric pressure, sp.gr. 0.9617 at 15°/4°; it forms a sparingly soluble crystalline picrate, m.p. 139.5° (corr.), and a soluble hydrogen tartrate which on crystallisation suffers partial resolution into its optically active isomerides (Slimmer, *l.c.*). Of the acyl derivatives of *L*-valine, the formyl derivative



obtained by heating *dl*-valine with 1½ times its weight of formic acid crystallises in large rhombic plates from water, sinters at 137° and melts at 140°–145° (corr.), is readily soluble in hot water, alcohol or acetone (Fischer, Ber. 1906, 39, 2322); the benzoyl derivative



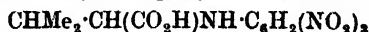
crystallises in plates, m.p. 132.5° (corr.), is readily soluble in alcohol or ether, sparingly so in water (Slimmer, *l.c.*); the phenylisocyanate derivative $CHMe_2.CH(CO_2H)NH\cdot CO\cdot NHPh$ forms colourless plates, soluble in 130 parts of hot water, m.p. 163.5° (corr.) with decomposition, is readily soluble in hot alcohol, sparingly so in ether, and is converted into phenylisopropylhydantoin



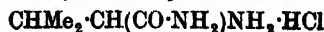
by boiling with hydrochloric acid; this compound crystallises from ether in long needles, m.p. 124°–125° (corr.), and is sparingly soluble in hot water, readily so in alcohol or ether (Slimmer, *l.c.*); the carbamino derivative



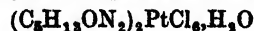
crystallises in needles, m.p. 176°, is soluble in 213 parts of water at 20°, and forms crystalline barium, mercury and silver salts (Lippich, Ber. 1908, 41, 2962); the picryl derivative



forms bright yellow needles, sparingly soluble in cold water, and has m.p. 171° (Hirayama, Zeitsch. physiol. Chem. 1909, 59, 290). *dl*-Valinamide $CHMe_2.CH(NH_2)CONH_2$, obtained by the action of liquid ammonia on the ester prolonged over a period of three months, crystallises from benzene in colourless prisms, m.p. 78°–80° (corr.), and yields a β -naphthalenesulphonic derivative $C_{15}H_{15}O_3N_2S$, m.p. 256°–257° (corr.), a carbethoxy derivative $C_8H_{11}O_2N_2$, m.p. 143°–144° (corr.) (Königs and Mylo, Ber. 1908, 41, 4427), and a hydrochloride



crystallising in the monoclinic system, and forming a crystalline platinumchloride



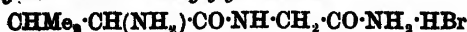
(Lipp, Annalen, 1880, 205, 1). *dl*-Valine anhydride $C_{10}H_{15}O_2N_2$, obtained by heating *dl*-valine, or by heating the ethyl ester under pressure at 180°–190°, forms long colourless needles, m.p. 303° (corr.) (Fischer and Schenkel, Annalen, 1907, 354, 1).

When α -bromoisovalerylglycinamide is

beated at 120° with alcoholic ammonia, it yields a mixture of *valylglycine anhydride* (*diketiso-propylpyperazine*)



needles from hot water, m.p. 245°, and the *hydrobromide of valylglycinamide*



microscopic needles from alcohol-ether, m.p. 235° (Bergell, Zeitsch. physiol. Chem. 1916, 97, 293). α -Amino- β -hydroxyisovaleric acid has been synthesised from ethyl β -dimethylacrylate, it melts with decomposition at 218°; the *methoxyl derivative* $\text{OMe} \cdot \text{CMe}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ forms colourless lustrous plates, m.p. 250°–260° (decomp.); the naphthalene β -sulphonyl derivative $\text{C}_{10}\text{H}_7\text{O}_2\text{NS}$ forms small colourless needles, m.p. 281° (Schrauth and Geller, Ber. 1922, 55, 2783).

Valinol $\text{CHMe}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{OH}$, prepared by reducing valine ethyl ester, is a colourless oil with a strong odour, b.p. 181°–186°/720 m.m.; the *hydrochloride*, m.p. 114°, is very hygroscopic.

Dimethylvalinol, prepared by reducing ethyl α -dimethylaminoisovalerate (b.p. 160°), gives with methyl iodide *valinecholine* in the form of its iodide, m.p. 195°; the *aurichloride*



forms yellow leaflets, m.p. 225°, the *platinochloride*, brownish-red prisms, m.p. 210°–211° (Karrer, Gisler, Horlacher, Locher, Mäder and Thomann, Helv. chim. Acta, 1922, 5, 469).

d-Valine is most conveniently obtained from the two to three weeks old etiolated seedlings of *Lupinus luteus* and *Lupinus albus*; contamination with leucine, which is very difficult to separate from valine, can be obviated by removing the cotyledons from the young plants before they are dried (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 312). *d*-Valine is prepared from the synthetic compound by the fractional crystallisation of the brucine salts of the formyl derivative (Fischer, Matsubara and Hilpert, Ber. 1906, 39, 2320).

d-Valine crystallises in colourless, shining six-sided plates. It melts in a closed capillary tube at 315° (corr.); when heated in an open tube it sublimes and decomposes partially with formation of the anhydride. It dissolves in 11 parts of water at 16.5°. The taste is first slightly sweet, then bitter (Fischer, Matsubara and Hilpert, l.c.). The natural compound obtained from *Lupinus luteus* has $[\alpha]_D^{16} + 28.2^\circ$ in 20 p.c. hydrochloric acid (0.5 grm. in 10 c.c.); from *Lupinus albus* $[\alpha]_D^{16} + 27.9^\circ$ in 20 p.c. hydrochloric acid (0.5012 grm. in 10 c.c.) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 299). The synthetic compound prepared by hydrolysing the formyl derivative has $[\alpha]_D^{20} + 28.75^\circ$ in 20 p.c. hydrochloric acid, or $[\alpha]_D^{20} + 6.42^\circ$ in aqueous solution (Fischer, Matsubara and Hilpert, l.c.). For the practically quantitative separation of *d*-valine and *d*-alanine by the alternate crystallisation of valine as the free amino acid and of alanine as the phospho-

193).

Salts and derivatives of d-valine.—The *copper salt* $(\text{C}_6\text{H}_{11}\text{O}_2\text{N})_2\text{Cu}$, blue crystalline plates, soluble in 52 parts of methyl alcohol at 18°. The *hydrochloride* $\text{C}_6\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl}$, small prismatic crystals readily soluble in water or alcohol, the *platinochloride* is also readily soluble (Schulze and Barbieri, J. pr. Chem. 1883, 27, 337); the *picrolonate* has m.p. 170°–180°, and $[\alpha]_D^{20} + 23.4^\circ$ (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127).

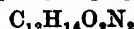
Formyl d-valine



obtained by the resolution of *dl*-formyl-valine through the brucine salt, forms small prisms, sinters at 150° and melts at 156° (corr.), and has $[\alpha]_D^{20} + 12.8^\circ$ to 13.27° in alcoholic solution *d*-valine *phenylcarbimide*



forms small microscopic prisms, m.p. 147° (corr.) with decomposition (Fischer, Matsubara and Hilpert, l.c.), m.p. 154° (Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 303), and yields the *d*-phenylisopropylhydantoin



on treatment with concentrated hydrochloric acid. This forms colourless thin prisms, m.p. 131°–133° (corr.), and has $[\alpha]_D^{20} - 97.5^\circ$ in alcoholic solution (Fischer, Matsubara and Hilpert, l.c.); m.p. 124° (Schulze and Winterstein, l.c.); *chloroacetyl-d-valine*



has m.p. 113°–115° (corr.) $[\alpha]_D^{20} + 15.8^\circ$; *glycyl-d-valine* $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHPr}^s \cdot \text{CO}_2\text{H}$ has m.p. 254° (corr.), $[\alpha]_D^{20} - 19.7^\circ$ in aqueous, -10.5° in hydrochloric acid or -6.9° in sodium hydroxide solution; it forms a crystalline *hydrochloride* and a *copper salt*. The *hydrochloride* of the *methyl ester* $\text{C}_6\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{HCl}$ is converted by methyl alcoholic ammonia into *glycyl-d-valine-anhydride* $\text{CH}_2 < \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CHPr}^s$, m.p. 266°

(corr.), $[\alpha]_D^{20} + 20.8^\circ$ in glacial acetic, $+32.7^\circ$ in aqueous or $+41^\circ$ in alcoholic solution; 1-*valyl-d-valine* $\text{C}_{10}\text{H}_{18}\text{O}_4\text{N}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ becomes anhydrous at 95°/12–15 mm. over phosphoric oxide; has m.p. 308° (corr.), and $[\alpha]_D^{20} - 70.6^\circ$ to -74° ; the *hydrochloride* of the *methyl ester* yields on treatment with methyl alcoholic ammonia the *trans-valine-anhydride* $\text{CHPr}^s < \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{array} > \text{CHPr}^s$ prisms, m.p. 316°–318° (corr.), which is optically inactive (Fischer and Scheibler, Annalen, 1906, 363, 136).

l-Valine is obtained by the resolution of the racemic formyl derivative through the brucine salt (Fischer, Matsubara and Hilpert, l.c.); by the action of ammonia on *d*- α -bromoisovaleric acid (Fischer and Scheibler, Ber. 1906, 41, 2891); and by the selective action of yeast on *dl*-valine (Ehrlich, Biochem. Zeitsch. 1906, 1, 8; 1908, 8, 438).

l-Valine is soluble in 17.1 parts of water at 5°, possesses a markedly sweet taste, and has $[\alpha]_D^{20} - 6.06^\circ$ in 24 p.c. aqueous solution.

—29.04° in 20 p.c. hydrochloric acid solution (Fischer, Matsubara and Hilpert, l.c.). A specimen obtained from yeast had $[\alpha]_D^{20}$ —27.62° in a 4.61 p.c. solution of 20 p.c. hydrochloric acid.

1-Formylvaline $\text{CHMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CHO}$ crystallises in small prisms, sinters at 150° and melts at 156° (corr.); it has $[\alpha]_D^{20}$ —12.93° to 13.07° in alcoholic solution, or +16.9° in aqueous solution; 1-valine phenylisocyanate $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_2$ has m.p. 147° (corr.) decomp., and $[\alpha]_D^{20}$ —19.02° in absolute alcoholic solution, and yields 1-phenylisopropylhydantoin $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$ on treatment with hydrochloric acid. It has m.p. 131°–133° (corr.) and $[\alpha]_D^{20}$ +97.22° in absolute alcoholic solution. For iso-valine, α -amino- α -methylbutyric acid, v. Gadamer and Rukop (J. pr. Chem. 1914, [ii.] 90, 405). M. A. W.

VALONIA (Valonée, Fr.; Valonea, Acker-doppen, Orientalische Knoppfern, Ger.). An important tanning material. Is the acorn cup of certain species of oak, usually *Quercus Aegilops* (Linn.), and probably *Q. macrolepis*, *Q. graeca*, *Q. Ungeri*, and *Q. coccifera* (Linn.). The former is most prolific in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, whereas the *Q. macrolepis* forms great forests in Greece. These acorn cups have a diameter up to about 1½ ins., and in good condition possess a bright colour.

The fruit ripens in Asia Minor about July or August, and the trees are then shaken, and the material left on the ground to dry; this is subsequently collected into heaps, and allowed to ferment for some weeks, until the acorn contracts and falls from the cup. The acorn, which contains but little tannin, is employed for feeding purposes.

In Greece distinct qualities of valonia are known, the best (*chamada*) collected about April before the fruit is ripe, a second (*rhabdisto*) in September or October, and a third little used inferior variety (*charcola*).

Smyrna valonia may contain 40 p.c., Greek 19–30, and Candia valonia 41 p.c. of tannin matter, which consists of a mixture of a gallo-tannin and an ellagitannin. Valonia is, indeed, an excellent source for the preparation of ellagic acid, because it so readily yields a product easy to purify. Extract of valonia frequently undergoes fermentation with deposition of ellagic acid, and to avoid this the employment of antiseptics is to be recommended.

Valonia is especially suited for the manufacture of sole leather, and together with gambier and other materials for dressing leather, but is little employed for dyeing purposes (cf. Procter, Principles of Leather Manufacture, 259). A. G. P.

VANADINITE. A mineral consisting of lead chloro-vanadate $(\text{PbCl})\text{Pb}_4(\text{VO}_4)_3$, crystallised in the hexagonal system and isomorphous with apatite and pyromorphite (q.v.). The formula requires 19.4 p.c. V_2O_5 , but this is often partly replaced by phosphoric and arsenic oxides; and the variety *endlicheite* forms a passage to the species *milneite* (lead chloro-arsenate). The mineral forms small hexagonal prisms usually terminated simply by the basal plane; at times the crystals are curved and barrel-shaped. Cleavage, warty, and cauliflower-like mass

occur. The colour is usually yellowish or brownish, but crystals from Arizona are bright scarlet. Sp.gr. 6.6–7.2. When touched with a drop of nitric acid a yellow coating of vanadic oxide is formed on the crystals; this affords an easy test for recognising the mineral.

Vanadinite is a mineral of secondary origin in the upper portions of lodes of lead ore, and it sometimes occurs in association with gold. It was formerly found in some quantity at Wanlockhead in Dumfriesshire and near Klagenfurt in Carinthia; and now abundantly in several of the mining districts of Arizona and New Mexico. It has been met with at Broken Hill in Northern Rhodesia, and in Morocco. Important localities in Arizona are the Red Cloud mine in Yuma Co., the Mammoth gold mine in Pinal Co., the Globe district in Gila Co., and in Pima Co. and Yavapai Co., &c. In New Mexico at the Sierra de los Caballos near Lake Valley in Sierra Co., Magdalena in Socorro Co., Georgetown in Grant Co., &c. It is also of abundant occurrence at Santa Marta in Badajoz, Spain.

In New Mexico and Arizona, and also in Spain, the mineral is mined as a source of vanadium. The concentrate containing the vanadinite, together with descloizite, is treated in lead-lined vats with dilute sulphuric acid heated by steam, and the vanadium obtained in solution as sulphate, the lead remaining in the insoluble residue. The solution is decanted and evaporated, and the vanadium salt heated to give vanadic oxide. The bulk of this product appears to be used in the manufacture of vanadium-steel, and to a limited extent also as a pigment. Other minerals that have been worked for vanadium are carnotite, descloizite, patronite, and roscoelite (q.v.). L. J. S.

VANADIUM. Sym. V. At.wt. 51.0. This element was discovered by Del Rio (Gilbert's Ann. 1801, 71, 7) in a lead ore, *vanadinite*, from Zimapan in Mexico; the discovery was confirmed by Sefström (Pogg. Ann. 1830, 21, 48), and by Wöhler and Berzelius (*ibid.* 1831, 22, 1; cf. Collet-Descotils, Ann. Chim. 1805, [i.] 53, 260). Upon the work of Berzelius was based the view that vanadium was allied to chromium and molybdenum and, like them, yielded an acidic trioxide, and this idea was current till Roscoe, in 1867, showed that the substance believed to be the metal in earlier investigations had been either an oxide or a nitride, and that the compounds of vanadium in general showed that the element belonged to the phosphorus group. According to Aston, vanadium is simple with an atomic weight of 51.

Occurrence.—Minerals containing a large proportion of vanadium are rare, but the metal is very widely distributed in small quantities. Vanadium occurs as vanadic acid in *vanadine* with the native copper of Lake Superior, and in *alaite* (Nenadkevitch, Bull. Acad. Sci. St. Petersburg, 1909, 185); as lead vanadate, with lead chloride, in *vanadinite*; as *descloizite*, a basic lead and zinc vanadate; as hydrated vanadate of lead and copper in *mottramite* and *peitavite*; as vanadate of copper in *turnite* (Nenadkevitch, l.c.); as lead vanadate containing zinc and manganese in *degehenite*, *arconite*, and *eusynelite*; as vanadate of lead and arsenic in *endlicheite*; as bismuth vanadate in *pucheris*; as the basic

oxide V_2O_5 in the vanadium muscovite *roscoelite* (Hillebrand, Turner and Clarke, Amer. J. Sci. 1899, [iv.] 7, 451); as vanadate of copper, barium, and calcium in *volborthite*; and as vanadium sulphide V_2S_5 with sulphur, in *patronite* (Hillebrand, *ibid.* 1907, [iv.] 24, 141; Hewett, Eng. & Min. J. 1906, 82, 385; Trans. Amer. Inst. Min. Eng. 1910, 40). See also Vanadium Ores [Monographs on Mineral Resources prepared under the direction of the Imperial Institute], John Murray, London, 1924.

Vanadium is present in magnetites and in most other iron ores (Pope, Chem. Soc. Abstr. 1900, ii. 409), and becomes concentrated in the residues from their treatment, especially by the Thomas-Gilchrist process. It is said to be diffused, with titanium, through all primitive granite rocks (Dieulaufait; Hillebrand, Amer. J. Sci. 1898, 6, 209; 7, 294), and has been found by Deville in *bauxite*, *rutile*, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands. Jorissen has found vanadium in the coal of Liège (Bull. Acad. Roy. Belg. 1905, 178). Scacchi has observed its presence in incrustations on the Vesuvian lava of 1631, and Donath has found as much as 0.16 p.c. of vanadic acid in a sample of commercial caustic soda (Dingl. poly. J. 240, 318). It occurs in the sun and has been found in stony meteorites (Hasselberg, Vetensk. Akad. Svenska. 1899, 56, 131).

Extraction.—Ammonium metavanadate was formerly prepared on a commercial scale by the Magnesium Metal Co. at Patricroft near Manchester.

The mineral employed was *mottramite* $(PbCu)_3(VO_4)_2 \cdot 2PbCu(HO)_2$, which occurs in the copper-bearing Keuper beds at Alderley Edge and Mottram St. Andrew's, in Cheshire, as a film on the grains of sandstone. The sand is digested in concentrated hydrochloric acid, and the acid liquid is withdrawn. The solution, with the washings of the residue, is concentrated and evaporated with an excess of ammonium chloride, forming ammonium metavanadate, which, being insoluble in a concentrated solution of ammonium chloride, is precipitated. After being freed from copper and iron by repeated crystallisation, it is gently roasted in a porcelain vessel, with production of vanadium pentoxide. This is suspended in water and subjected to a current of ammonia gas, with formation of ammonium metavanadate, the solution being separated from the silica, phosphates, &c., which are not affected by ammonia, is crystallised until free from phosphates, and gently ignited to produce pure vanadium pentoxide (v. Roscoe, Phil. Trans. 1867, 158, 1).

The chief ores from which vanadium is or may be derived are patronite, carnotite, roscoelite, vanadinite and asphaltite. The chief deposits of vanadium ores, mainly carnotite, in the United States are in South-Eastern Utah and North-Western Colorado, but at present the only vanadium produced from native ore is obtained as a by-product from carnotite worked for its radium content. The principal source of supply at present is in Peru, where deposits occur at *Uchire* *Passo*, about 30 miles to the north-west of the Cerro de Pasco copper mines; here it is found in the coal deposits as a

black mineral resembling slaty coal; it contains about 30 p.c. of free sulphur, with 40 p.c. vanadium sulphide (patronite). After burning out the free sulphur the ore contains from 30 to 52 p.c. of vanadium oxide (V_2O_5). The asphaltite deposits of Peru frequently contain considerable amounts of vanadium, the ash yielding from 25 to 40 p.c. of vanadium oxide.

Vanadium ores are also worked in New Mexico, and carnotite, roscoelite, and vanadinite deposits are found in Colorado, Utah, Nevada, Arizona, and Oklahoma, mainly for the production of ferro-vanadium and vanadium steel. Small quantities of vanadium are also obtained from Argentina (*rafaelite*), Chile (*chileite*), South-West Africa (*mottramite*), and Spain (*vanadinite*).

Two consignments of 25 and 30 tons, respectively, of vanadinite concentrate, averaging 13 p.c. V_2O_5 , from the Kafir's Krall mine in the Transvaal, constitute the first important shipment of this ore from the Union.

To extract it from vanadinite the mineral is fused with potassium nitrate, alone or mixed with sodium carbonate, the mass is lixiviated, and the solution acidified, or, better, evaporated with ammonium chloride in order to precipitate alumina and silica. From the clear solution barium chloride and ammonia precipitate the barium salts of vanadic, chromic, and molybdic acids, &c., and on treating the product with sulphuric acid, followed by ammonia and water, the vanadium goes into solution as ammonium metavanadate, which is finally precipitated by the addition of ammonium chloride. Vanadic acid may also be separated from mixtures of sodium vanadate and silicate by the addition of more vanadic acid. This precipitates the silica and leaves only fairly pure sodium vanadate in solution (Herrenschmidt, Compt. rend. 1904, 139, 862).

Gin (Proc. Seventh Int. Cong. Appl. Chem. London, 1909) smelts the vanadinite in the electric furnace with 6 p.c. of its weight of carbon, which is sufficient to reduce the base metals, leaving the vanadium in the slag in the form of trioxide. The slag is pulverised and gently heated in a current of air until the trioxide is oxidised to tetroxide; at this stage sodium carbonate and a little nitrate are added to complete the oxidation to vanadic anhydride; the mass is then fused, cooled, pulverised and treated with boiling water, which dissolves the sodium metavanadate together with the phosphate, silicate and aluminate. The cooled solution is treated with carbon dioxide to precipitate silica, and then ammonium carbonate is added and the solution concentrated until ammonium metavanadate is precipitated. This is washed, dried, again washed with water acidified with nitric acid, and calcined to obtain vanadic acid. When electric-furnace treatment is inadmissible, it may be replaced by treatment in a water-jacket furnace, in which case the lead and copper are separated, and the slag is oxidised on the hearth of a reverberatory furnace and mixed with sodium carbonate and nitrate. Or, alternatively, the vanadiferous slag is melted with sodium bisulphate in an iron or steel pan; when the reaction has ceased, the mass is run off on to plates of silicon-steel, pulverised, digested with water in a water-jacketed

with an agitator, steam being introduced during the process. The copper, silver, and arsenic are precipitated from the solution by hydrogen sulphide, ammonia added and the iron and alumina removed. The solution now contains the vanadium in the form of thiovanadate, which is converted into vanadium sulphide by neutralising with dilute acid, and the sulphide is converted into vanadic acid by roasting (J. Soc. Chem. Ind. 1911, 30, 218).

Vanadium can be separated from arsenic or phosphorus by precipitation of vanadic acid from an acidified vanadate solution. A vanadinite concentrate containing 10.24 p.c. V_2O_5 , 0.28 p.c. As, and 0.27 p.c. P, was fused with sodium carbonate, sodium hydroxide, and charcoal. The lead present was reduced to the metallic state and the slag extracted with hot water. After acidifying with sulphuric acid the solution was boiled with live steam for several hours. A 97 p.c. recovery of vanadic acid free from arsenic and phosphorus was obtained (H. A. Doerner, J. Ind. Eng. Chem. 1923, 15, 1014; J. Soc. Chem. Ind. 1923, 42, 1182 A.).

Determination of phosphorus in vanadium ores.—Precipitation of the phosphorus as ammonium phosphomolybdate from a solution containing relatively large quantities of vanadic acid yields an orange-brown precipitate which contains considerable amounts of vanadic acid. The method recommended by Treadwell (Kurzes, Lehrbuch der Analytischen Chemie, 6th ed.), involving previous reduction of vanadic acid to vanadyl sulphate, is also unsatisfactory for determining small quantities of phosphorus in vanadium ores; the precipitate is greenish-yellow, and the results are too high. The most satisfactory of several procedures tested was found to be the following: 10 grms. of finely-divided ore is dissolved in 75 c.c. of hydrochloric acid and 25 c.c. of water, and the solution is oxidised with nitric acid and evaporated with 30 c.c. of sulphuric acid (1 : 1) until strong, white fumes are evolved. The cold mass is dissolved in 100 c.c. of water, and the sand and lead sulphate are removed by filtration. To the filtrate 50 c.c. of strong nitric acid and 1 gm. of fine tin powder are added, and the mixture is shaken till the latter has dissolved, then set aside overnight in a hot place. The liquid is diluted with 400 c.c. of hot water and filtered. The precipitate is heated in a nickel crucible, and the residue fused with 5 grms. of potassium cyanide, which reduces tin and arsenic to the metallic form. The fused mass is dissolved in water, the solution filtered, and the filtrate boiled with hydrochloric acid to expel all hydrocyanic acid. It is transferred to a graduated flask, treated with potassium ferrocyanide until a spot test gives a brown colour with uranium acetate, when it is diluted to 500 c.c. 450 c.c. is filtered through a dry paper, treated with a solution of an aluminium salt containing about 0.1 gm. of metal, then with a slight excess of ammonia. The precipitate, which contains all the phosphoric acid, is collected, washed free from chloride and ferrocyanide, and dissolved in hydrochloric acid. The solution is evaporated to remove silica, and the filtrate is evaporated with nitric acid to expel chlorine compounds. The phosphoric acid is eventually precipitated as ammonium molybdate and determined in

the usual manner (Kriesel, Chem. Zeit. 1923, 47, 177; J. Soc. Chem. Ind. 1923, 314A).

According to Wits and Osmond (Bull. Soc. chim. 1882, [ii.] 38, 49; Compt. rend. 95, 42), the slags produced while working the Thomas-Gilchrist process at the Crenot ironworks contain nearly 1.5 p.c. of vanadium, the quantity of that metal thus concentrated amounting to 60,000 kilos (nearly 59 tons) annually. They recommend the following process for the separation: 1 kilo of the roughly broken slag is treated with a quantity of hydrochloric acid insufficient to attack the whole (about 1 litre of acid of 21°–22°Bé.) without stirring, 3 litres of water being added, and the whole remaining at rest for 2 days. The solution, having a sp.gr. of about 27°Bé. at 36°, is decanted and diluted to 15°Bé., and the silica is removed. The solution contains the vanadium in the hypovanadic condition, and may be used at once for the production of aniline black. If it is desired to produce hypovanadic phosphate, the solution is nearly neutralised and about 250 c.c. of saturated ammonium acetate solution is added. The bluish-grey precipitate produced, containing phosphates of iron, aluminium, and vanadium, is re-dissolved and again treated with ammonium acetate, the precipitate containing about 20 p.c. of vanadium.

If the slag contains less than 1.5 p.c. of vanadium, the hydrochloric acid solution is neutralised by the addition of a further quantity of finely-powdered slag. The solution becomes colourless, and a greyish granular precipitate separates, containing the whole of the vanadium and smaller proportions of the other less soluble phosphates. The precipitate is re-dissolved and re-precipitated as before. For the preparation of ammonium metavanadate, the phosphatic precipitate is roasted at incipient redness, and the ochreous-yellow mass of impure pentoxide is dissolved with the aid of ammonia, boiled until colourless and filtered, the ammonium metavanadate being precipitated by the addition of excess of ammonium chloride. From 4 kilos. of slag containing 1.5 p.c. of vanadium, about 250 grms. of ammonium metavanadate may be produced. It is a colourless transparent salt, or white powder, difficultly soluble in water, insoluble in a concentrated solution of ammonium chloride and in ether. It was formerly used, in conjunction with sodium chlorate, as an oxygen-carrier in the formation of the finest aniline black, only an extremely small quantity of the salt being required for a large amount of aniline.

Später attempted (1896) to employ the ash of an anthracite from Yauli (Peru) containing 28 p.c. of vanadium, but was unsuccessful.

From minerals in which it occurs with uranium, vanadium may be extracted by fusing with potassium hydrogen sulphate, lixiviating the mass and concentrating the solution thus obtained. The solution is reduced with zinc and the vanadium precipitated with ammonia and ammonium carbonate (Gin. Elektrochem. Zeit. 1906, 13, 119).

Haynes states (Mines and Minerals, 1900, 30, 139) that vanadium is extracted from carnotite, in West Colorado, by dissolving out the uranium and vanadium with hot sodium carbonate solution, precipitating the uranium with caustic soda, and throwing down the vanadium from the mother liquor as calcium vanadate.

also Barker and Schlundt, *J. Soc. Chem. Ind.* 1916, 35, 175.

Fleok and Haldane recommend that the crushed ore be treated with 15–20 p.c. sulphuric acid, the acid liquid neutralised by the addition of fresh ore, and the clear solution fractionally precipitated with limestone, whereby a complex mixture, rich in vanadium, is obtained, from which the element may be extracted by any ordinary method (U.S. Pat. 880752).

It is probable that in future American carnotite ore will for the most part be delivered to the reduction works as concentrates. The most usual process for dealing with these is as follows. They are first boiled in autoclaves with soda ash and water, with stirring, for 6–10 hours. This converts radium and barium salts into the carbonates, 90 p.c. of the uranium present into sodium uranyl carbonate, and 30 p.c. of the vanadium into sodium vanadate. The treated concentrate is settled, decanted, filter-pressed, and washed free from sulphate. The filtrate and washings contain the uranium and vanadium salts and are evaporated. The cake is acidified with hydrochloric acid and boiled, pressed in wooden filters, and washed. The cake is discarded. The filtrate contains radium and vanadium, and the former is precipitated as radium barium sulphate and removed on vacuum filters. The cake is washed and boiled with soda ash, caustic soda and water, the resulting carbonates are pressed and washed, converted into chlorides, and are then ready for fractional crystallisation. The utmost care must be taken against contamination by sulphates during the stages of this process. The uranium is separated from vanadium by crystallisation as sodium uranyl carbonate, dissolved in water, acidified, and boiled. Any vanadium present is removed by addition of a small quantity of ferrous sulphate, and the uranium precipitated as ammonium uranate. The vanadium in the acid solution from the barium radium sulphate precipitation is precipitated with lime, and the calcium vanadate added to the solution remaining from the sodium uranyl carbonate crystallisation, and the whole boiled with sodium carbonate and a small quantity of manganese dioxide. The solution, containing 95–98 p.c. of the vanadium, is filtered, almost neutralised with sulphuric acid, and freed from phosphate by precipitation with sodium aluminate. The solution is concentrated and vanadic acid precipitated by boiling with a slight excess of sulphuric acid. By this process a minimum yield of 80 p.c. of each product is obtained from carnotite (K. B. Thews and F. J. Heinle, *J. Ind. Eng. Chem.* 1923, 15, 1159–1161; *J. Soc. Chem. Ind.* 1924, 43, 55 B).

Preparation of metallic vanadium.—Roscoe gave two methods for the preparation of the metal; (a) the reduction of vanadium nitride in hydrogen, which never gives a pure product; and (b) the reduction of anhydrous, oxygen-free vanadium chloride in dry hydrogen. For a long time the latter method was the only one known by which the pure metal could be obtained (v. Roscoe and Schorlemmer, *Treatise on Chemistry*), but it can be also prepared by the reduction of vanadium pentoxide with 'mischmetal', a mixture of alkaline earth metals extracted from the residues from the manufacture

of thorium (Weiss and Aichel, *Annalen*, 1904, 337, 380). The mixture of mischmetal and pentoxide is placed in a magnesia crucible and fired; the heat of reaction is sufficient to melt the reduced metal, which is afterwards found as a compact mass in the crucible (Muthmann, Weiss and Riedelbauch, *ibid.* 1907, 355, 58).

It was formerly supposed that Goldschmidt's aluminium reduction method would not give pure vanadium from the pentoxide (Koppel and Kaufmann, *Zeitsch. anorg. Chem.* 1905, 45, 352), but under certain conditions Vogel and Tamman have, by this method, obtained a regulus containing 99 p.c. vanadium, with a little silicon and aluminium (*ibid.* 1909, 44, 225).

According to Ruff and Martin (*Zeitsch. anorg. Chem.* 1912, 25, 49), vanadium trioxide melting at about 2000°, gives better results than the pentoxide.

Reduction of the oxide with metallic calcium according to Muthmann's method, gives product containing only 91–93 p.c. of vanadium. A purer regulus is obtained by reducing with a mixture of calcium and aluminium (Prandtl and Bleyer, *ibid.* 1909, 64, 217).

Vanadium produced by the reduction of the pentoxide in the electric furnace contains 10–25 p.c. of carbon and consists chiefly of vanadium carbide VC, a silvery-white, highly crystalline and extremely hard substance of sp.gr. 5.405 and m.p. 2705°. A product containing less carbon can be obtained by conducting the operation in an atmosphere of hydrogen (Moissan, *Compt. rend.* 116, 1225; 122, 1297; *Zeitsch. anorg. Chem.* 14, 174).

The pure metal can also be obtained by the electrolysis of a solution of sodium vanadate in hydrochloric acid, using carbon electrodes and a current density of 0.018–0.020 amp. per sq. m., and maintaining the temperature about 80° (Cowper-Coles, *Eng. and Min. J.* 67, 744; von Bolton, *Zeitsch. Elektrochem.* 1905, 11, 45).

On the small scale it can be obtained by passing a mixture of hydrogen and vanadyl chloride vapour over incandescent platinum wire, when metallic vanadium is deposited as a silver-grey coating, or by passing the chloride over sodium hydride. The reduction of vanadium trichloride with sodium yields a product containing about 96 p.c. of metal and of D₄, 5.819.

Properties.—Pure vanadium is a silver-white metal, similar in appearance to cast iron, and crystallises in hexagonal rhombohedra, like the other elements of its group. Its hardness is 7.5 on Mohr's scale, and it is as brittle as glass. Its sp.gr. is 5.688 at 18.7° (sp.gr. 5.5 at 15°/15°, Roscoe), and its specific heat is 0.124 (Matignon and Monnet, *Compt. rend.* 134, 542; Muthmann, Weiss and Riedelbauch, *l.c.*), which, assuming the atomic heat to be 6.4, confirms the atomic weight of 51. Heat of combustion of 1 gram. (to V₂O₅) is 2456 cal.

The melting-point is very high, but the data given by various investigators are not in agreement. Werner von Bolton, using the photometric method of Lammer, found it to be 1880°. Vogel and Tamman give it as 1780°, and 1790° (*Zeitsch. anorg. Chem.* 1908, 33, 73); Ruff and Martin 1715°. The melted metal readily dissolves both the trioxide and the pentoxide, and the

mixtures melt at higher temperatures than the metal.

It is stable in moist or dry air at ordinary temperatures, and a polished surface retains its lustre for weeks. It is unacted upon by bromine water, aqueous alkali solutions, hydrochloric acid, or cold sulphuric acid. It is dissolved by hydrofluoric acid or hot sulphuric acid forming green solutions, and is attacked by nitric acid or *aqua regia*. Melted potash or saltpetre rapidly dissolve the metal with formation of an alkali vanadate. Metallic vanadium reduces solutions of mercuric chloride and bromide, cupric chloride and bromide, and ferric chloride to the lower haloid salts, and it precipitates the metal from solutions of auric chloride, silver nitrate, platonic chloride, iridium tetrachloride, &c.

Alloys of vanadium can be prepared in the electric furnace by the reduction of the pentoxide in presence of a second metal or its oxide (Moissan, *Compt. rend.* 1896, 122, 1297). By fusing vanadic acid with aluminium in the necessary proportions, Czako (*Compt. rend.* 1913, 156, 140) has prepared alloys of aluminium and vanadium, and has isolated crystals of Al_3V and AlV . The hardness of the alloys increases with the vanadium content up to 60 p.c., after which it diminishes. The chief industrial use of vanadium is in the preparation of special steels, which are largely used for motor-car work; it is introduced into the molten steel as *ferro-vanadium*, an alloy prepared by electric-furnace methods. The addition of 0.1–0.25 p.c. of vanadium to chromium, manganese, or other open-hearth or crucible steels greatly increases the elastic limit and the ultimate tensile stress without reducing the ductility (J. Kent Smith, *J. Soc. Chem. Ind.* 1906, 291; cf. Auchy, *J. Ind. and Eng. Chem.* 1909, 1, 455).

Colloidal solutions of vanadium have been prepared by Svedberg (*Ber.* 1906, 39, 1712). According to Prandtl and Hess (*Zeitsch. anorg. Chem.* 1913, 82, 103) they are best obtained from the solutions of the vanadic esters, especially *tert.* butyl orthovanadate, as the alcohol is easily removed by boiling. Riedel (*Chem. Zentr.* 1914, i. 1738) found that *iso-amyl* orthovanadate ($C_5H_{11}VO_4$, b.p. $161^\circ/19$ mm.) is the most convenient ester. This is boiled in water until a homogeneous dark red solution is obtained. After removing the amylene hydrate by ether the deep red solution contains about 8 p.c. vanadic acid.

OXIDES OF VANADIUM.

There are five oxides of vanadium, analogous to the oxides of nitrogen—

- Vanadium suboxide, V_2O ;
- “ monoxide, hypovanadious oxide, V_2O_3 ;
- “ sesquioxide or trioxide, V_2O_5 ;
- “ dioxide, hypovanadic oxide, V_2O_4 (VO_2);
- “ pentoxide, vanadic anhydride, V_2O_5 .

The first three of these act as basic oxides, forming salts with acids; the last two behave both as weak basic oxides and acid-forming oxides.

Vanadium suboxide V_2O is obtained as a brown powder by the exposure of finely divided

metallic vanadium to the air. No salts of this oxide have been prepared.

Vanadium monoxide V_2O_3 , or VO (*vanadyl*) is obtained as a lustrous grey solid by reducing the higher oxides with metallic potassium, or by passing the vapour of vanadyl trichloride with hydrogen over red-hot carbon, or by heating the solid oxychloride $VOCl$ to a red heat in hydrogen. It has sp.gr. 3.64, is brittle and conducts electricity. At a red heat it burns in air to form the trioxide, and it combines directly with chlorine to form the oxytrichloride. This oxide was supposed by Berzelius to be the metal. It is a black amorphous powder D¹⁴ 5.758.

Vanadium monoxide dissolves in acids to form the corresponding salts, which have a blue or violet colour and act as powerful reducing agents. The solution in hydrochloric acid has been suggested as a reagent for the removal of arsenic from hydrochloric acid gas in the process of manufacture, the arsenic being reduced to the free state and remaining suspended in the liquid (D. R. P. 164355).

Vanadium trioxide V_2O_3 , obtained by reducing the pentoxide with hydrogen or carbon at a red heat, is a black powder of sp.gr. 4.7, m.p. 2000° . Heat of formation 302 ± 10 cal. (Ruff and Friedrich). In air it oxidises, slowly at the ordinary temperature, quickly when heated, forming the dioxide V_2O_4 . It is insoluble in most acids.

Vanadium dioxide V_2O_4 , or VO_2 , is prepared by the oxidation of the trioxide or by the partial reduction of the pentoxide. It is a steel-coloured powder composed of dark indigo-coloured crystals. It dissolves in acids to form solutions of vanadyl salts of a bright blue colour, and in alkalis to form *vanadites* (v.i.). A hydrate, $V_2O_4 \cdot 7H_2O$, or $V_2O_4(OH)_4 \cdot 5H_2O$, is obtained as a greyish-white precipitate by adding sodium carbonate to a solution of a vanadyl salt. At 100° it loses 4 molecules of water, forming $V_2O_4 \cdot 3H_2O$.

Hypovanadic acid (*vanadious acid*) $H_4V_2O_6$ has been prepared by boiling a solution of the dioxide VO_2 in aqueous sulphurous acid. It is a pink crystalline powder (Gain, *Compt. rend.* 1906, 143, 823; see also *ibid.* 1154), and can exist in a green isomeric form (Gain, *ibid.* 1907, 146, 403; *Ann. Chim.* 1908, [viii.] 14, 224).

The salts in which VO_2 is the acidic oxide are derived from the partial anhydrides $H_2V_2O_6$ and $H_4V_2O_6$.

Potassium and sodium vanadites



are prepared by adding excess of caustic alkali to a solution of vanadyl sulphate or chloride (v. Koppel and Goldmann, *Zeitsch. anorg. Chem.* 1903, 36, 281). They form reddish-brown crystalline scales and dissolve in water to dark-brown solutions.

Vanadium pentoxide V_2O_5 is the final product of most commercial processes for the extraction of vanadium from its ores. The pure oxide is best prepared by decomposing vanadyltrichloride with water and fusing the product, or by the decomposition of ammonium metavanadate by

(Matignon, *Chem. Zeit.* 1906, 29, 266; also Beard, *Ann. Chim. anal.* 1906, 1 of formation 427 ± 7 cal. (Gibbs)

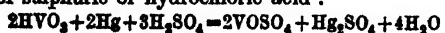
Friedrich, *Zeitsch. anorg. Chem.* 1914, 39, 273.

Vanadium pentoxide forms large rhombic prisms, of a fine ruby-red colour by transmitted light, of sp.gr. 3.85, soluble in about 1000 parts of water with formation of a yellowish, tasteless solution which reddens litmus; this appears to be a colloidal modification of vanadic acid. At 668° (Carnelley) it fuses, forming a red liquid, which recrystallises in needles, with incandescence, on cooling. When the molten acid is poured into water it yields a solution of the colloidal modification (Müller, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 302).

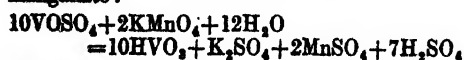
When prepared by heating ammonium metavanadate, treating the residue with nitric acid and drying at a gentle heat, it is a yellow, hygroscopic powder which forms hydrates with 1, 2, and 8 molecules of water, and is soluble in water to the extent of 8 parts in 1000. When the oxide is heated at 440°, or fused, two different sparingly soluble modifications are formed (Ditte, *Compt. rend.* 1885, 101, 698).

The properties of colloidal vanadium pentoxide have been studied by Dumanski (*J. Russ. Phys. Chem. Soc.* 1924, 54 703; *Chem. Soc. Abstr.* 1924, ii, 195).

Vanadium pentoxide is reduced to V_2O_4 by the action of SO_2 , or by evaporation with hydrochloric acid or hydriodic acid in absence of air; to V_2O_3 by magnesium and hydrochloric acid, or by hydrogen in the dry way; to V_2O_2 by zinc and hydrochloric acid (Glasmann, *Ber.* 1905, 38, 600; Chapman, *Analyst*, 1907, 32, 250); or by shaking with mercury in presence of sulphuric or hydrochloric acid:



If a sufficiency of sodium chloride is present the whole of the mercury is precipitated as mercurous chloride, and a blue solution is obtained which may be quantitatively titrated with permanganate:



(McCay and Anderson, *J. Amer. Chem. Soc.* 1922, 44, 1018). The determination of vanadium by reduction with hydrogen peroxide and titration with permanganate has been studied by Hotherhall (*J. Soc. Chem. Ind.* 1924, 43, 270 T, 853 B). Vanadic acid volatilises with hydrochloric acid or to a slight extent when heated with alkaline chlorides.

The pentoxide was formerly used in the preparation of aniline black, and it acts as a carrier of oxygen in many reactions, e.g. the electrolytic oxidation of organic compounds in acid solution (Meister, Lucius and Brüning, *D. B. P.* 172654), and the oxidation of sugar to oxalic acid or of stannous to stannic chloride (Ludwig, Mooser and Lindenbaum, *J. pr. Chem.* 1907, [ii.] 75, 146; *D. B. P.* 183022).

For the analysis of commercial vanadic acid, see Cheneau (8th Internat. Cong. Appl. Chem. 1913, 1, 123; *J. Soc. Chem. Ind.* 1912, 31, 921).

The Vanadic Acids and their Salts.

Orthovanadic acid H_3VO_4 has not been prepared.

Metavanadic acid HVO_3 may be obtained by boiling copper metavanadate with aqueous sulphurous acid. A mixture of brown and yellow

crystals is first produced, the former being redissolved on continued boiling with excess of sulphurous acid. The remaining yellow crystals consist of metavanadic acid. The acid may also be prepared by addition of a solution of ammonium metavanadate to one of copper sulphate containing excess of ammonium chloride, until a permanent precipitate is produced, and heating for a few hours at 75°. The whole of the vanadium is slowly precipitated, the colour being finer when precipitation is slow (Gerland, *Ber.* 1876, 9, 874). Metavanadic acid forms brilliant golden or orange-coloured scales, which are used as a pigment in place of gold bronze under the name 'vanadium bronze.'

Pyrovanadic acid $H_2V_2O_7$, prepared by the action of nitric acid on an acid vanadate, is a brown precipitate which when air-dried has above composition (von Hauer, *v.i.*).

Hexavanadic acid $H_4V_6O_{17}$, formed when a solution of pervanadic acid is allowed to stand, is known only in solution (Düllberg, *Zeitsch. physikal. Chem.* 1903, 45, 170).

The following sodium vanadates are known, and may be taken as typical of the vanadates in general—

- Sodium metavanadate, $NaVO_3$;
- " orthovanadate, Na_2VO_4 ;
- " pyrovanadate, $Na_2V_2O_7$;
- " tetravanadate, $Na_4H_2V_4O_{17}$;
- " hexavanadate, $Na_4H_4V_6O_{17}$.

(v. also von Hauer, *J. pr. Chem.* 1856, [i.] 69, 385; 1859, 76, 156 and 929; 1860, 80, 324; Carnelley, *Chem. Soc. Trans.* 1873, 323). In solution the metavanadates are most stable, and the orthovanadates least stable, the pyrovanadates being intermediate. This is the reverse of the order of stability of the phosphates. At high temperatures orthovanadates are the most stable salts, being produced, e.g., by fusing alkali carbonates with vanadium pentoxide. The alkali pyrovanadates, prepared by fusing the pentoxide with excess of alkali carbonate and crystallising from water, are soluble, whilst the pyrovanadates of heavy metals are mostly insoluble.

The alkali metavanadates are obtained by boiling a solution of alkali carbonate with the pentoxide, and are colourless salts which give yellowish-red anhydro-salts on treatment with acid. The metavanadates of heavier metals are usually yellow. Pure silver metavanadate is precipitated on addition of silver nitrate to a neutral solution of an alkali vanadate (Browning and Palmer, *Amer. J. Sci.* 1910, 30, 230).

A test which distinguishes between ortho- and meta-vanadates depends on the colour of the copper salts of the acids which are blue-green and light yellow respectively.

A series of double stannates and vanadates of sodium has been described by Prandl and Rosenthal (*Ber.* 1907, 40, 2125). Mixed alkali tungstates and vanadates by Prandl and Hecht (*Zeitsch. anorg. Chem.* 1915, 92, 196). Heteropolyvanadates have also been prepared by Rosenheim and Pieck (*Zeitsch. anorg. Chem.* 1916, 98, 223).

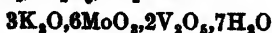
By introducing vanadium pentoxide into a boiling aqueous solution of iodic acid, the salts $V_2O_5 \cdot I_2O_5 \cdot 4H_2O$ and $V_2O_5 \cdot 2I_2O_5 \cdot 16H_2O$ may be formed. By ————— potassium and ammonium salts of the acids

$2R_2O_3 \cdot 2V_2O_5 \cdot 3P_2O_5 \cdot xH_2O$ are produced. Phosphates give rise to such salts as



and $R_2O_3 \cdot 2V_2O_5 \cdot P_2O_5 \cdot xH_2O$ (Rosenheim and Yang, *Zeitsch. anorg. Chem.* 1923, 129, 181; *Chem. Soc. Abstr.* 1924, 126, ii, 54).

A number of molybdeno-vanadates such as $4K_2O \cdot 4MoO_3 \cdot 3V_2O_5 \cdot 7H_2O$ and



have been prepared (Canneri, *Gazz. chim. ital.* 1923, 53, 779; *J. Chem. Soc. Abstr.* 1924, 126, i, 118).

Ammonium metavanadate NH_4VO_3 is the most important salt of vanadic acid. It may be prepared by dissolving vanadium pentoxide in excess of aqueous ammonia and then, by evaporation or by adding alcohol or excess of ammonium chloride, it is thrown out of solution as a white crystalline powder.

Pure ammonium metavanadate (*d* 2.326) is prepared by saturating with ammonia moist vanadium pentoxide and crystallising from a very dilute ammonia solution. One hundred parts of water dissolve 5.18 parts of the salt at 15° and 10.4 parts at 32°; it is only slightly soluble in hot alcohol and in ether. When heated in a vacuum to 135°–210°, the salt yields anhydrous ammonium triivanadate; above 210°, lower oxides of vanadium are formed. On boiling an aqueous solution, soluble ammonium divanadate and the insoluble triivanadate are formed. By the action of 4 p.c. acetic acid on boiling solutions of ammonium metavanadate, the divanadate



is obtained, which on desiccation loses $2H_2O$. Use of 10 p.c. acid gives the triivanadate $3V_2O_5 \cdot (NH_4)_2O \cdot 2H_2O$ (*d* 2.594), desiccation of which gives an anhydrous red salt (*d* 2.163). The previously described yellow anhydrous triivanadate has *d* 3.029. When the acetic acid is replaced by nitric, hydrochloric, or sulphuric acid, indefinite acid ammonium vanadates are formed, the composition varying with the concentration of the acid added. With a large excess of hydrochloric acid, reduction of the vanadate also takes place (*M. Lachartre, Bull. Soc. chim.* 1924, [iv.] 35, 321; *Chem. Soc. Abstr.* 1924, 126, ii, 409).

A 'vanadium ink' is produced by the addition of gallic acid to a mixture of neutral ammonium metavanadate and gum water. This ink is not destroyed by acids, alkalis, or chlorine but does not appear to be permanent. Soerensen (*J. Soc. Chem. Ind.* 1, 185) recommends the use of a solution of 1 lb. neutral ammonium metavanadate in 10 gals. of water for producing a permanent black dye on leather which has been tanned with nut galls.

A 'drier' for linseed oil may be prepared by ammonium metavanadate with rosin or oil. Vanadium is said to be superior to lead in drying power and gives smoother and tougher films than manganese or cobalt. According to Gardner (*Circ.* 149, *Paint Manufacturers Assoc., U.S.*, April, 1922) the time of drying of linseed oil siccated with vanadium is not markedly different from that of oil siccated with other known driers.

Paravanadic acid HVO_3 , prepared by adding finely powdered vanadium pentoxide to a solution of hydrogen peroxide acidified with sulphuric acid, forms yellow crystals soluble in water, giving a deep-red solution (Werther, *J. pr. Chem.* 1861, 83, 195; Pissarjewsky, *Zeitsch. physikal. Chem.* 1903, 43, 173). The potassium salt KVO_3 forms a yellow microcrystalline precipitate (see also Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.* 1899, 19, 504; Pissarjewsky, *ibid.* 1903, 32, 341; Melikoff and Kasanezky, *ibid.* 1901, 28, 242; Melikoff and Jelchmaninoff, *Ber.* 1909, 42, 2291; Anger, *Compt. rend.* 1921, 172, 1355).

Vanadiselenious acid $3V_2O_5 \cdot 4SeO_3 \cdot 4H_2O$ and its salts have been described by Frandl (*Ber.* 1905, 38, 1305).

Vanadium trifluoride $VF_3 \cdot 3H_2O$ crystallises in dark-green octahedra from a solution of the trioxide in hydrofluoric acid. Addition of potassium fluoride precipitates the double potassium salt $2KF \cdot VF_3 \cdot H_2O$ as a bright green crystalline powder.

Vanadium tetrafluoride VF_4 , a brownish-yellow hygroscopic powder, deliquescent to a blue liquid, is produced by the action of hydrogen fluoride on the tetrachloride.

Vanadyl difluoride VOF_2 is prepared by heating vanadyl dibromide in a current of hydrogen fluoride. It is a yellow powder of sp.gr. 3.396 at 19°.

Vanadyl trifluoride VOF_3 is formed by the action of hydrogen fluoride on vanadyl trichloride. It forms yellowish-white hygroscopic crusts of sp.gr. 2.459, deliquescent to a brownish-yellow solution. Melts at 300° and boils at 480°. May be sublimed in a current of oxygen.

Vanadium pentafluoride VF_5 , obtained as a white sublimate by heating the tetrafluoride in nitrogen. Is readily soluble in water, alcohol, chloroform, acetone and light petroleum. Sp.gr. 2.177; b.p. 111.2°/758 mm (Ruff and Lickfett, *Ber.* 1911, 44, 2539).

Numerous double fluorides have been described (see Petersen, *J. pr. Chem.* 1889, [ii.] 40, 193, 271; Piccini and Giorgis, *Gazz. chim. ital.* 1888, 18, 186; Baker, *ibid.* 1878, 388; Costăchescu, *Ann. Sci. Univ. Jassy*, 1910, 6, 117).

Vanadium tetrachloride VCl_4 is formed by the action of excess of chlorine on the metal or the mononitride. It is prepared the vapour of vanadyl trichloride with over red-hot sugar charcoal, or by the action of chlorine on the impure metal obtained by Goldschmidt's method (Koppel, Goldmann and Kaufmann, *Zeitsch. anorg. Chem.* 1905, 45, 245), and is separated from admixed oxychloride by fractional distillation. It is readily obtained by the action of chlorine on finely powdered vanadium carbide. It is best prepared by heating the trichloride in a stream of chlorine (Ruff and Lickfett, *Ber.* 1911, 44, 506), or by passing chlorine over heated ferro-vanadium:



(Mertes, *J. Amer. Chem. Soc.* 1913, 35, 671). Heat of formation 165 ± 4 Cal.

It is a deep brown-red, viscous liquid which fumes in air. It boils at 154°, and when heated or exposed to light loses chlorine, forming the trichloride (*v.i.*). It has sp.gr. 1.8384 at 20° and V.D. 8.09 at 205°. Water decomposes it.

with formation of a blue solution of vanadyl chloride. It is soluble in carbon tetrachloride.

The pentachloride does not appear to exist.

Vanadium trichloride VCl_3 is obtained by the decomposition of the tetrachloride, by passing the vapour of the tetrachloride with hydrogen through a red-hot tube, or by heating the trisulphide in chlorine (Halberstadt, Ber. 1882, 15, 1619). It is prepared by passing first the vapour of carbon disulphide and then dry chlorine over heated vanadium pentoxide, or more easily by heating vanadyl trichloride or vanadium tetrachloride with sulphur (Ruff and Lickfett, l.c.). Hydrogen chloride reacts at $300^\circ\text{--}400^\circ$ with vanadium to give the trichloride (Meyer and Backe, Zeitsch. anorg. Chem. 1924, 135, 177). Heat of formation 187 ± 8 Cal.

The trichloride thus obtained forms beautiful purple tabular crystals, resembling chromium trichloride. Heated in air, it decomposes yielding the pentoxide. Heated in nitrogen it is decomposed into the tetrachloride and dichloride. When heated in hydrogen it does not volatilise, but is reduced to the dichloride. Its sp.gr. is 3.0, and it is extremely hygroscopic.

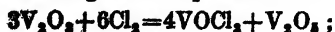
The hydrated salt $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ is obtained by evaporating *in vacuo* a solution of the trioxide in hydrochloric acid (Locke and Edwards, Amer. Chem. J. 1898, 20, 594), or by reducing electrolytically a solution of the pentoxide in hydrochloric acid and saturating the resulting solution with hydrogen chloride (Piccini and Brizzi, Zeitsch. anorg. Chem. 1899, 19, 394). It is a green crystalline powder, and when heated begins to decompose before all the water has been driven off.

Vanadium dichloride VCl_2 is prepared by reducing the trichloride, by heating to redness a mixture of the tetrachloride and hydrogen, or by heating the silicide VSi_2 in chlorine (Moissan and Holt, Compt. rend. 1902, 135, 78; Ruff and Lickfett, l.c.). Heat of formation 14 ± 74 Cal.

It forms deliquescent, apple-green hexagonal plates having a micaceous lustre; it dissolves in water to form a solution which bleaches strongly, and is a more powerful reducing agent even than chromous chloride (Piccini and Marino, Zeitsch. anorg. Chem. 1902, 32, 68).

When the solid is heated in hydrogen the pure metal is obtained (Roscoe).

Vanadyl trichloride VOCl_3 (vanadium oxytrichloride) is prepared (1) by the action of chlorine on the trioxide, some pentoxide being formed according to the equation



(2) by heating the pentoxide to a dull red heat in a stream of chlorine; (3) by heating a mixture of the pentoxide and carbon in a current of chlorine; (4) by passing dry hydrogen chloride over a mixture of vanadium and phosphorus pentoxides at 60° (Ephraim, Zeitsch. anorg. Chem. 1903, 35, 66); (5) by chlorinating a mixture of the pentoxide and sulphur; (6) by heating the trichloride in a current of oxygen. Heat of formation 200 ± 4 Cal.

The product is usually dark-coloured from the presence of the tetrachloride, and is best purified by distillation over metallic sodium in an atmosphere of carbon dioxide.

A solution in acetic acid may be obtained by the action of dry hydrogen chloride on a solution

of the pentoxide in glacial acetic acid (Koppel and Kaufmann, *ibid.* 1905, 45, 352).

Pure vanadyl trichloride is a lemon-yellow mobile liquid; b.p. 127.2° , sp.gr. 1.86534 at $0^\circ/4^\circ$ (Thorpe). In contact with moist air it evolves dense red fumes. Water decomposes it with formation of vanadic and hydrochloric acids, and with a large quantity of water it yields a yellow solution (see Agafonoff, J. Russ. Phys. Chem. Soc. 1903, 35, 649). Heated in a current of ammonia it yields the mononitride. At 70° it combines with ether yielding the compound $\text{VCl}_3(\text{OC}_2\text{H}_5)_2$, crystallising in red needles (Bedson, Chem. Soc. Trans. 1876, i, 309), and it forms a compound with pyridine.

Vanadium may be quantitatively volatilised as the trichloride by heating its compounds: current of carbon tetrachloride vapour (Jannasch and Harwood, J. pr. Chem. 1909, [ii.] 80, 127).

Vanadyl dichloride VOCl_2 , crystallising deliquescent green tablets, is formed when the oxytrichloride is heated with zinc at (Thorpe), or with hydrogen at a red heat. latter method of reduction yields vanadyl monochloride VOCl , a flocculent brown powder, insoluble in water, and divanadyl monochloride $\text{V}_2\text{O}_2\text{Cl}$, a yellow crystalline powder. Double compounds of VOCl_2 with the hydrochlorides of pyridine and quinoline, have been described (Koppel, Goldmann and Kaufmann, Zeitsch. anorg. Chem. 1905, 45, 345).

Divanadyl tetrachloride $\text{V}_2\text{O}_2\text{Cl}_4 \cdot 5\text{H}_2\text{O}$ is obtained as a brown, amorphous deliquescent mass by the evaporation of a solution of the pentoxide in hot concentrated hydrochloric acid. It dissolves in water to a blue solution which is turned brown by hydrochloric acid or alcohol, possibly owing to the formation of different hydrates (Crow, Chem. Soc. Trans. 1876, ii, 453).

Another oxychloride $\text{V}_2\text{O}_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ is obtained by similar methods as a dark-green deliquescent solid (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium tribromide VBr_3 is prepared by the action of dry bromine on the metal on the mononitride, on vanadium carbide V_4C_3 , or a mixture of the trioxide and carbon at a red heat. It is a deliquescent solid which is very unstable and loses bromine even at the ordinary temperature.

The hydrated bromide $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ is prepared in a similar manner to the corresponding chloride (*q.v.*).

Vanadyl tribromide VOBr_3 , prepared by passing bromine vapour over the heated trioxide, is a dark-red liquid, sp.gr. 2.967 at 0° , b.p. 130° under 100 mm. Heated to 180° it suddenly decomposes into free bromine and vanadyl dibromide VOBr_2 , a brownish-yellow powder. This on further heating yields VOBr , a violet powder, of sp.gr. 4.0, which is eventually decomposed into vanadium tribromide and vanadium trioxide (Ruff and Lickfett, Ber. 1911, 44, 2534).

Vanadium triiodide (hydrated) $\text{VI}_3 \cdot 6\text{H}_2\text{O}$ is prepared in the same manner as the corresponding bromide.

Divanadyl tetriodide $\text{V}_2\text{O}_2\text{I}_4 \cdot 6\text{H}_2\text{O}$ is obtained as a dark-coloured deliquescent solid by the action of hydriodic acid on vanadium pentoxide (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium monosulphide VS, obtained by heating the sesquisulphide in hydrogen, is a brown powder soluble in nitric acid.

Vanadium sesquisulphide (vanadium trisulphide) V_2S_3 , is prepared by heating the trioxide in a current of hydrogen sulphide or the pentoxide in the vapour of carbon disulphide. It is a greenish-black powder (Kay, Chem. Soc. Trans. 1880, 728; cf. Wedekind and Horst, Ber. 1912, 45, 262).

Vanadium pentasulphide V_2S_5 is obtained as a black powder by heating the trisulphide with sulphur. This sulphide is acidic and gives rise to a series of *thiovanadates*, which are best prepared by passing hydrogen sulphide into cooled solutions of the corresponding vanadates.

Vanadyl sulphite $6VO_2 \cdot 4SO_3 \cdot 9H_2O$ is obtained as a dark blue crystalline powder by reducing barium vanadate with sulphur dioxide. Gain has described a sulphite $4VO_2 \cdot 3SO_3 \cdot 10H_2O$, crystallising in silky blue needles (Compt. rend. 1906, 143, 823; see also *ibid.* 1907, 144, 1157).

Vanadous sulphate $VSO_4 \cdot 7H_2O$ is best prepared by acting with sulphur dioxide on a suspension of vanadium pentoxide in sulphuric acid and then reducing the solution electrolytically. On evaporation *in vacuo* the salt is obtained in reddish-violet monoclinic crystals which appear to be isomorphous with ferrous sulphate. The solution of the salt is a powerful reducing agent and bleaches strongly.

Vanadous sulphate forms a series of double salts with the alkali sulphates (see Piccini, Zeitsch. anorg. Chem. 1899, 19, 204; Piccini and Marino, *ibid.* 1902, 32, 55; Marino, *ibid.* 1906, 50, 49; Rutter, *ibid.* 1907, 52, 368; and Zeitsch. Elektrochem. 1906, 12, 230).

Vanadium sesquisulphate $V_2(SO_4)_3$, prepared by reducing a solution of vanadium pentoxide in sulphuric acid with magnesium, or by the electrolytic reduction of vanadyl sulphate, forms a green solution from which green crystals of the acid salt $V_2(SO_4)_3 \cdot H_2SO_4 \cdot 12H_2O$ separate out. By dissolving this salt in water, adding sulphuric acid and heating at 180° in a current of carbon dioxide, the sesquisulphate separates out as a yellow crystalline powder, insoluble in water (Stähler and Wirthwein, Ber. 1905, 38, 3978). Alkali vanadium sulphates of the form $MV(SO_4)_2$ have also been prepared (Rosenheim and Mong, Zeitsch. anorg. Chem. 1925, 148, 25; Chem Soc. Abstr. 1925, 128, i, 1411).

Several *vanadium alums* have been prepared.

Vanadyl sulphate $V_2O_5 \cdot (SO_4)_2$ is prepared (a) in the insoluble form by dissolving the dioxide VO_2 in sulphuric acid and heating the solution at 260° (Gerland, Ber. 1877, 10, 2109; Koppel and Behrendt, Zeitsch. anorg. Chem. 1903, 35, 154); (b) in the soluble form by heating the insoluble form with water at 130° , or by dissolving the dioxide in sulphuric acid, evaporating, and treating the residue with alcohol. Both forms are blue, and by crystallisation of the soluble form under different conditions hydrates with 13, 10, 7, 4, 3, and 2 molecules of water are obtained.

Strongly acid solutions deposit the acid sulphate $(V_2O_5)_2H_2(SO_4)_2$, crystallising with molecules of water. When heated it gradually loses water, yielding various lower hydrates, and, finally, at 190° , the *anhydrous salt*



which forms microscopic green tetragonal crystals, sparingly soluble in water (Koppel and Behrendt, *loc. cit.*; Gain, Compt. rend. 1906, 143, 1154).

Divanadyl trisulphate $(VO_2)_2(SO_4)_3$ is obtained in ruby-red octahedra by boiling the pentoxide with excess of sulphuric acid (see Ditte, *ibid.* 1886, 102, 77). Other basic salts, e.g. $(VO_2)_2O(SO_4)_2$ and $VO(OH)SO_4$, have been described (see Gerland, Ber. 1878, 11, 98).

Vanadium pyrophosphate $V_2(P_2O_5)_3 \cdot 30H_2O$ is formed as a flocculent green precipitate when an alkaline pyrophosphate solution is added to a solution of vanadium ammonium alum (Rosenheim and Triantaphyllides, Ber. 1915, 48, 582).

Vanadium mononitride VN may be obtained by the direct union of its elements or by heating ammonium metavanadate or the pentoxide to whiteness in a current of ammonia. It is a brown powder, oxidised to the blue oxide when heated in air.

Vanadium dinitride VN_2 is a black powder obtained by the action of ammonia on vanadyl trichloride.

Many phosphovanadic and arsenovanadic acids are known, giving rise to numerous derivatives (see Ditte, Compt. rend. 1886, 102, 757; Gibbs, Amer. Chem. J. 1886, 7, 118, 209; Friedheim, Ber. 1890, 23, 1530, 2600; Gain, Compt. rend. 1907, 144, 1271; Mawrow, Zeitsch. Chem. 1907, 55, 147). Blum has described a series of phosphovanadic molybdates (J. Amer. Chem. Soc. 1908, 30, 1858).

Vanadium boride VB is formed by heating a mixture of its constituents in the electric arc. It is a hard metallic looking substance. Stable towards alkalis and acids but readily decomposed by fused alkali hydroxide.

Vanadium carbide VC, obtained by heating the pentoxide with carbon in the electric furnace, forms hard crystals of sp.gr. 5.405; m.p. 3100° Abs.

Vanadium silicides. Two silicides are known: V_2Si , sp.gr. 5.48; and VS_i , sp.gr. 4.42. Both are obtained in the electric furnace from the oxide and silicon. They are hard, crystalline substances, having a metallic lustre (Moissan and Holt, Compt. rend. 1902, 135, 78, 493; Meyer and Backa, Chem. Soc. Abstr. 1924, ii, 558).

A vanadium aluminium silicide V_3 has been described by Manchot and Annalon, 1907, 357, 129).

For *vanadic esters and other organic vanadium compounds*, see Hall, Chem. Soc. Trans. 1887, 51, 751; Prandtl and Hess, Zeitsch. anorg. Chem. 1913, 82, 103; Barbieri, Atti R. Accad. Lincei, 1914, [v.] 23, ii, 408; Mertens and Fleck, J. Ind. Eng. Chem. 1915, 7, 1037.

Detection and estimation of vanadium.—Vanadium may be detected *qualitatively* by the behaviour of its compounds on oxidation and reduction, yellow or red solutions of vanadates yielding blue solutions of vanadyl salts on reduction with zinc and acid. Addition of ammonium chloride to a solution of a vanadate precipitates white ammonium metavanadate. The most delicate test known for vanadium consists in adding hydrogen peroxide and ether to a solution of a vanadate acidified with sulphuric acid; a yellow or red colour is produced in the aqueous layer (G. Werther, J. pr. Chem.

1903, [L.] 88, 195; Campagne, Chem. Zentr. 1904, [L.] 1167). Vanadium may also be detected spectroscopically (see Purvis, Trans. Camb. Soc. 1906, 20, 193; Pollok, Sci. Proc. Roy. Dubl. Soc. 1909, 11, 331).

For the arcspectrum of vanadium, see W. F. Meggers (J. Washington Acad. Sci. 1923, 13, 317-325).

Vanadium is usually estimated volumetrically by oxidation methods after other reducible metals have been eliminated. See art. ANALYSIS, and also Hartmann (Zeitsch. anal. Chem. 1925, 66, 16).

For the volumetric estimation of vanadium in steel, see A. T. Etheridge (Analyst, 1923, 48, 588).

Atomic weight.—The atomic weight of vanadium was estimated by Roscoe (Phil. Trans. 1868, 158, 1) to be 51.23; by Prandtl and Bleyer (Zeitsch. anorg. Chem. 1909, 65, 152; 1910, 67, 257) as 51.07; by McAdam (J. Amer. Chem. Soc. 1910, 32, 1603) as 50.96; and by Briscoe and Little (Chem. Soc. Trans. 1914, 105, 1310) as 50.95.

VANADIUM INK v. VANADIUM.

VANADIUM MICA v. ROSCOELITE.

VANILLA is the dried fermented pod of certain orchids, indigenous to Mexico, but also found in Java, Réunion, the Seychelles, Brazil, Peru, on the banks of the Orinoco, Parahyba and other rivers of South America.

The chief cultivated variety is *V. planifolia* (Andr.), which is grown on a considerable scale in Mexico, Réunion, Mauritius, Madagascar, the Seychelles, and in Java. The long fleshy stem of the plant clings by its aerial rootlets to trees, and bears a greenish-white flower. The fruit is a pulpy pod, about 6-12 ins. long and half an inch thick. In Mexico the plant is cultivated by planting cuttings at the feet of trees left in a clearing of the forest; these root in a few weeks and bear in the third year. In Réunion and in the Seychelles the plants are trained on trellis-work supported by trees, and are fertilised by hand. Care has to be taken to gather the pods at the proper time of maturity, as if over-ripe they split in drying, and if under-ripe they are deficient in flavour.

The fruit is usually gathered in the late autumn when full grown, but just before it ripens.

The curing of the fruits consists essentially of a slow process of drying in warm air, using either artificial or solar heat, but the details vary in different countries; thus in Mexico the gathered pods are allowed to lie in heaps until they begin to shrivel, after which they are heated, either by exposure to the sun or in ovens, when they gradually acquire a dark-brown colour. In Réunion and Madagascar the pods are immersed in boiling water for a few seconds, and then exposed to the sun for a few weeks in woollen cloths until they acquire the proper brown colour. As they become dry, they discharge a viscid liquid from the upper end, and are pressed from time to time to promote its flow. They are usually packed for the market in small bundles of fifty or one hundred in each. The yield of vanilla beans in Madagascar and dependencies for the season 1921-22 was 309,000 lbs., and in Réunion and Mauritius 121,000 and 2000 lb., respectively.

It has also been suggested to use

chloride in the drying of the beans (J. Soc. Chem. Ind. 1898, 180).

For literature on the culture and curing of the vanilla beans, v. *ibid.* 1893, 707; *ibid.* 1896, 679; *ibid.* 1900, 847; *ibid.* 1901, 1048; *ibid.* 1906, 1117; *ibid.* 1909, 1002; Fr. Pat. 367285, 1906.

Those who habitually handle vanilla beans are often subjected to a cutaneous affection in the form of an eruption on the hands, face, or neck, which causes intense irritation; this is probably due to the oily juice which exudes from the beans. To avoid the affection, good ventilation of the factories and thorough washing of the hands are recommended (Claverie, J. Soc. Chem. Ind. 1908, 1082).

Commercial vanilla beans are almost 15-20 cm. long and 6-9 mm. thick. They are of a flattened cylindrical shape, tapering towards each end, wrinkled and flexible. The varieties, chiefly the Mexican, are the largest; they are very dark, glossy, and frost or (i.e. become covered with white crystals) very quickly. The inferior varieties are shorter, lighter in colour, and do not frost much.

Vanillons are the cured fruits of uncultivated vanilla plants; they are usually of poor quality. The unripe beans are said to contain coniferin and two enzymes, one of which converts coniferin into coniferyl alcohol and glucose, and the other oxidises the former to vanillin (Lecomte, Compt. rend. 1901, 133, 745).

Best Mexican vanilla beans contain 1.60-1.86 p.c. vanillin, Bourbon 1.91-2.90, Java 2.75, German East African 2.16, Ceylon 1.48, Tahiti 1.55-2.02, but the flavour of vanilla does not depend merely on the quantity of vanillin it contains (Busse, Zeitsch. Nahr. Genussm. 1899, 2, 519). The best qualities of vanilla beans contain less actual vanillin than the cheaper varieties.

In addition to vanillin, the beans also contain vanillic acid $C_8H_7(OH)(OCH_3)CO_2H$, resins, fat, sugar, and 4-5 p.c. ash (Winton and Silverman, J. Soc. Chem. Ind. 1902, 1300; U.S. Pat. 931805; *ibid.* 1909, 1062; Gautier and Kling, Ann. Falsif. 1910, 3, 200). Anisyl alcohol and anisaldehyde have also been detected (Walbaum, Chem. Zentr. 1909, ii. 2181).

When the green vanilla pods are exposed to ultra-violet rays, they emit a smell of vanillin, the process being accelerated by a rise in temperature and by previous immersion in dilute manganous chloride (Pougnet, Compt. rend. 1911, 152, 1184).

Tincture or essence of vanilla is formed by extracting the ground or cut up vanilla (10 parts) with a mixture of alcohol and water, and mixing the extract with 20 parts of refined sugar, the whole being made up to 100 parts.

The extracts obtained from several varieties of vanilla and tonka beans, using isopropyl alcohol, ether, acetone, and carbon tetrachloride, when compared with that obtained with ethyl alcohol showed that the alcoholic solvents are much superior as regards quality of extract, carbon tetrachloride giving the poorest extract. It is possible, however, that a preliminary extraction with ether or carbon tetrachloride, followed by extraction with a dilute solution of alcohol, may give satisfactory extracts (J. W. Sale, J. Ind. Eng. Chem. 1923, 15, 758-759; J. Soc. Chem. Ind. 1923, 43, 367 A-368 A).

The chief adulterant in vanilla extracts is either artificial or from tonka beans; imitation extracts may be obtained from 3 parts of vanilla, and 1 part of tonka beans, but most commercial imitations contain no vanilla, and are made up of artificial vanilla and coumarin and extract of tonka beans, the whole being coloured with caramel (Winton and Silverman, *l.c.*). In the preparation of inferior extracts weak alcohol and alkali are employed; these can be distinguished from good extracts by shaking a few c.c. with 3 volumes of water, when, if no alkali has been employed, a flocculent red precipitate will be formed. With hydrochloric acid a good extract should give only a slight turbidity (Hess, *J. Amer. Chem. Soc.* 1899, 21, 719).

Vanilla in the form of its tincture, is employed for flavouring chocolate and confectionery. It is also largely used in the manufacture of liqueurs and perfumes. See also Vanille, Vanilline, Vanille-Extraiten. W. L. Utermark, Amsterdam: Kolonial Instituut, 1922.

VANILLIN (4-hydroxy-3-methoxybenzaldehyde $C_8H_8(OH)(CHO)(OCH_3)$) is contained in vanilla beans (*v. VANILLA*); in *Habenaria nigra* (R. Br.) (Lippmann, *Ber.* 1894, 27, 3409); in dahlia tubers (*ibid.* 1906, 39, 4147); in the woody parts of plants (*ibid.* 1904, 37, 4521); in the fruit and roots of *Avena sativa* (L.) (Rawton, *Compt. rend.* 1897, 125, 797). It also occurs in many other plants, in resins, balsams, and other substances (Campani and Grimaldi, *Bull. Soc. chim.* 1890, [iii.] 3, 458; Weld, Tollens and Lindsey, *Ber.* 1890, 23, 2990; Thomas, *Arch. Pharm.* 1899, 237, 271; Knittl, *ibid.* 256; Itallie, *ibid.* 1901, 239, 506). Vanillin may be obtained from vanilla pods by disintegrating the latter with sand and extracting with ether or a mixture of ether and alcohol (Tiemann and Haarmann, *Ber.* 1876, 9, 1287).

Vanillin may be obtained artificially by oxidising coniferin or coniferyl alcohol with chromic acid; by oxidising eugenol or, better, isoeugenol with air (Fr. Pat. 316526, 1902; Eng. Pat. 4909, 1902; *J. Soc. Chem. Ind.* 1902, 722; *ibid.* 1903, 439). According to A. Lowy and Catherine M. Moore (*Am. Electrochem. Soc. Trans.* 1922, 42, 273), contrary to the claim of D. R. P. 92007 (1897), no appreciable proportion of vanillin could be obtained by the electrolytic oxidation of isoeugenol. The latter is highly susceptible to oxidation to a wide variety of possible products and vanillin itself is readily oxidised electrolytically (*Sci. Abstr.* 1924, 27, 575). In the oxidation of the sodium salts of isoeugenol, or of acetyl isoeugenol in presence of aromatic amino carboxylic acids, extracting acetylvanillin from the products of the reaction, converting this into the bisulphite compound and treating successively with acid and sodium hydroxide (Sievers and Givaudan & Co., Swiss Pat. 89063); with ozone or ozonised air (Trillat, *Compt. rend.* 1901, 133, 822; *Bull. Soc. chim.* 1903, 29, 45; Fr. Pat. 326775, 421784, 1909; U.S. Pat. 829300, 1906; *J. Soc. Chem. Ind.* 1903, 819); with peroxides (Eng. Pat. 11952, 1894; 14923, 1896; *J. Soc. Chem. Ind.* 1895, 806; *ibid.* 1897, 633); electrolytically (Eng. Pat. 1624, 1895; *ibid.* 1896, 48, 323).

Ozonised air on a commercial scale have not been uniformly successful, owing to the formation of a resin as a result of the reaction being a very rapid one. In the new process the plant consists of a series of four towers partly filled with splash plates or balls. The first two contain a mixture of isoeugenol and aqueous sodium bisulphite, while the third and fourth are smaller and contain sodium carbonate and hydroxide respectively. Ozonised air is drawn through the towers and the vanillin dissolves in the bisulphite solution as formed. After 8 hours the aqueous layer is run off, the bisulphite compound decomposed with the requisite quantity of sulphuric acid (determined by titration of test sample), rendered slightly alkaline with sodium carbonate, and extracted with benzene. The crude vanillin recovered from the benzene solution is crystallised three times from water, the last crystallisation being from water completely free from iron. The power required for ozonisation is given as $\frac{1}{2}$ kva. per oz. of vanillin (B. G. Wood, *Met. & Chem. Eng.* 1923, 28, 806; *J. Soc. Chem. Ind.* 1923, 42, 626A).

A 95 p.c. yield and a much purer product is said to be obtained by oxidising eugenol, isoeugenol, coniferin, or coniferyl alcohol, simultaneously with air and ultra violet rays at 50°–60° (D. R. P. 224071; *J. Soc. Chem. Ind.* 1910, 1036).

The conversion of isoeugenol to vanillin by ozonised air has been studied by Briner, Patry, and E. De Luserna (*Helv. Chim. Acta*, 1924, 7, 62), by conducting a current of ozonised air at varying concentrations of ozone (5 p.c. to 19 p.c.) into a solution of isoeugenol in carbon tetrachloride, at temperatures from 15°–150°. The highest oxidation efficiency obtained, in terms of ozone consumed, was 20 p.c. at the lowest temperature. At higher temperatures the efficiency falls off rapidly and the quantity of resinous by-product formed increases (*Chem. Soc. Abstr.* 1924, 126, i, 290).

Vanillin may also be prepared by dissolving 14.2 kilos protocatechuic aldehyde in concentrated sodium carbonate solution, and mixing it with 12.6 kilos of dimethyl sulphate. The whole is heated on the water-bath, acidified, and extracted with ether. The latter is evaporated, and the vanillin extracted from the residue with chloroform (*J. Soc. Chem. Ind.* 1902, 274; see also *ibid.* 1897, 633; *ibid.* 1894, 1218; *ibid.* 1895, 1061).

Pure vanillin may be synthesised by the following method, the yield being 70–80 p.c. of the theoretical: 1 gm. molecule of a methyl or ethyl ester of mesoxalic acid or of any α -diketonic acid (or of the free acid) is added to a solution of 250 grms. of zinc chloride in 500 grms. of glacial acetic acid. The whole is kept at the ordinary temperature for 15 hours, after which it is heated at 50° for some hours, and then diluted with water and shaken with ether. The ethereal extract is washed with dilute aqueous sodium carbonate, distilled with steam to remove guaiacol (if present) and oxidised with copper chloride or acetate, vanilloylcarboxylic acid being formed. The latter, when heated with an equal weight of dimethyl-*p*-toluidine at 170°, yields vanillin, which is extracted from the acidified mixture.

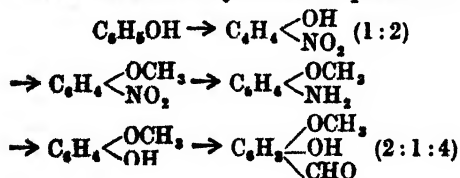
and. 1909, 140, 928). Vanillin may also be synthesised by treating guaiacol with hydrocyanic acid, hydrochloric acid, and zinc chloride in the presence of infusorial earth (D. R. P. 189037; Chem. Zentr. 1908, i, 73).

A nearly theoretical yield of vanillin sodium hydrogen sulphite is obtained when dry hydrogen is passed through a boiling mixture of vanilloyl chloride-*p*-toluenesulphonic ester (154 pts.), dry xylene (1000 pts.), and palladised barium sulphate (5 p.c., 30 pts.) until evolution of hydrogen chloride ceases (Eng. Pat. 131161).

Vanillin has also been prepared by other methods.

The process of the Ozone Vanillin Co. (U.S. Pat. 829100) consists in passing ozonised air into a mixture of isoeugenol and sodium bisulphite solution of 30°Bé. The vanillin produced unites with the bisulphite from which it is easily separated. The production in the United States in 1919 was 134,700 lbs., valued at \$1,365,900 (Census of Industrial Products). Gattefossé and Morel describe a method of producing vanillin from phenol which consists in nitrating the phenol, separating the ortho- and para-derivatives by steam distillation, methylating the ortho-nitrophenol by dimethyl sulphate in presence of caustic soda to produce *o*-nitroanisole, which is then reduced by zinc powder in presence of calcium chloride to *o*-aminoanisole. This is converted by diazotisation into guaiacol, which by treatment with formaldehyde and hydroxylaminobenzenesulphonic acid yields vanillin.

These reactions may be thus represented :



Literature.—Tiemann, Ber. 1891, 24, 2877; Augier and Boissien, Bull. Soc. chim. 1895, 13, 519; Bouveault, *ibid.* 1898, [iii.] 19, 75; Verley, *ibid.* 1901, [iii.] 25, 48; J. Soc. Chem. Ind. 1896, 556, 740; *ibid.* 1902, 68; *ibid.* 1908, 644; Stok, Ber. 1904, 37, 4149; Frdl. 1877-87, i, 563-590; 1890-94, iii, 894-900; 1894-97, iv, 1273-1291; 1897-1900, v, 101, 110; 1902-04, vii, 755; 1905-07, viii, 1280, 1281; 1907-10, ix, 162, 1130, 1166.

Vanillin forms white needles having a strong characteristic taste and smell, m.p. 80°-81°, b.p. 285° (without decomposition in a stream of carbon dioxide) or 170°/15 mm. It is soluble in 90-100 parts of water at 14°, and in 20 parts at 75°-80°; it is readily soluble in ether, alcohol, and chloroform. Curves of solubility in aqueous alcohol and aqueous glycerol are given by Mange and Ehler (J. Ind. Eng. Chem. 1924, 16, 1258). The aqueous solution is acid, and gives a blue-violet colour with ferric chloride. When treated with ferrous sulphate and bromine water, vanillin is coloured bluish-green, then yellow (Pharm. J. 1897, 58, 167). Vanillin in hydrochloric acid gives characteristic colour reactions with phenols, ketones, and other substances; thus with acetone and its homologues a rose colour is formed, which becomes green on warming (Rosenthaler, Zeitsch. anal.

Chem. 1905, 44, 292). A nitric acid solution of vanillin on standing yields a small quantity of hydrogen cyanide (Jorissen, J. Soc. Chem. Ind. 1910, 1036).

When oxidised with ferric chloride, nitric acid, or with fungus extract, or with gum arabic solution, vanillin forms *dehydrovanillin*.



white needles, m.p. 303°-304° (Tiemann, Ber. 1885, 18, 3493; v. Lerat, Bull. Soc. chim. 1904, [iii.] 31, 270; Bourquelot and Marchadier, *ibid.* 1248; Bentley, *ibid.* 1900, [iii.] 24, 942).

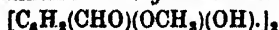
Vanillin may be estimated by converting it into its hydrazone by treatment with a hydrazide (Hanuš, Zeitsch. Nahr. Genussm. 1900, 531, 657; *ibid.* 1905, 10, 585); or by converting it into its bisulphite derivative, decomposing the latter with sulphuric acid, removing the sulphur dioxide with a stream of carbon dioxide, extracting the vanillin with ether; the ether is evaporated and the residue weighed (Busse, *ibid.* 1899, 2, 519; Doherty, J. Roy. Soc. N.S.W. 1914, 47, 157). For other methods, see J. Soc. Chem. Ind. 1893, 718; *ibid.* 1903, 514. Or it may be estimated colorimetrically by adding a phosphotungstic phosphormolybdic acid solution to an acid solution of vanillin, and comparing the intensity of the blue colour produced with that formed under like conditions by a standard solution of vanillin. For details, see Folin and Denis, J. Ind. Eng. Chem. 1912, 4, 670. Or 1 c.c. of the vanilla essence is extracted with ether, the extract evaporated over the water-bath, and the aqueous solution filtered and diluted to 50 c.c. in a Nessler glass. Ten drops of freshly prepared bromine water and ten drops of 10 p.c. ferrous sulphate are then added, and the green colour matched against a 0.2 p.c. solution of pure vanillin. Methods for determining vanillin are critically reviewed by Radcliffe and Sharples (Perf. Ess. Oil Rec. 1924, 15, 396, 437; 1925, 16, 20, 51, 87, 156, 197, 271, 353, 387).

A refractometric determination of vanillin in vanilla sugar may be made by shaking 3 grms. of the sugar with 3 c.c. of ether for 1 minute, and allowing to settle. The butyro-refractometer readings of the ether used and that of the ethereal solution of vanillin are then taken. The difference multiplied by 0.4 gives the percentage of vanillin in the sugar. The temperature of the prism should be the same for both readings.

A volumetric method of determining vanillin depends on the formation of a hydro-derivative by the interaction of vanillin and *p*-toluidine dissolved in 80 p.c. alcohol. This compound contains the original hydroxyl group of the vanillin, and is therefore soluble in alkali, giving a yellow solution. A measured excess of standard alkali is added, followed by a comparatively large volume of cold water. The addition of standard acid first neutralises the excess of alkali and then liberates the anhydro-derivative from its sodium salt. The first drop of acid which liberates the derivative produces yellow turbidity, the free derivative being practically insoluble in the liquid phase. The volume of alkali required for the titration of the vanillin is thus obtained. Accurate results are obtained when benzoic acid is present as an adulterant in quantities up to 10 p.c. but

with higher percentages of acid it is advisable to use a gravimetric method. No sample of first-class vanillin contains more than 1 p.c. of acid (as vanillic acid), though some of the samples had been kept in cardboard containers for 10 years. The gravimetric method suggested comprises the precipitation of vanillin as the semi-carbazone from dilute acetic acid solution. The precipitate is easy to wash and filter and may be dried in a water oven for 6-8 hours, without losing a weighable quantity by volatilisation. The vanillin may be separated from impurities, such as piperonal, by dissolving the semi-carbazone in ammonia solution. Vanillin semi-carbazone, by virtue of its hydroxyl group, forms a soluble ammonium salt, giving a yellow solution, whilst piperonal semi-carbazone is insoluble. Test analyses in which piperonal was added to vanillin gave results agreeing with the actual percentage to within 1 part in 450. The oxidation of samples of purified vanillin exposed to air, moisture, and light was practically negligible. With vanillin in solution, however, oxidation proceeds much more rapidly, while solutions of vanillin in alkali behave similarly to alkaline pyrogallol solution. The following corrected melting-points are given: vanillin semi-carbazone, 232°C.; piperonal semi-carbazone, 218°C.; vanillin-*p*-nitrophenylhydrazones, 148°C. (S. B. Phillips, *Analyst*, 1923, 48, 367-373; *J. Soc. Chem. Ind.* 1923, 42, 948 A).

Oxidising agents, in particular ferric chloride, convert vanillin into *dehydrodivanillin*



m.p. 302°-305°C., and the precipitation of the latter can be observed from aqueous solutions containing as little as 1 in 10,000 of vanillin. 20 c.c. of the solution to be tested is heated in a bath containing a solution of calcium chloride at 130°-140°C., and two fractions of 10 c.c. of distillate are collected. Further quantities of 10 c.c. of water are added to the residue and distilled off, until nine or ten such fractions have been collected. These fractions are tested with ferric chloride, it being easily possible to detect and characterise 0.01 grm. of vanillin in the 20 c.c. of sample taken (*cf.* *Chem. Soc. Abstr.* 1923, ii. 887; H. Herissey and P. Delauney, *J. Pharm. Chim.* 1923, 28, 257-262; *J. Soc. Chem. Ind.* 1923, 42, 1197 A).

For other methods, see Fellenberg, *Chem. Zentr.* 1916, ii. 391; Dox and Plaisance, *Amer. J. Pharm.* 1916, 88, 481; Estes, *J. Ind. Eng. Chem.* 1917, 9, 142.

Vanillin is frequently adulterated with coumarin, acetanilide, and with acetyl isoeugenol (Heas and Prescott, *J. Amer. Chem. Soc.* 1899, 21, 256; see also *J. Soc. Chem. Ind.* 1898, 1976; *ibid.* 1899, 604).

According to Winton and Lott (*ibid.* 1910, 1268) genuine vanillin may be distinguished from imitations by determining the lead number which, for the former, should lie between 0.29 and 0.34.

DERIVATIVES OF VANILLIN.

Vanillin forms salts with zinc, lead, sodium, and manganous of the type $(C_6H_4O_3)_2M'$ (Tiemann and Haarmann, *Ber.* 1874, 7, 614).

Bromovanillin $C_6H_4Br(OMe)(CHO)(OH)$, m.p. 187°-188°, crystalline yellow leaflets (Tiemann

and Haarmann, *l.c.*); the corresponding iodo compound has m.p. 174° (Bentley, *Amer. Chem. J.* 1900, 24, 172).

2-Nitrovanillin has m.p. 137°, 5-nitrovanillin, m.p. 176° (Bentley, *l.c.*; Paschorr and Sumuleanu, *Ber.* 1899, 32, 3405).

Vanillin forms an *aldoxime*, m.p. 121°-122° (Decker and Klausner, *ibid.* 1904, 37, 520); a *phenylhydrazone*, m.p. 105° (Tiemann and Kees, *ibid.* 1885, 18, 1662); an *azine*, m.p. 174°-176° (Knöpfer, *Monatsh.* 1909, 30, 29); an *acetyl* derivative, m.p. 77° (Paschorr and Sumuleanu, *l.c.*); a *benzoyl* derivative, m.p. 75° (Wörner, *Ber.* 1896, 29, 143); also a *di-* and *trithio* derivative, in which the oxygen of the aldehyde group is replaced by sulphur, m.p. 129°-130°, 235°-237°, respectively (Manchot and Zahn, *Annalen*, 1905, 345, 320; Wörner, *l.c.*). *Vanillinacetic acid* $CHO \cdot C_6H_4(OMe)O \cdot CH_2 \cdot CO_2H$ has m.p. 188° (Gassmann and Krafft, *Ber.* 1895, 28, 1871).

Vanillin-*p*-phenetidine (*eupyrin*)



is formed by the interaction of vanillin and *p*-phenetidine at 140°; m.p. 97°. It is said to have hypnotic and antineuralgic properties (*D. R. P.* 91171, 96342; *Frdl.* 1894-97, iv. 1183, 1185).

Benzaldivanillin forms microscopic needles, m.p. 221.5°-222.5° (Rogoff, *Ber.* 1901, 34, 3881; *ibid.* 1902, 35, 1961).

Methyl ether of vanillin (veratraldehyde) $(CH_3O)_2C_6H_3CHO$ may be obtained by the methylation of vanillin, and by other methods. It is best to dissolve 1 mol. of vanillin in less than the equivalent quantity of 10 p.c. methyl sulphate on the water-bath, 1 mol. of potash in solution is then added in drops. When the reaction is over the solution is made slightly alkaline when it separates into two layers. The upper layer is extracted with ether, and on distilling off the latter, the pure aldehyde is obtained (Decker and Koch, *Ber.* 1907, 40, 4794). It has m.p. 47° (Juliusberg, *ibid.* 119), and possesses hypnotic properties. The corresponding *ethyl* derivative $CH_3O \cdot C_6H_4(OC_2H_5)CHO$ has m.p. 64°-65° (Tiemann, *Ber.* 1875, 8, 1120). Homologues of vanillin have also been prepared (*Eng. Pat.* 10112, 1895; *J. Soc. Chem. Ind.* 1895, 595).

o-Vanillin (*m*-methoxysalicylic aldehyde) $(CHO : OH : OMe = 1 : 2 : 3)$ is, in the pure state, a solid which crystallises from water in pale yellow needles, m.p. 45.5°, b.p. 265°-266°. It dyes wool and silk from an acid bath a golden or lighter yellow, but the shades are not fast to soap (Noelting, *Bull. Soc. Ind. Mulhouse*, 1909, 79, 401; *J. Pharm. chim.* 1908, 28, 173).

It gives a phenyl-hydrazone, m.p. 139°-131° and a large number of other derivatives. *Cf.* Perkin and Robinson, *Chem. Soc. Trans.* 1914, 105, 2376; Mosimann and Tambor, *Ber.* 1916, 49, 1261.

The root of a species of *Chlorocodon* of Uganda, where it is termed *Murundo*, contains an odorous constituent $C_6H_4O_3 \cdot OMe$, m.p. 41°-42°, b.p. 257°-258°, which forms thin, colourless plates, is isomeric with vanillin, and yields an *azine*, m.p. 138°, and a phenyl-hydrazone, m.p. 137°-138° (Goulding and Pelly, *Chem. Soc. Proc.* 1908, 62).

VANTHOFFITE. The presence of this double salt, $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$, in the abraum-salts at Wilhelmshall near Stassfurt, was detected by plotting on curves the results of several analyses of material from an apparently homogeneous specimen, which was found to consist of a mixture of vanthoffite, loewite, apthitalite, halite, &c. Such intimate intermixtures of minerals of different kinds are really of the nature of rocks, and they must be studied by the methods of petrography; namely, by the examination of thin sections in the polarising microscope, and by separating the individual minerals with the help of heavy liquids (e.g. mixtures of methylene iodide and benzene or tetrabromoethane and toluene). Similar mixtures containing vanthoffite have also been found in the Berlepsch mine at Stassfurt. The mineral has also been observed as nodules embedded, with loewite, in bloedite at Hall in the Tyrol. It is colourless with a vitreous lustre, and a flat-conchoidal fracture; sp.gr. 2.7; H. 3½. The mineral is named after J. H. van't Hoff, who, when its occurrence in the salt deposits was discovered, succeeded in preparing it artificially. When crystals of bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) are heated in contact with their mother-liquid to above 70° they are transformed first into loewite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) and then into the anhydrous salt $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$. L. J. S.

VAPOUR DENSITY *v.* SPECIFIC GRAVITY.

VAREC. *Kelp v.* IODINE.

VARIOLARIN *v.* LICHENS.

VARISCITE. One of the many minerals consisting of hydrated aluminum phosphate, here with the formula $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$. It forms concretionary and compact nodular masses, sometimes with a minutely crystallised (orthorhombic) surface. The colour is bright apple-green (due to chromium); sp.gr. 2.5-2.6; H. 4-5. It was first found in 1837 in Saxon Voigland (the ancient Variscia), and within recent years has been mined in considerable quantities (3½ tons in 1909, and 2½ tons in 1910) at several places in Utah and Nevada. It is used as a gem-stone, taking the place of green turquoise (D. B. Sterrett, Min. Res. U.S. Geol. Survey, Annual Reports for 1910 and earlier). L. J. S.

VARNISH (Syn. *Vernis*, Fr.; *Lac*, *Firniss*, Ger.). A varnish may be described as a homogeneous fluid, which, when applied by any suitable means in a thin layer over the surface of any object, dries either by the evaporation of the volatile solvent, or by the combined evaporation of the volatile solvent and the oxidation of the component oils and resins to a more or less impervious elastic film of varying degrees of hardness and of generally good weather-resisting properties.

Varnishes, in the drying of which heat is applied in a well-ventilated compartment to expel the solvent and to complete the oxidation so that the film is uniform like glass, are termed stoving varnishes. The simplest form of varnish is the spirit varnish, which is merely a solution of a more or less elastic solid in a volatile solvent. Spirit varnishes dry the most rapidly, but are liable to be brittle and eventually to crack and peel off unless plasticised by the addition of suitable soluble elastic substances. Oil varnishes are, to a large extent,

free from this defect;

contain, binding and softening the resin, and although they take longer to dry, they are generally more lustrous and durable. When varnish is used as the vehicle or medium for the application of a pigment or a pitch to an object, an enamel is produced. Such enamels dry with a gloss, and save labour by combining painting and varnishing in one operation. The solvents employed in making the various varnishes are chiefly turpentine, naphtha and petroleum spirit, kerosene and white spirit, methylated spirit and, recently, higher aliphatic alcohols, e.g. isopropyl, butyl and amyl alcohols. Linseed oil is the drying oil in most general use, but tung oil (China wood oil) is coming more into demand. Walnut and poppy oils are artists' media. The solids, i.e. resins, &c., mostly employed in oil varnish making are: 1. Copal, incl. Kauri, Manila and Congo; 2. Rosin, incl. its glyceryl ester; 3. Asphaltum, including the various pitches. Recently synthetic resins have been tried in the form of coumarone resins and phenol formaldehyde resins incorporated with rosin (Albertols). The resins are solid bodies, generally more or less coloured, amorphous usually with a vitreous lustre, which melt as a rule at comparatively low temperatures often with decomposition. They are insoluble in water, but partially or wholly soluble in a number of solvents, e.g. alcohol, ether, acetone, carbon tetrachloride, benzene, light petroleum, turpentine, &c. In practice the varnish maker is more concerned with the properties of the varnish film than of the original resin, and although, generally speaking, the hardest resin gives the hardest film, the properties of the film are greatly affected by the other ingredients of the varnish and the skill with which they are incorporated.

Resins.—The resins have been classified into hard, medium and soft. Among the hard resins appear Zanzibar and Amber. The medium resins include Kauri, West African and Gold Coast copals. Among the soft resins are Manila (East Indian) and South American resins. Among the spirit varnish resins shellac, dammar, sandarac are hard resins, whereas mastic and rosin are medium, and elemi, oleo-resin turpentine and Burgundy pitch are soft. The solubility of a resin may be said to be in inverse proportion to its hardness. The hard resins and semi-hard resins are but very slightly soluble in their original condition at the ordinary temperature, but they are easily dissolved by turpentine, linseed oil, and other solvents, by previously heating them in such a manner as to cause them to lose by destructive distillation 10-25 p.c.

to the resin dealt with. This partial destructive distillation of the harder resins is necessary before they will dissolve in oil or other solvents. The temperature to which the resins must be heated before they become soluble, is higher in the case of the hard resins than of the soft resins.

Oil Varnishes.—The first process in preparing an oil varnish is selection of the gum; the pieces are sorted out by hand and graded according to their colour and general soundness, and so the gum gives the hardening properties to the varnish and is the most expensive constituent, great

case is encountered in its solution. The selected gum is melted or 'run,' whereby depolymerisation occurs, and then caused to unite with the oil. The gum is heated in a pot of copper, or of iron with a copper bottom, or of aluminium over a rapid fire, until it is perfectly liquid at about 260°-300°C.; a hood or lid is placed over the pot, which is connected to large flues in which the varnish 'fumes' are condensed. The drying oil, specially chosen for varnish making and clarified, is heated and added cautiously at the right moment to the 'run' gum, the whole being kept well stirred, and the heating continued until the mixture is perfectly clear. The driers are added in several ways, either in the form of a lead and manganese soap dissolved in oil or as solid lead and manganese compounds, and the mixture boiled with stirring until the driers are incorporated. The pot is then removed from the fire, and when sufficiently cooled, turpentine or white spirit is added gradually, stirring all the while until the whole is thoroughly mixed. Much inflammable vapour is evolved during these operations, and it is necessary that the varnish house should be so constructed that the vapours do not come in contact with fire.

After the addition of the thinners the varnish is strained into a tank, and allowed to stand until clear for use. The time required for this varies, and as all varnishes improve by age, the longer they are tanked the better. In some cases the driers, consisting of litharge and dry white copperas (cryst. ZnSO_4), are churned at the ordinary temperature with the varnish and the excess of undissolved solids is allowed to settle in tanks. Old varnishes produce surfaces of much greater lustre than new ones. The good qualities of a varnish largely depend on the efficient mixing of the gum and oil; if these are thoroughly incorporated the varnish will be free from spots and blemishes on its surface, while, if well boiled, a varnish is said to flow more freely and to dry more rapidly. Excessive boiling, however, causes the varnish to stouten and thus to require more thinners to bring it to a working consistency, and the resulting fluid, being poorer in its non-volatile constituents, yields a thinner and less lustrous coat. No strict rule on this point can be given, as some oils and gums stouten more rapidly than others, and the final result has to be manipulated according to circumstances.

The drying of oil varnishes varies considerably according to composition, and within certain limits to the proportion of metallic driers present as well as to the objects to which they have to be applied; thus a gold size may dry in a few minutes, while body or coach varnishes require 12-24 hours, and even then should be allowed 2 or 3 days to harden.

Of recent years many attempts have been made to prepare oil varnishes without previous fusion of the gum. Only one has led to successful results, viz. that in which naphthalene under pressure is employed. By this process, which was patented in 1894, the copals are dissolved in naphthalene by heating under pressure to 250°-300°C.; linseed oil or other drying oil is added to the solution and the naphthalene is distilled off. The varnishes obtained by this process are satisfactory and of

good hardness. The objections to the autoclave processes are the capital outlay and the length of time taken in rendering the gum soluble. Other special solvents for copals have been suggested, e.g. linseed oil acids, amyl alcohol, terpineol, &c., but they have met with no success. The effect of the solvent materials on the finished product is deleterious, unless they can be completely removed, which is not feasible. The weight of the gum 'run' in one operation has been steadily on the increase, and nowadays the old charge of $\frac{1}{2}$ cwt. is increased to over 1 cwt. and the whole operation can be performed with complete safety, if proper precautions are taken.

The number of varieties of oil varnishes is large; as many as 200 may be listed, each having its own special use. There is no general classification, although long and short oil varnishes, based on the proportion of resin to oil, is the most acceptable. The most important classes are, coachbuilders' varnishes, including those for carriages, motor cars and railway work; boat, marine and spar varnishes; decorators' varnishes for inside and outside work. Other classes include furniture varnishes, clear and black stoving varnishes and black japans containing pitch. Coachbuilders' varnishes (body and carriage varnishes) must give films which are dust dry within 12 hours and do not crack nor show 'bloom'; moreover, they will retain their lustre for several years, if washed from time to time and occasionally polished with wax. Undercoating varnishes, harder than finishing varnishes, must be sufficiently dry in 10-15 hours to admit of being lightly rubbed down previous to the application of an elastic finishing coat. A film of a blooming varnish shows after a time an opacity which may become permanent. Such surfaces have been found to be strongly polar. Blooming is not confined to oil varnish films. The general formulae of coachbuilders' varnishes may be summarised as follows:

	Resin	Oil	Thianox
Finishing body varnish	60 lbs.	15 gals.	15 gals.
Elastic coach varnish	60 "	12 "	12 "
Hard elastic varnish	60 "	10 "	12 "
Quick hard drying varnish	60 "	8 "	12 "

Undercoating varnishes show bloom when not covered by an elastic finish. Boat varnishes should give a water-resisting film and should not become opaque on immersion in water; these, as well as seaplane varnishes, generally contain China wood oil. Whilst a film of linseed oil never attains a degree of hardness to withstand abrasion, China wood oil gives a harder and more weather-resisting coating. Owing to the rapid gelatinisation of wood oil on heating, copals are largely replaced by rosin and rosin glyceride. Decorators' varnishes for inside and outside work differ slightly in the proportions of gum and oil; the inside varnishes must have good flow, be free from bloom, but great weather-resisting power is not required; for outside work, varnishes on the lines of the carriage varieties are employed. The undercoating varnishes are termed *stoving* or *rubbing*

varnishes, drying rapidly so that in 12 hours they may be rubbed down to a flat surface upon which the finishing variety may be applied. The proportions of gum to oil may be 1:1.25. They are liable to bloom and not durable to weathering unless protected by an elastic finishing coat. Other varieties of decorators' varnishes include: church oak, drying with a hard film, not softening appreciably up to 40°C., suitable for church seats; floor varnish, softer than church oak, with a gum and oil proportion of 1:1.4 or 1:1.67; front door varnish, which must combine elasticity with hardness and lustre; furniture varnish containing rosin: oil=1:1.10, in which rosin is often introduced, and thin coats are applied, rubbing down between each coat until the requisite brilliance is obtained.

Black Japans and Bituminous Varnishes occupy a special position, since they have for their characteristic ingredients a bitumen or asphalt. Both gum resin and oil may or may not be present, as the asphaltic substances differ far more widely in their hardness and elasticity than the various gum resins, and their properties can be modified with greater facility. The most important bituminous varnish in the higher branches of the decorative craft is known as black japan. The term "japan," as applied to substances which promote the drying of a paint film, denotes generally liquids which dry to a hard film possessing considerable coherence. Japan driers give a harder film than the oleo-driers, which are elastic and of a drying-oil character, whilst japan driers are of the nature of a resin varnish containing resin, or rosin with lead and manganese. The specific purpose of black japan is in the production of a brownish-black ground of special translucence or depth, thus differing from pigmented preparations (black enamels), which appear to reflect their depth of colour from the surface only. The main use of black japan in the coach-building trade is for panel work. The varnish is obtained by amalgamating specially treated oil of great drying power with suitable bitumens, in the same manner as described in the manufacture of copal varnish. Black japan itself rarely possesses great elasticity or weather resistance, so that it requires a coating of a suitable finishing varnish. The art of the varnish maker consists in the preparation of a mixing of great degree of depth and intensity of colour without employing so high a proportion of bitumen that the solubility of the latter in the ensuing coat takes place, a condition manifesting itself by the appearance on the finished work of a greenish fluorescence. It is difficult to give a general formula for these coatings, as the quality depends on the selection of the materials. The proportions may be roughly stated as equal quantities of hard resin, asphaltum or petroleum pitch, and boiled oil with turpentine, and white spirit thinners.

Air-drying Black Enamels are made on a far plan to the coachmakers' black japans, but consist of materials which are not so carefully selected, e.g. asphaltum, rosin, boiled oil, and petroleum thinners. Some contain only pitch, oil, and turpentine, and are known as **household blacks**, for which the following formula may be considered as fairly represen-

tative: 45 lb. pitch, 6 galls. boiled oil, and 6 lb. litharge, boiled until stringy and then cooled and thinned with 25 galls. turpentine or petroleum. It is evident that the varieties of blacks will be large in number and will have special names according to their requirements. They may be bright or dead; e.g. Berlin black for grates and fenders, in which the introduction of a black pigment such as carbon black produces a matt appearance. Coach and motor builders require a quick black for iron work, drying in about an hour, a black petrol-resisting varnish of brilliant lustre, drying and hardening quickly, and a dead black metal priming, capable of standing great heat, for the exteriors of cylinders of motor cars.

Black Stoving Enamels are of great variety and a similar classification holds, as in the of resin oil varnishes as to elasticity, body viscosity, and temperature of stoving coating, under-coating and finishing, dipping and spraying modifications are use.

The marked difference between clear varnishes and black stoving enamels lies in the presence of bitumen. The remaining components are drying oils with their attendant driers and thinners, chiefly kerosene, since the temperature of stoving is higher than that of resin-oil varnishes, viz. 150°-177°C. Some black stoving enamels contain no resin or rosin, but generally a certain proportion is present; but it is difficult to identify the resins in the presence of a mixture of bitumens, especially if stearine pitches have been used. Flow and surface are important properties. The finishing coat must have a high lustre and hardness, and should show no runs or rivelling at the edges under the conditions of application, dipping, brushing, or spraying. The production of quality coatings demands careful selection of the components and of the proportions in the mixings. If an under-coating be used it must be adherent to the surface and be rust preventative, providing also a grip for the coat. The under-coatings possess small elasticity, great hardness, good hiding power, but no lustre. They may contain a pigment such as carbon black instead of bitumen, whose function is to leave a dull uniform surface for the finishing coat. The composition and mode of preparation is variable. Among the many published formulae a mixing containing asphaltum, resin, and boiled linseed oil in the proportions of 10; 2.5; 50, with petroleum or turpentine may be considered as fairly representative. The proportions will depend on the requirements and on the temperature of stoving. British Specifications for oil, black and shellac varnishes used in the trade have been issued by the British Engineering Standards Association.

Such black stoving enamels, largely used on ironwork, have great weather-resisting power, but recently cellulose air-drying black enamels have been put forward. It is impossible in the space available to consider adequately the great variety of decorative and protective coatings, as well as their advantages and defects.

For further details reference may be made to R. S. Morrell's *Varnishes and Compounds*, 1923; H. M. Langton, *Blacks and*

VARNISH.

Flückiger, 1923; H. Henton, Volatile Solvents and Thinners, 1925; T. H. Barry, A. A. Drummond and R. S. Morrell, Resins, Natural and Synthetic, 1926; The Analysis of Pigments, Paints and Varnishes, J. J. Fox and T. H. Bowles, 1926.

Spirit Varnishes.—The manufacture of spirit varnishes is much less complicated than that of the oil preparations, the former being simply solutions of one or more resins in various solvents. On the evaporation of the solvent a coating of varnish is obtained, consisting practically of the unchanged resins. The resins employed for this purpose are chiefly shellac, sandarac, soluble Manila, dammar, acaroid, elemi, benzoin, mastic and rosin. The solution of the resins is affected either cold or hot, as circumstances require, heat presenting the advantages of rapid solution and clearing, while the palest varnishes are obtained by the cold process. To facilitate solution the gum should be kept continually agitated, thus preventing the particles of gum from forming a mass. It will be readily seen that the larger the surface of the gum exposed to the solvent the quicker will be the solution. A revolving churn is used, and the rotation keeps the particles in motion and prevents them from caking together. When the gum is all dissolved the varnishes are set aside to settle, and are ready for use almost immediately. They dry very rapidly and are, generally speaking, harder and more brittle than oil varnishes, and as their drying is merely dependent on the evaporation of the solvent the addition of driers is not required. Within recent years many forms of artificial or synthetic resins have come into use. They may be broadly classified into (1) condensation resins—e.g. the formaldehyde-phenolic resins; (2) polymerisation resins—e.g. the coumarone resins, which are obtained by the treatment of certain distillates from coal tar naphtha. Condensation resins are such as are made by preliminary interaction of at least two chemical substances, generally involving elimination of water. Resinification may be completed by a polymerising action.

Formaldehyde phenolic resins.—The most important condensation resin is made from formaldehyde and phenolic compounds. Bakelite is the typical example. Amongst other trade products of similar character are—in America, Redmanol, Condensite, Amberite, Phenoform, Sibolite, Nuloid, Amberdeen, Abalac, etc.; in France, Melusite, Cerite; in Great Britain, Elo, Bakelacque. There is a marked difference in the properties of the formaldehyde phenolic resins compared with the natural resins. The natural resins can be melted, but not 'run,' and cooled, without great change in their solubility or fusibility, but the phenol synthetic resins on heating may, under certain conditions, pass more or less rapidly into solid infusible resins, charring at 300°C.; moreover, the resin becomes insoluble in all ordinary solvents and has acquired a remarkable increase in strength.

It is this marked change in properties which has made Bakelite products so valuable as substitutes for wood. The formaldehyde resins are of two distinct types—

analogous to the resins of the natural resins.

form the class of shellac substitutes (called Novolak by Baekeland). They are analogous to shellac in their solubility relationships; they are soluble in alcohol and insoluble in hydrocarbons. The second type of resin is that in which the resin is soluble and fusible only in an intermediate stage and becomes insoluble and infusible on heat treatment, being finally in the *resite* condition, passing through the intermediate *resitol* stage. Bakelite, Elo, and Bakelacque are examples of this latter type. Baekeland terms these latter resins *resinoids*, as they do not possess all the properties common to the natural resins.

For details as to preparation and further application reference must be made to Carleton Ellis, Synthetic Resins and their Plastics, 1923, and to the Chemistry of Natural and Synthetic Resins by Barry, Drummond and Morrell, 1926.

The chemical changes occurring during the manufacture of these substances are not yet understood, although considerable advance has been made during the last few years. The varieties of resin produced is dependent on the amounts of formaldehyde and phenol used and whether the catalyst is acidic or basic in character. Baekeland (J. Ind. Eng. Chem. 1909, 1, 159) uses ammonia as catalyst. An acid catalyst will tend to produce a soluble resin, whereas an alkali favours an insoluble resin. The greatest development of these resins has been in the direction of moulding and insulating compounds.

Formaldehyde-urea Resins.—Condensation products of formaldehyde with urea and thiourea have been used to give viscous products which may be gelatinised in several hours. The reaction takes place in two stages, a condensation phase followed by a polymerisation phase. The solid resins obtained are transparent, colourless, stable, taking a high polish, and may be used as substitutes for glass; Polloplas and the Beetle Products Company resins are examples. In Pollak's Schellan solutions the resin is maintained in water solution by alkali salts of weak acids, e.g. sodium acetate or a borax solution of shellac.

Coumarone Resins are obtained from the fraction of solvent naphtha 150°–200°C., and are polymerised as regards certain of their constituents by sulphuric acid to yield 25–40 p.c. of resin. These resins are not usually soluble in alcohol, and benzene, toluene, solvent naphtha, and turpentine are the best solvents. They are miscible with drying oils. The differences in the technical coumarone resins depend on the variable proportions of a coumarone present. The following is a formula for a coumarone oil varnish: China wood containing 15 p.c. of linseed oil is mixed with the resin in the proportion of 5–40 per 100 lbs. resin. The driers used are or manganese linoleates, and the thinner heavy refined coal-tar naphtha, b.p. 160°C. Typical varnish mixtures for coumarone are described by King, Bayard, Rhodes, (J. Ind. Eng. Chem. 1923) and R. S. Morrell (Varnishes and Resins, 1923).

Cellulose Ester Varnishes.—Cellulose esters are of any importance.

industry, viz. the nitrate and the acetate, formed by combination of cellulose with nitric acid and acetic acid respectively. These substances are soluble in certain mixtures of organic liquids, which have a comparatively high rate of evaporation, and when the solutions are spread on solid surfaces they rapidly become dry, leaving the cellulose ester in the form of a continuous film. By making certain additions to the original solutions, the hardness and adhesiveness of the films may be modified. Owing to the rapidity with which the solutions dry, they may be applied at ordinary temperatures, although a warm room is advantageous. As a rule a coating is dry under an hour. All organic protective coatings consist of highly polymerised structures. The degree to which the original cellulose is depolymerised or degraded in structure before and during the manufacture of the ester determines to a considerable extent the properties of the resulting varnish.

Nitrocellulose Varnishes.—The cellulose ester varnishes may be either transparent or opaque. The transparent varnishes may be coloured in practically any tint so as to give a coloured transparent lacquer coating. The opaque varnishes containing pigments may also be obtained in any colour, and are usually termed enamels. It is customary to include all solutions of cellulose esters used for protective or decorative coatings under the general term of cellulose varnishes. They may be applied by brush, but better results are obtained by dipping or by use of an air spray. Under proper conditions the solutions dry with a high polish, and the films resist water, petrol, soap, turpentine, weak acids and weak alkalis.

Cellulose nitrate lacquers.—The common metal lacquer usually contains not more than 5 p.c. of cellulose nitrate, in a mixture of solvents, and serves to delay the tarnishing of metal, not acting as a finishing material. In order to increase the solid content it was necessary to produce cellulose nitrate, which, when dissolved in suitable solvents, gave a solution of low viscosity. The addition of natural resins was found to impart adhesion and rubbing properties in varying degrees according to the resin employed and the amount used. The constituents of finishing lacquers may be: cellulose nitrate of low viscosity, resins to make the film glossy and hard, solvents which control the rate of drying, degree of gloss and viscosity of the lacquer, and plasticides to remain in the film after the solvents have evaporated and so to give it elasticity. Scrap celluloid as a substitute for cellulose nitrate has many drawbacks, and its use is not to be recommended. The resins are either of the soft or medium hard varieties. Butyl alcohol, ethyl, butyl and amyl acetates, ethyl lactate and amyl formate may be used as solvents. D. B. Keyes classifies the solvents into three groups: (1) low boiling solvents, reducing the viscosity of the lacquers and possessing a high rate of evaporation; (2) medium boiling, giving the lacquers the property of flow; (3) high boiling, acting as a solvent, preventing the precipitation of nitrocellulose or the resin.

The lacquers are best applied by brush or spray. The finished surface may be brushed on.

The order of application of the cellulose coatings, careful consideration of their elasticity must be taken, so as to prevent subsequent cracking of the film. Pigmented lacquers and enamels have been used for many years as protective coatings for bathroom fittings, cycle and motor lamps and furniture. The following proportions of cellulose nitrate, resin and plasticide have been found satisfactory for interior lacquer enamels: cellulose nitrate 12 parts; resins 6 parts; plasticide 2 parts. This ratio will give a hard and elastic film provided too much pigment is not added. For further details reference may be made to F. Sproston, *Cellulose Ester Varnishes*, 1925.

Cellulose acetate varnishes.—Solutions of cellulose acetate in a mixture of high and low b.p. solvents are used for tautening and weather-proofing linen fabric composing the wing surfaces of aeroplanes. A typical three-coat formula would be cellulose acetate 8.5 parts, acetone 50, alcohol 24, benzene 24, benzyl alcohol 2 and triphenyl phosphate 1.5. For durability the dopes must be specially pigmented and generally require a protective coating of a seaplane oil varnish.

Natural varnishes or lacquers.—Japanese lacquer is the milky juice exuding from the trunk of *Rhus vernicifera* (Tsi-chou, varnish tree). The tapping of the tree resembles that of *pinus* for turpentine oleoresin. The raw varnish, which is frequently adulterated with tung and perilla oils, is known in Japan as Ki-urushi. The peculiarity of the varnish is that it hardens only in a moist atmosphere and remains in a tacky condition to sunlight and heat. It is the most durable varnish known and resists the action of air and water excellently. It is stated to be the best protective coating for aeroplane propellers. The application of the lacquer is said to be dangerous to western workers owing to the peculiar poisonous properties of the *urushiol* in the resin. The resin has been investigated by Japanese chemists, who have synthesised hydrourushiol, the reduction product of the active principle of Japan lac. A concise account of Chinese and Japanese manufacture will be found in the Bulletin of the Imperial Institute, 1910, 8, 32; and in Stewart Dick's *Arts and Crafts of Old Japan*, 1908.

R. S. M.

VARVIGITE. *Hydrated manganese ore*
 $\text{MnO}_2 \cdot \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Rammelsberg), or



(Phillips) (v. MANGANESE).

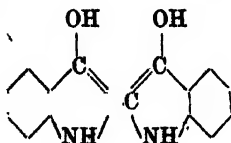
VASOTONIN. Trade name given to a combination of yohimbine and urethane which produces a fall of blood pressure, and appears to have considerable therapeutic value (China. Soc. Abstr. 1910, ii. 725).

VAT DYES. The term 'vat dye' is applied to those dyestuffs which, like indigo, are insoluble in water, dilute acids, and alkalis, but which, on being treated with suitable reducing agents, yield leuco compounds which are soluble in the hydroxides of the alkalis or of the alkaline earths, and in dyeing are taken up in such by textile fibres. By subsequent exposure to the air the leuco compound is oxidised to

and in the fibre, with the re-formation of the original colouring matter. The characteristic fastness of the colours thus produced is, in a large measure, due to the insolubility of the dyestuff.

Indigo (*q.v.*), which was formerly the only known vat dye, is by far the most important of this series of colouring matters, and has been used in dyeing from time immemorial. A blue, dyed with it on cotton, is still referred to as a 'vatted blue,' whilst in the woollen industry the term 'wooded blue' means a blue which is dyed either wholly or in part with indigo.

In preparing or 'setting' the indigo vat, various methods are employed in practice to bring about the reduction of the indigotin. This is effected either by purely chemical or by bacteriological means, but in either case the product of the reaction is the same, viz. indigo white, $C_{16}H_{11}N_2O_2$, or graphically,



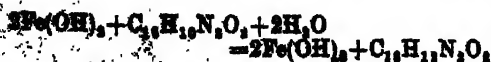
which dissolves in caustic soda with the formation of either the mono- or di-sodium salt ($C_{16}H_{11}N_2O_2Na$ or $C_{16}H_{10}N_2O_2Na_2$), according to the amount of caustic soda present in the bath. It has been shown that indirubin and thioindigo red also require 2H for reduction, and by analogy it is presumed that the other indigoid dyestuffs behave similarly. In aqueous solution, the mono-sodium salt of indigo white has been shown to be an electrolyte, though it is not so strongly ionised as sodium chloride (Knecht and Batey, J. Soc. Dyers, 1910, 171).

The so-called chemical vats are distinguished, according to the reducing agent employed, as the copperas, the zinc, and the hydrosulphite vats. They are used in cotton dyeing, but the hydrosulphite vat also finds a limited application in wool dyeing. In the setting of any indigo vat, it is essential that the indigo should be in a finely divided state. The 20 p.c. artificial indigo paste contains the colouring matter in a sufficiently finely divided condition for the purpose, but the natural product must be ground, before use, to an impalpable powder.

The *copperas vat* depends upon the reducing action of ferrous hydroxide, and is made up of indigo, copperas and slaked lime. The lime reacting with the copperas forms ferrous hydroxide



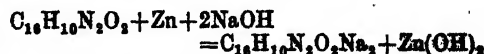
which in turn reduces the indigotin to indigo white:



which then dissolves in the excess of lime present to form the soluble calcium salt. In the *copperas vat*, there is always a large amount of sediment, and to prevent this settling into con-

with the goods during dyeing, deeper vessels are required than with the other chemical vats. At the present time, the copperas vat is not largely used in this country, the main reasons being that its use involves a considerable loss in indigo, and the sediment in the vat is very bulky. On the other hand, the blues obtained in the copperas vat are faster than those obtained in the zinc or hydrosulphite vats.

In the *zinc vat*, zinc powder is the reducing agent. For satisfactory working, this should contain not less than 80 p.c. of metallic zinc. The vat is set with indigo, zinc powder and lime (or caustic soda). The reduction may be regarded as taking place as follows:



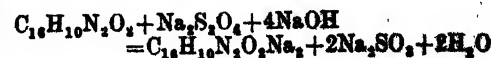
although, according to Binz (Chem. Ind. 11, 1902), it is probable that combination of the indigotin with the alkali takes place first, with the formation of a compound



which then reacts with the zinc, forming the same products as shown in the above equation.

This vat is the one which is most largely used in cotton dyeing.

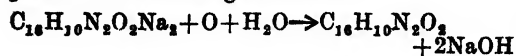
The *hydrosulphite vat* depends upon the reduction of the indigotin by sodium hydrosulphite, which is usually prepared by stirring zinc dust into commercial sodium bisulphite, in the proportion of a pound of the former to a gallon of the solution; and after allowing to stand for some time, adding to the solution an excess of milk of lime. The so-called 'stock vat' or concentrated vat is made by dissolving the indigo in this muddy liquid. (A product of this kind, containing about 3 p.c. of indigotin, was formerly sold under the name of 'reduced indigo.') This stock vat serves either for making up or for replenishing the dye vat proper. The reduction by means of sodium hydrosulphite may be regarded as taking place according to the following equation:



By employing artificial indigo paste, caustic soda, and the solid commercial sodium hydrosulphite, which is now placed on the market in an almost pure condition and at a reasonable price, it is possible to obtain a vat practically free from sediment.

The dyeing of cotton in the indigo vat is in itself a comparatively simple operation, although the management of the vats requires careful supervision and considerable practical experience. In hank dyeing, the wetted-out hanks are immersed in the vat and turned by hand under the surface of the liquid until thoroughly impregnated with the vat liquor, after which they are withdrawn and wrung, the liquor being returned to the vat. The hanks are then exposed freely to the air, in order to allow of the oxidation of the indigo white to indigotin. By repeating this operation several times, the shade becomes successively darker, and its depth will

one and the same or in different vats. Although it is possible to obtain a dark shade by a single dip in a strong vat, this is not practised, because it would result in a large proportion of the indigo being loosely fixed and much of it would be lost in washing off; besides, the resulting blue would 'rub off' very badly. The oxidation of the indigo white taken up by the fibre from the vat is usually regarded as taking place in the following manner:—



though under chosen conditions it has been shown by Herzog and Manchot that auto-oxidation may take place, resulting in the formation of equal molecular proportions of indigotin and hydrogen peroxide (Annalen, 316, 318). This interesting observation may account, according to Crowther, for the presence of isatin in the hydrosulphite vat (J. Soc. Dyers and Col. 1911, 146). It is further evident that the dyed cotton material removes a considerable amount of alkali from the vat. Where lime is used in the vat in place of caustic soda, an accumulation of calcium carbonate on the fibre occurs through air exposure, and the goods therefore soured, after dyeing, in dilute sulphuric acid. In the dyeing of cotton warps and of piece goods, the material is guided through the vat by means of submerged rollers, so that it passes many times up and down between the time of entering and leaving; excess of liquor is expressed at the point of exit by means of a pair of squeezing rollers. In case it is desired to give the pieces two or more 'dips' in the same vat, they are stitched together, end to end, so as to form a continuous band, and, after leaving the vat, are passed up and down over a series of loosely running wooden rollers (which are usually placed immediately above the vat in order to economise space) for a sufficient length of time to allow of the oxidation of the indigo white before they re-enter the vat.

The reason why indigo white should be taken up from its aqueous solution by the cotton fibre is imperfectly understood. It has been suggested that it is a case of mutual precipitation between colloids, but as it has been definitely shown (see above) that indigo white lacks some of the most essential properties of a colloid, this theory cannot hold good. In any case, the affinity of indigo white for cotton is but slight, as, when once taken up, it can be completely removed by continued washing with cold, air-free water, whereas a boiling solution of dilute caustic soda removes it from the fibre almost instantaneously. The affinity of indigo white for cotton appears to be similar in character to that of tannic acid for this fibre (Knecht and Nair, *ibid.* 1912, 28).

If the cotton to be dyed in indigo or other vat dyes has been previously mercerised, darker shades are obtained than on untreated cotton. The same applies with regard to indigo and certain indigoid dyestuffs if the cotton has been previously dyed manganese bronze or has been steeped for some time in strong nitric acid (see *Mercerising*). In the latter case, the increase in depth is due in a greater measure to slight nitration of this fibre than to the mercerising effect of the acid.

Indigo dyed on cotton is sometimes associated with other colours. Thus, if a light shade of indigo is 'topped' or subsequently dyed chrome yellow, pleasing and very fast shades of green result. The old-fashioned 'fast black' was obtained by a combination of a heavy shade of indigo and catechu brown. The dyeing of a black of this description was practised by the Incas of Peru prior to the Spanish invasion.

Indigo dyed on cotton is usually regarded as fast to washing and to light. Strictly speaking, however, these qualities are only relative, for by repeated washing in soap or continued exposure to light, the colour (especially in light shades) gradually fades. But in fading it always retains the characteristic colour of indigo and does not change, as is the case with most other blues, to an unsightly grey or drab. It is noteworthy that the fastness of indigo to light may be considerably enhanced by treating the dyed fabric for a few minutes in a boiling dilute solution of copper sulphate.

In Egypt, Persia, India, China, Japan, and other Eastern countries, where dyeing is still almost entirely a household industry, fermentation vats are generally used for cotton dyeing. Such vats are occasionally used in this country for the dyeing of goods for certain markets. The fermentation vat imparts a certain peculiar smell to the goods dyed in it, and unless they possess this smell, the natives in some markets will not accept them as indigo-dyed. A product known as indigo essence, consisting of a mixture of the methyl ethers of α -naphthol and β -naphthol, is put on the market for the purpose of imitating this smell on material dyed blue with dyes other than indigo.

The dyeing of wool with indigo differs from the dyeing of cotton in that whereas cotton is invariably dyed cold, the temperature of the vat for wool dyeing must be maintained at from 50° to 55°. Another point of difference is that in the case of wool, the time of immersion in the vat has to be much longer than in the case of cotton.

For wool dyeing, especially where fermentation vats are used, natural indigo is generally preferred to the artificial product.

Only one of the vats generally used in cotton dyeing can be used with advantage in wool dyeing, viz. the hydrosulphite vat. This is set with indigo, sodium hydrosulphite and ammonia. Although the cost of working this vat is greater, as far as materials are concerned, than that of the fermentation vats, this is more than compensated by its greater output. It is, however, only suitable for light to medium shades of blue.

The fermentation vats, of which a considerable variety are in use in different countries and sometimes in one and the same country, might appear at first sight to depend for their action upon different principles. But it is probable that in all cases the action depends upon a bacterial decomposition (butyric acid fermentation) of the carbohydrates, in which hydrogen is generated. Various substances containing carbohydrates, such as bran, flour, sugar, meal or dates, are used along with lime, potash, or soda for the purpose. The setting and management of fermentation vats require considerable skill and experience, and in all large works these matters are under the sole

control of the 'blue dyer,' upon whose intelligence and efficiency the prosperity of the works depends.

The fermentation vat mostly used in this country is the so-called *woad vat*, which is set in a vessel having a capacity of from 1600 to 3000 gals. with indigo, woad, bran, madder and lime, the temperature being maintained at 60°. The fermentation will have set, as a rule, in from three to five days, and the vat will then be ready for use. Once set, a woad vat simply requires replenishing, from time to time, with the necessary additions of indigo, lime, and bran, and may remain in use continuously for many years. It should be explained that in this vat the woad, which in former times (before the introduction of indigo from India) was the only indigo-bearing dyestuff used in this country and on the Continent, now acts solely by virtue of the bacteria which it contains, for in commercial woad there is, at the present day, no indigotin, the whole of the colouring matter having been destroyed by bacterial action.

Dyed on wool, indigo resists the action of light better than when dyed on cotton.

The disulphonic acid of indigotin, which is obtained by heating the dyestuff to about 100° with excess of concentrated sulphuric acid, is known commercially as indigo extract or, in the form of its sodium salt, as indigo carmine. It dyes wool 'at the boil' from a bath containing sulphuric acid and Glauber salt a much brighter shade of blue than that obtained in the vat, but the colour is neither fast to light nor to soap, and goods so dyed cannot be classed as being dyed with indigo.

Silk is seldom dyed in the indigo vat, although fast and pleasing shades can be obtained in this way.

Indigo in printing.—In textile printing, notably in calico printing, indigo may be regarded as the most important individual dyestuff in use at the present time. This is partly due to the favour which it finds with the public as being pleasing to the eye and relatively fast, and partly to the variety of styles to which it lends itself in this branch of textile colouring. Effects are obtained with indigo in printing in three entirely different ways, viz. by direct printing, by the discharge process, and by the resist process.

In direct printing, the indigo is not printed on to the fabric in the reduced condition (a process which would obviously suggest itself at once to any one acquainted with its properties and its application in dyeing) owing to practical difficulties which this mode of application entails. The process in actual use is the so-called *glucose process*, in which glucose and caustic soda serve as the reducing agent. The pieces are first prepared by padding in a solution of glucose and are then dried. The finely ground indigo is made up with strong caustic soda thickened with maize starch and British gum. This is printed on to the prepared calico and the goods are run through a rapid ager containing air-free moist steam, the time required for this treatment being about half a minute. During the steaming, the indigo is reduced to indigo white which dissolves in the caustic soda and penetrates into the fibres. By subsequent exposure to air, the indigo white slowly oxidises

back to indigo blue. The operations of preparing in glucose and drying may be dispensed with by adding to the printing colour a suitable reducing agent such as the formaldehyde compound of sodium sulphoxylate (hydrosulphite NaF). This has no action on indigo in the cold, but reduces it on steaming for two to three minutes. The goods are then exposed to the air as in the glucose process.

Indigo may also be produced on the fibre in printing (or in dyeing) by means of *indigozol*, a product discovered by Messrs. Sunder and Bader, and recently introduced by Messrs. Durand and Huguenin. The new product is a comparatively stable compound of indigo white, soluble in water and in caustic soda. The printed or padded pieces are run through a weak bath of nitrite of soda and acid, when the indigo instantly develops on the fibre. The blues obtained in this way are faster to rubbing than those obtained in other ways.

In the discharge process, which lends itself to a greater variety of effects, the whole piece is first dyed to the required depth of blue in the vat and the colour is then removed locally either by destroying it by means of oxidising agents or by reducing it to the leuco compound and removing this by means of boiling dilute alkali. The former process, which is the one chiefly employed, consists in printing sodium chromate, suitably thickened, on to the blue fabric. After printing, the goods are run through a warm solution of sulphuric and oxalic acids, when in consequence of the liberation of chromic acid, the indigo is oxidised to isatin and this is removed in the subsequent washing, a white pattern on a blue ground resulting. For coloured discharges, the chromate is mixed with albumen and a suitable pigment, such as vermilion or chrome yellow, and the goods are run, after being printed, through the mixture of acids at a temperature high enough to coagulate the albumen. The fixation of the pigment and the destruction of the indigo thus take place simultaneously. The process is capable of many modifications. Thus, in order to obtain a bright scarlet on a blue ground, the indigo-dyed fabric is padded first with an alkaline solution of β -naphthol, dried and printed with a colour containing diazotised *p*-nitraniline and sodium dichromate. The *p*-nitraniline red thus formed resists the action of the chromic acid formed when the pieces are run through acid and a bright red on a blue ground results.

Indigo may also be discharged by printing on sodium nitrate and running the goods through warm sulphuric acid of 100°Tw. (Freiberger's process).

In the reduction discharge process, the pieces are printed with the formaldehyde compound of sodium sulphoxylate with or without the addition of a catalyst such as anthraquinone. They are then steamed in the rapid ager to reduce the indigo and immediately run through a boiling bath of caustic soda, soda ash, or sodium silicate. The indigo white is thus completely removed and there is no tendering of the discharged places, as is invariably the case when the chromate discharge is used.

In the resist process, the fabric is first printed with a mechanical or with a 'chemical resist,' and is then dyed in the vat. Wherever the resist

has been printed no colour is fixed, and a white pattern on a blue ground results. In the East, and also to some extent in European print works, wax is used as the resist. After dyeing it is removed by soap and alkali. When the goods are handled (as in dyeing) after the wax has been printed on, the latter cracks in places so that in the dyeing some of the reduced indigo liquor penetrates through the fissures, with the result that fine blue veins are afterwards seen in the pattern. This defect is characteristic of all true Battick work, which the modern printers are at pains to imitate.

The 'chemical resist' mostly used at the present time is a very thick colour containing copper sulphate, lead nitrate, and China clay, usually thickened with flour and British gum and with or without the addition of such mechanical resists as tallow or rosin. As with the wax resist, the dyeing is best conducted in the zinc vat. By increasing the amount of lead nitrate in this resist so as to exceed its equivalent in copper sulphate, and running the goods after dyeing through sodium dichromate, lead chromate is formed in the resisted parts and a yellow pattern on a blue ground results.

VAT DYES OTHER THAN INDIGO.

Although it has long been known that indirubin (an isomeride of indigotin which occurs in almost all natural indigos) can be dyed in the same manner as indigo, it has never found any technical application, partly on account of the shade it yields being undesirable and partly for other reasons. The tetrabromo (5:7:5':7') derivative, obtained by brominating the artificially prepared dyestuff in nitrobenzene solution is, however, a useful vat dye, and comes into the market under the designation *Ciba Heliotrope B*. *Indophenol*, which was discovered in 1882 by Koechlin and Witt, is also a vat dye, and although it was a commercial article in the '90's it was never much used, mainly because it produced loose colours, and it is now entirely obsolete.

The enormous development in the vat colour industry that has taken place during the last few years may be traced, on the one hand, to the discovery of indanthrene blue by Bohn in 1901, and on the other hand to the synthesis of thioindigo red by Friedländer in 1905. At the present time there are well over one hundred individual dyestuffs which may be strictly classed as vat dyes, without taking into account the large number of sulphide colours (*q.v.*) which, in a sense, might also be classed as vat dyes. It would obviously be out of place to embody the whole of our present knowledge of the vat dyes in this work, as that would require an amount of space which would not be commensurate with the general interest attaching to the subject. In the following, it will therefore be understood that the examples given are only typical of the various classes. For further information on the subject of vat dyes, see Engi, *Chem. Zeit.* 1908, 1178; Bohn, *Ber.* 1910, 987; Staebli, *Chem. Zeit.* 1910, 731 *et seq.*; Friedländer, *ibid.* 1911, 640; Masera, *Färber-Zeit.* 1911, 336; Grandmougin and Battagay, *Ela. Text. Bl.* 1910; Malloch, *J. Soc. Dyers*, 1910, 26; Ermen, *ibid.* 1910, 56 and 236; E. de Barry Barnett,

ibid. 1913, 185; L. E. Vlies, *ibid.* 1914, 22; Truttwin, *Enzyklopädie der Küpenfarbstoffe*, 1920; J. F. Thorpe and C. K. Ingold, *Vat Colours*, 1923; The 'Colour Index' of the Society of Dyers and Colourists, edited by F. M. Rowe, 1924; Knecht, Rawson and Loewenthal, *A Manual of Dyeing*; Knecht and Fothergill, *The Principles and Practice of Textile Printing*, 1924.

These vat dyes may be classed under two headings, viz. as (a) indigoid dyestuffs, and (b) anthraquinonoid dyestuffs. The former come into the market under various trade names such as indigos of various brands, the Durind colours (British Dyestuffs Corporation), anthrene colours (British Alizarine Co.), the Ciba colours (Soc. of Chem. Ind., Basel), while the latter are represented by the anthrene colours (British Dyestuffs Corporation), the Caledon colours (Solway Dyes Co.), and the Cibanon colours (Soc. of Chem. Ind., Basel). V. INDIGOID DYESTUFFS, Vol. III. p. 620.

The bromo derivatives of indigotin are brought into the market under different designations, such as indigo pure R.B.N., ciba blue, indigo K2B, and generally yield, in dyeing and in printing, either redder or greener shades of blue than indigo itself, according to the amount of bromine which they contain. Thus *indigo R* is 5 bromoindigo, *ciba blue 2B* is 5:7:5':7'-tetrabromoindigo, and *indigo KG* consists mainly of 4:5:7:4':5':7'-hexabromoindigo. There is no object to be gained in substituting more than five hydrogen atoms in the indigo molecule, as the leuco compounds of the more highly halogenated derivatives are so sparingly soluble as to preclude their practical application. The 6:6'-dibromoindigo synthesised by Friedländer, and shown by him to be identical with the *Tyrian purple* of the ancients, is not a commercial article. It is interesting to note that the 6:6'-dibromoindigo dyes an amethyst shade (Tyrian purple) whereas the isomeric 5:5'-dibromoindigo (*indigo RB*) dyes blue. The position occupied by the halogen atoms in the molecule is of importance in other instances. Thus the entrance of the halogen atoms in the para-position with reference to the nitrogen atoms causes but little alteration in the colour, although the shades are brighter than those from indigo itself. If the halogen atoms occupy the para-position to the CO groups, the dyes obtained are redder in shade than indigo.

Of homologues of indigo, the 7:7'-dimethylindigo (*methyl indigo B*), and the 5:5'-dimethylindigo (*methyl indigo R*) are the most important commercial representatives. The former dyes cotton a greener and the latter a redder shade of blue than indigo itself.

Thioindigo red B or thionaphthene indigo

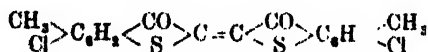


was discovered in 1905 by Friedländer and is obtained by fusing *o*-carboxyphenylthioglycollic acid with caustic potash to form thioindoxyl, which is then oxidised to the dyestuff. This dye results from the action of dichloroethylene on thioacetylic acid, followed by treatment with sulphuric chlorhydric. The discovery of this product marked the beginning of

a new era in the history of organic colouring matters, for it opened up a new field and has resulted in the introduction of a large number of new and valuable vat dyes. Like artificial indigo and most other commercial vat dyes, thioindigo red B comes into the market in the form of a 20 p.c. paste. The pure colouring matter is readily obtained from the dried paste by crystallisation from benzene or toluene in well-defined dark red crystals. Its solution in benzene is red and shows a characteristic intense yellow fluorescence. In concentrated sulphuric acid it dissolves with a bluish-green colour; but on pouring the solution into water, the original dyestuff separates. By warming with fuming sulphuric acid, it is sulphonated and the soluble sulphonic acid thus obtained dyes wool from an acid bath a full bluish shade of red. Unlike indigo, thioindigo red is not affected by oxidising agents, remaining unaffected by chromic acid, alkaline ferrocyanide and bleaching powder; whilst, on the other hand, it is more readily reduced than indigo. It has been shown that the reduction of thioindigo red to its leuco compound is analogous to that of indigo, two atoms of hydrogen or their equivalent being required for one molecular weight of the dyestuff (Knecht, J. Soc. Dyers, 1906, 156). Like indigo white, the leuco compound dissolves readily in caustic alkalis, forming a yellow vat from which it is taken up by the cotton fibre, the red reappearing on exposure to the air.

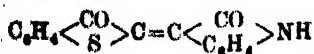
Of derivatives of thioindigo red, the following may be mentioned:

Thioindigo red B.G (dichlorothionaphthene indigo) $C_6H_4Cl<\underset{S}{CO}>C=C<\underset{S}{CO}>C_6H_4Cl$; *thioindigo red 3B* (dichlorodimethylthionaphthene indigo)



thioindigo violet 2B (dichlorodimethyldimethoxythionaphthene indigo); *thioindigo orange R* (6:6'-diethoxythionaphthene indigo); and *thioindigo gray* (7:7'-diaminothioindigo). In general it may be said that the introduction of substituents such as OH, OCH₃, OC₂H₅, SCH₃, SC₂H₅, NH₂, &c., in the para- position to the sulphur atoms produces a deepening of the shade to blue-violet, greenish-black, &c. Substitution in the meta- position to the sulphur atoms produces yellower shades—orange, orange-brown and scarlet. Halogenation darkens the shade of thioindigo red.

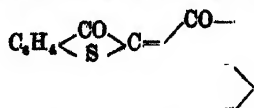
Thioindigo scarlet R



obtained by the action of thioindoxyl on isatin contains the characteristic groupings of thioindigo red and of indirubin. When acted upon by bromine in sulphuric acid solution it yields a dibromo derivative which is placed on the market under the name of *thioindigo violet K*. The tribromo-amino derivative represents *thioindigo brown G*.

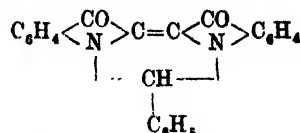
Ciba scarlet G (also known as *thioindigo scarlet 3G*) is a non-nitrogenous product, ob-

tained by the condensation of thioindoxyl with acenaphthene quinone and has the constitution



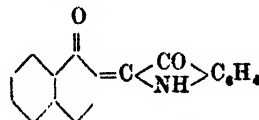
By the bromination of this dyestuff, *Ciba red R* results.

Of other indigoid dyestuffs, mention may be made of *Ciba yellow 3G*, which is obtained by boiling indigo with benzoyl chloride and copper powder in nitrobenzene, and to which the constitution



has been described. The complete change from blue to yellow is remarkable.

By the condensation of α -naphthol with α -isatinchloride, a compound is obtained with the following *orthoquinonoid* structure



and is, in a sense, also indigoid in character. The tribromo derivative is known as *Alizarin indigo 3R*. The corresponding compound from alpha anthrol and dibromoisatin is known as *Alizarin indigo G*.

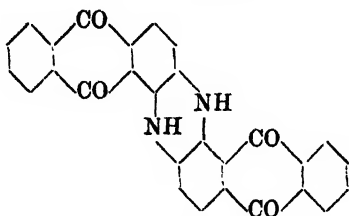
The indigoid dyestuffs all behave very much like indigo towards reducing agents, i.e. they yield leuco compounds (corresponding to indigo white) which dissolve readily in caustic alkalis, and in this condition show affinity for the textile fibres. The affinity of the different dyestuffs for the cotton fibre varies, however, in each case, so that their successful application, especially in the production of mixed shades, requires a considerable amount of practical experience. The reducing agent employed for these colouring matters (in fact for all vat dyes other than indigo) is invariably sodium hydrosulphite, for although it is not the most economical, it is the most effective and convenient reagent for the purpose and yields vats which are free from sediment. In principle, the dyeing of cotton with these dyestuffs is the same as the dyeing of indigo in the hydrosulphite vat. The optimum temperatures vary, however, according to the individual dyestuff, from the ordinary temperature (as used for indigo) to temperatures as high as 70°. The range of shades obtainable contains almost every colour of the spectrum, and some of these vie in brilliancy with the basic colours. Most of the colours are characterised by great fastness, and are in this respect superior to indigo. Hitherto no indigoid black has been produced.

Although originally applied to dyeing and printing on cotton and other vegetable methods have been devised by which colouring matters can be successfully applied in wool dyeing, by substituting ammonium

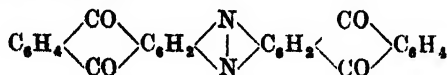
the caustic soda in the vat or neutralising the effect on the fibre of the caustic soda by the addition of some soluble oil (see H. Kämmerer, J. Soc. Dyers, 1913, 68).

In calico printing, the indigoid dyestuffs can be applied by methods similar to those employed for indigo, with the exception of the chromic acid discharge, which cannot be used owing to these dyestuffs being either not affected at all by chromic acid, on the one hand, or yielding imperfect discharges on the other. They can, however, be discharged by means of the formaldehyde compound of sodium sulfoxylate. For further information on the use of these colours in calico printing, see N. Evans, J. Soc. Dyers, 1913, 144.

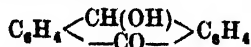
Anthraquinonoid dyes.—The first of these dyestuffs brought into the market was *indanthrene blue*, a product formed by the action of molten caustic potash on β -aminoanthraquinone, and possessing the constitution



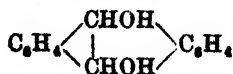
It is a dark blue compound insoluble in water, dilute acids, alkalis and most ordinary organic solvents. It can be obtained in well-defined crystals from its solution in quinoline or by sublimation. Oxidising agents convert it into the yellow azine



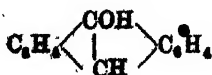
(containing 2 atoms of hydrogen less), but this is readily reconverted into the dyestuff by the action of reducing agents. Acted upon by hydrosulphite in presence of an excess of caustic soda, indanthrene blue yields a blue vat from which cotton and other vegetable fibres can be dyed in exceedingly fast shades of blue. The composition of the leuco compound of indanthrene blue and other anthraquinonoid vat dyes is not known with certainty, but it is evident from the behaviour of anthraquinone, alizarin and the non-nitrogenous anthraquinonoid dyes that reduction takes place in the $-\text{CO}-$ group, resulting in the formation of compounds analogous to oxanthranol



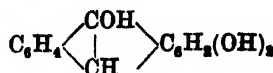
or the isomeric anthrahydroquinone



where in either case 2H would be required for the reduction. The further reduction to anthranol



requires 4H or its equivalent. In this connection it may be mentioned that in the quantitative estimation of alizarin by titration with titanous chloride in presence of sodium tartrate (J. Soc. Dyers, 1915, 241) the analogous reduction to desoxyalizarin

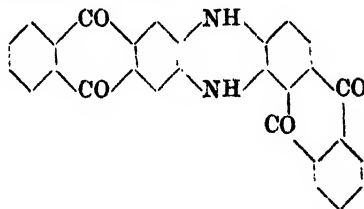


takes place, 4H being required.

To what extent the four $-\text{CO}-$ groups of indanthrene blue suffer reduction in the formation of a 'vat' is not known at the present time, and this applies also to the other ant' quinonoid dyes.

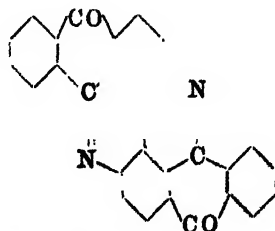
Halogen derivatives (Cl and Br) of indanthrene blue are also commercial articles and yield in dyeing greener shades of blue which are fast to bleaching powder than ordinary indanthrene blue (v. INDANTHRENE), as the introduction of halogen atoms renders the oxidation to the azine less easy. *Indanthrene blue GCD* and *indanthrene blue GC* are the dichloro and dibromo derivatives respectively of indanthrene blue.

By the condensation of alizarin with 2:3-diaminoanthraquinone, a compound having the following constitution



is obtained, halogen derivatives of which come into the market under the names *algol blue* and *algol green*.

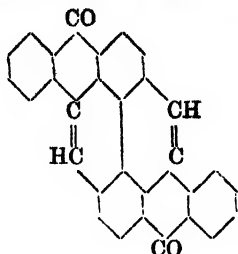
Flavanthrene or *indanthrene yellow* is formed as a by-product in the manufacture of indanthrene blue, but is obtained in much better yield, according to D. R. P. 138119, by the oxidation of β -aminoanthraquinone with antimony pentachloride in boiling nitrobenzene, or by the action of manganese peroxide in nitric acid solution (D. R. P. 141355). Flavanthrene has been shown to possess the constitution



and comes into the market in the form of a yellow paste. With caustic soda and hydrosulphite (or other reducing agents) it yields a deep cobalt-blue vat from which cotton takes up the leuco compound and is dyed, after exposure to the air, a fast yellow. The halogen derivatives of flavanthrene dye redder shades than flavanthrene itself.

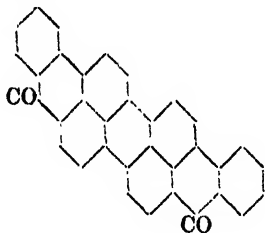
That nitrogen and sulphur are not essential

constituents of vat dyes is shown by the fact that *pyranthrone* or *indanthrene golden orange G*

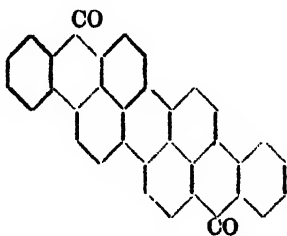


obtained by the condensation of two molecules of 2:2'-dimethyl-1:1'-dianthraquinonyl behaves in exactly the same manner towards reducing agents and in dyeing as the other vat dyes of this series. By the introduction of halogens into this dyestuff the shade is altered towards red. Thus, the brominated product represents *indanthrene scarlet G*.

By the alkaline condensation of two benzanthrone molecules, vat dyes are obtained, the simplest representative of which (*violanthrene BS*) is represented by the constitution

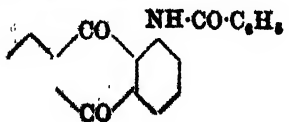


which, when nitrated, yields *indanthrene green*. This vat dye produces a green on cotton which is not very fast to light. *Indanthrene violet RT*, which dyes very fast shades, is a halogenated violanthrene. *Violanthrene R extra* is obtained by fusing halogen derivatives of benzanthrene with alcoholic potash. It is represented by the constitution

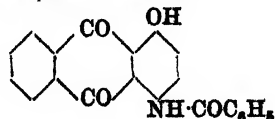


Indanthrene violet RR and *indanthrene violet B* are the dichloro and dibromo derivatives of this violanthrene.

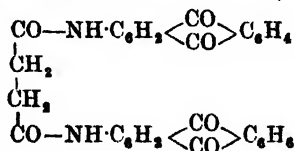
Some of the dyestuffs of this series are derivatives of aminoanthraquinones and are represented by comparatively simple constitutional formulae. Thus, *algal yellow WG* is α -benzoylaminoanthraquinone



whilst *algal pink R* is the benzoyl derivative of a hydroxyaminoanthraquinone

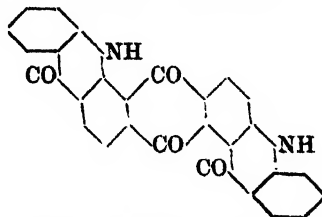


A variety of shades are produced by the introduction of further groups such as OCH_3 , NH_2 , additional OH groups, &c., into the anthraquinone molecule, followed by benzoylation. Succinyl derivatives are also used. An example of these is the dyestuff known as *algal yellow 3G*, which is the succinyl compound of diaminoanthraquinone



It is noteworthy that the arylaminoanthraquinones do not act as vat dyes for cotton, although some of them are, in the form of the sulphonic acids, valuable wool dyes. In this connection it may be mentioned that whereas alizarin is quantitatively reduced by titanous chloride in presence of Rochelle salt to desoxyalizarin, alizarin orange cannot be reduced further than to β -aminoalizarin.

Another class of anthraquinonoid dyes, the anthraquinone acridones, are obtained by condensing 1:2 chloroanthraquinone carboxylic acids with aromatic amino compounds, followed by treatment with concentrated sulphuric acid. *Indanthrene violet 2B* is a member of this class. It is represented by the constitution



Some of the sulphide colours (*q.v.*) are also classed as vat dyes, though they do not appear to bear any relationship to the indigoid or anthraquinonoid dyestuffs as far as constitution is concerned. The points of similarity are the use of hydrosulphite to form a vat and the fastness of the resulting colours on cotton. Of these dyestuffs the best known is *hydron blue*, which is obtained by melting the indophenol of carbazol (from *p*-nitrosophenol and carbasol) with a sodium polysulphide rich in sulphur. The dyeing is done at an elevated temperature (50° - 70°), and shades are obtained which resemble indigo, though they are claimed to be faster. Some vat dyes obtained from anthracene or its derivatives, such as *algal brown B*, *indanthrene olive G*, and the *cibanon* colours are also sulphide dyes of unknown constitution.

The anthraquinonoid dyes are employed in cotton dyeing much in the same way as the indigoid dyes. Generally speaking, they require, however, a much larger amount of caustic soda in the vat and are not dyed cold, but at a

temperature of 50°-80°. In dyeing light shades, the dye-bath is generally exhausted under these conditions. After dyeing, the goods are soaped hot, a process which in most cases considerably enhances the brilliancy of the colour. With some of the colours, the fastness to bleaching powder is increased by steaming under pressure after dyeing. Although no black anthraquinonoid dyestuff is known, a black of extraordinary fastness can be obtained on cotton by dyeing it first indanthrene green and then subjecting the dyed material to the action of bleaching powder. The colours obtained with the dyes of the anthraquinonoid series are generally somewhat faster to light than those obtained with the indigo dyes. They are not applicable to wool dyeing owing to the necessity of keeping the vat strongly alkaline with caustic soda, with the inherent risk of damaging or destroying the fibre. It has been suggested that a preliminary treatment of the wool with formaldehyde would obviate this difficulty.

In calico printing, the anthraquinonoid dyes are largely used for some of the best classes of work. The usual method of using the indanthrene colours is to print a colour containing the vat dye, stannous chloride, ferrous sulphate and thickening, and after drying to pass rapidly through a hot strong solution of caustic soda. The fixation may also be effected in one operation by using a printing colour containing the vat dye, hydrosulphite-formaldehyde and soda ash, after which the goods are steamed for 5-7 mins. in air-free steam. The glucose process, as described for indigo, is also applicable to vat dyes in general.

In steaming or 'ageing' the vat dyes, it sometimes happens that the colours do not develop satisfactorily on subsequent exposure to the air, and faulty goods thus result. This is due to over-reduction of the vat dye to a stage at which neither air contact nor oxidising agents will develop the colour. See Reinking: Exothermic reactions in the rapid ager, *J. Soc. Dyers*, 1922, 306.

By the introduction of the vat dyes the public demand for fast colours, especially in dyes and printed cotton and linen fabrics, has been met, and it is now possible to obtain by means of them almost any shade fast to washing, light, perspiration, rubbing, and even bleaching powder. It should, however, not be taken for granted that a vat dye is of necessity a fast colour. Those on the market have, however, generally been carefully tested and selected by the makers and usually possess this attribute. Many of the vat dyes are so fast that they can be put through the full bleaching process for cotton pieces without suffering any material diminution of intensity and brilliancy, and advantage is taken of this in the production of white fabrics with coloured stripes or figures. Whereas it was formerly necessary, in order to obtain these effects, to bleach both warp and weft before weaving, the bleaching is now largely effected in the piece and considerable economy is realised. With the exception of indigo, the vat dyes are still too expensive to admit of their being employed for any but the best class of work. This is due in part to the high cost of manufacture, but more especially to the fact that most of them are tinctorially weak, as com-

pared with, for instance, the basic and direct cotton colours. Even indigo itself shows this drawback, but most of the other vat dyes show it to a greater extent.

For the identification of the vat dyes in dyed and printed fabrics, see A. G. Green and G. H. Frank (*J. Soc. Dyers*, 1910, 83), also G. E. Holden (*ibid.* 1909, 47), A. G. Green, W. Gardner, L. Lloyd, and G. H. Frank (*ibid.* 1913, 227), and J. I. M. Jones and W. Kilby (*ibid.* 1925, 127). Indigo can readily be distinguished from the other vat blues by dissolving the fabric in warm 80 p.c. sulphuric acid. The solution is poured into water and filtered through a small asbestos filter. After washing and drying, the residue on the filter is heated to about 100° with concentrated sulphuric acid and again poured into water and filtered. Under these conditions, the indigo is sulphonated and passes into the filtrate with a bright blue colour, whereas the other vat blues remain unaffected. E. K.

VAUQUELINITE. Native lead and copper chromate.

VAUXITE AND PARAVAUXITE. These occur on wavellite in brecciated tin-veins in rhyolite at Llallagua, Oruro. Vauxite occurs as radiating aggregates of sky-blue, triclinic crystals with $a:b:c=1.1510:1:1.2624$, $\alpha=99^\circ 32'$, $\beta=102^\circ 14'$, $\gamma=110^\circ 14'$; $d\ 2.375$, $H\ 3\frac{1}{2}$; refractive indices $\alpha\ 1.551$, $\beta\ 1.555$, $\gamma\ 1.562$, optically positive. Paravauxite forms colourless, triclinic crystals of prismatic habit with good $b\ (010)$ cleavage; $a:b:c=0.5058:1:0.6882$, $\alpha=97^\circ 42'$, $\beta=110^\circ 22'$, $\gamma=100^\circ 56'$; $d\ 2.291$, $H\ 3$; refractive indices $\alpha\ 1.554$, $\beta\ 1.558$, $\gamma\ 1.573$, optically positive. Analyses by J. E. Whitfield gave I for vauxite and II for paravauxite.

FeO	MnO	Al ₂ O ₃	P ₂ O ₅	H ₂ O at 104°	H ₂ O above 104°
I. 19.34	0.18	14.89	31.33	3.68	30.24
II. 15.47	—	17.89	29.80	16.40	20.34

The minerals are readily soluble in hydrochloric acid. The water content of the paravauxite varies considerably with the humidity of the atmosphere. Formulas:

Vauxite: $4\text{FeO}, 2\text{Al}_2\text{O}_3, 3\text{P}_2\text{O}_5, 24\text{H}_2\text{O} + 3\text{H}_2\text{O}$.

Paravauxite:

$5\text{FeO}, 4\text{Al}_2\text{O}_3, 5\text{P}_2\text{O}_5, 26\text{H}_2\text{O} + 21\text{H}_2\text{O}$.

(Samuel G. Gordon, *Proc. Acad. Nat. Sci. Philadelphia*, 1923, 75, 261-270; *Chem. Soc. Abstr.* 1923, 124, ii. 646).

VEGETABLE BUTTER v. **BASSIA OILS**; also **OILS, FIXED, AND FATS**.

VEGETABLE ETHIOPS. A form of charcoal obtained by the incineration of *Fuci*.

VEGETABLE FATS v. **OILS, FIXED, AND FATS**.

VEGETABLE IVORY. The fruit of *Phyt. elephas macrocarpa* (Ruiz. and Pav.) found in Colombia, South America.

VEGETABLE PARCHMENT v. *Parchment paper*, art. **CELLULOSE**.

VEGETABLE SPERMACEI. *Insect waxes*, v. **WAXES**.

VELOCITY OF REACTION v. **CHEMICAL AFFINITY**.

VELLOSINE v. **PERERO BARK**.

VENETIAN CHALK v. **STRAITTE**.

VENETIAN LAKE. *Crimson lake* v. **PIGMENTS**.

VENETIAN RED. *Ferric oxide*.

VENETIAN WHITE. A white lead pigment containing a large percentage of barium sulphate.

VENTILAGO MADRASPATANA (Gerten.) is a large climbing shrub belonging to the order *Rhamnaceae*, the root-bark of which furnishes a dyestuff much valued in Southern India. It is very common in the Western Peninsula from the Konkan southwards, as well as in Ceylon and Burma, and, according to Lostard, it is collected in Mysore at certain periods of the year and exported to other districts of India.

The following are a few of its vernacular names: pitti (*Hindi*); raktapita (*Bengali*); pappili-chakka, surralpattai (*Tamil*); poplichukai (*Kan*); lokandi, kanwai (*Bomb*).

The root-bark appears as dark purplish-brown scales, ribbons, or filaments, the dust from which, when it is ground to powder, irritates the throat in a marked manner. When treated with boiling water or alcohol it gives a red solution, which on addition of caustic alkali, changes to a deep crimson.

Perkin and Hummel (Chem. Soc. Trans. 1894, 65, 923), who examined this dyestuff, extracted the root-bark with carbon disulphide, and obtained in this manner a resinous colouring matter, *ventilagin*, together with the crystalline non-tinctorial substances described below.

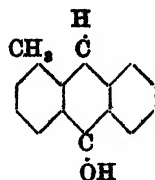
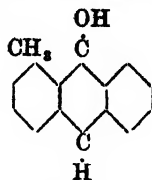
Ventilagin $C_{11}H_{14}O_6$ consists of a reddish-brown brittle resin which, when distilled with zinc-dust, gives *a*-methyl-anthracene, and when treated with zinc-dust in alkaline solution behaves as a derivative of methyl-anthraquinone. Dilute alkalis dissolve it with a purple-violet coloration, and the corresponding salts are obtained as violet precipitates on adding sodium or potassium chlorides to these solutions. According to Perkin and Hummel, ventilagin is possibly allied to alkanin $C_{11}H_{14}O_4$, the colouring matter of alkanet, *Anchusa tinctoria* (Lam.), and may differ from this merely by the possession of two additional hydroxyl groups.

Emodin monomethyl ether $C_{15}H_{12}O_5$, m.p. 200°, consists of orange-red needles, and is identical with that subsequently isolated from the root of the *Polygonum cuspidatum* (Sieb. and Zucc.) (Perkin, Chem. Soc. Trans. 1895, 67, 1084). A similar, if not identical, substance was isolated by Schwabe (Arch. Pharm. 1888, 26, 569), and by Thorpe and Miller (Chem. Soc. Trans. 1892, 64, 6) from the bark of the *Rhamnus frangula* (Linn.), and it is also present in rhubarb and the *Rumex ecklonianus* (L.) and Goa powder.

Trihydroxy-a-methyl-anthranol monomethyl ether (A), $C_{15}H_{12}O_6$, colourless needles, decomposes about 260° before melting, and is soluble in alkaline solutions with a yellowish-brown coloration. On gentle oxidation with chromic acid it is converted into emodin methyl ether, m.p. 300° (Lc), and the same reaction takes place when its alkaline solution is oxidised with hydrogen peroxide. It closely resembles the dehydro-emodin-anthranol monomethyl ether, subsequently isolated from Goa powder by Tutin and Clewer (Chem. Soc. Trans. 1912, 101, 290).

Trihydroxy-a-methylanthranol monomethyl ether (B), $C_{15}H_{12}O_6$, pale yellow needles, m.p. 172°, when oxidised with chromic acid is also

converted into the emodin methyl ether, m.p. 300°. As two methyl anthranols are capable of existence, the isomerism of these compounds may possibly be thus explained:—



Substance $C_{15}H_{12}O_5$, orange-red crystalline powder, m.p. 275°–280°, is soluble in alkaline solutions with an orange-red coloration, and when heated with zinc-dust gives a hydrocarbon which resembles *a*-methyl-anthracene.

Substance $C_{11}H_{12}O_5$ is a chocolate, crystalline powder, soluble in dilute alkali with a yellow coloration, and this solution, on exposure to air, deposits a blue amorphous precipitate.

Dyeing Properties.—On striped printed calico the root-bark gives with alumina mordant a claret-red, not unlike that of alizarin bordeaux; with iron mordant a greyish-lilac, which in strong colours approaches a black; and with a mixture of the two a very purplish dark chocolate. The colours are moderately fast to soap, although considerably behind the alizarin colours in this respect. On oil-prepared calico ventilago gives with alumina mordant a rich claret-brown, with chromium mordant a very black-purple, and with iron mordant a good purplish-black shade. On wool chromium mordant gives a good purplish-brown, alumina a bordeaux red, tin a brighter red similar to an alizarin red, and iron mordant gives dark dull purple and black. On silk similar colours are produced. No difficulty is experienced in dyeing with ventilago, and no additions to the dye-bath are necessary, except in the case of wool, with which it is desirable to add calcium acetate in order to correct the strong acidity of the mordanted fibre. Owing to the slight solubility of the colouring matter in water, the dyeing does not commence until the temperature reaches 70°–80°. The root-bark appears to contain from 8–10 p.c. of ventilagin.

A. G. P.

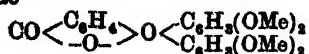
VERATRALBINE, VERATRIDINE, VERATRINE v. CEVADINE.

VERATROLE (*o*-dimethoxybenzene)



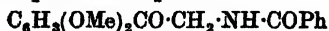
is best obtained by dissolving catechol (100 grms.) in methyl alcohol (200 grms.) mixed with 75 grms. of methyl sulphate. The mixture is cooled to –5°, and 150 grms. of potash dissolved in 350 grms. of water are then added all at once. In 3 mins. the methylation is complete. The product is diluted with water, extracted with ether, and the extract is dried and distilled (Perkin and Weizmann, Chem. Soc. Trans. 1906, 1856). Veratrole is also formed by the distillation of guaiacol with lead oxide (Pechorr and Silberbach, Ber. 1904, 37, 2149). Veratrole forms a crystalline mass, m.p. 15°, b.p. 205°. It yields a number of halogen derivatives (Cousin, Compt. rend. 1898, 127, 759; 1902, 135, 967; Ann. Chim. 1898, [vi] 13, 483); also nitro derivatives (Cousin, Compt. rend. 1902, 134, 290; 135,

967; Salway, Chem. Soc. Trans. 1909, 1163),
a *phthalide*



(Perkin and Weizmann, *l.c.*) and other compounds (Kropp and Decker, Ber. 1909, 42, 1184).

Veratrole reacts with hippuryl chloride in presence of aluminium chloride, forming a crystalline product, m.p. 155°



from which valuable therapeutic products are said to be obtained (D. R. P. 185596; Frdl. 1905-1907, 1184).

For other literature, see Simonsen, Chem. Soc. Trans. 1917, 111, 69, 220; 1918, 22, 782; Jones and Robinson, *ibid.* 1917, 111, 903.

VERBENALIN. A crystalline glucoside found in *Verbena officinalis* (Linn.), m.p. 181.5°; $\alpha_D = -180.3^\circ$. Hydrolysed by emulsin, yielding dextrose (Bourdier, J. Pharm. Chim. 1908, 27, 49, 101).

VERDIGRIS, VERT-DE-GRIS, VERT DE MONTPELIER. Basic acetates of copper v. ACETIC ACID.

VERDITE. An ornamental stone of a rich green colour consisting mainly of hydrated magnesium silicate coloured by chromium. It represents a serpentine rock more or less completely altered to talc. The chromium is probably present as the chrome-mica fuchsite, which was no doubt derived from chromite. The rock shows mottlings of yellowish-green and bluish-green with splashes of brown and yellow, and it takes a high polish. Sp.gr. 2.8; H. 3½. It occurs in the Jamestown series (Swaziland system) of chloritic and talcose schists; and is obtained from small quarries at several places on the banks of the Kaap and North Kaap rivers near Barberton in the Transvaal, and more particularly at the Verdite mines at Jamestown near Barberton, which are worked for talc with gold as a by-product (A. L. Hall, The Geology of the Barberton Gold Mining District, Union of South Africa, Geol. Survey, 1918, Mem. No. 9). L. J. S.

VERDITER, GREEN AND BLUE, v. COPPER.

VERIDIAN. Guignet's green v. CHROMIUM.

VERJUICE. A kind of vinegar containing malic acid made from the juice of the crab-apple.

VERMILION v. MERCURY.

VERMILIONETTE. A red pigment made by adding eosin to white lead, barium sulphate or zinc white.

VERNINE $\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}_3\cdot 2\text{H}_2\text{O}$ found by Schulze (Zeitsch. physiol. Chem. 1885, 9, 420) in seedlings of *Vicia sativa*, and later in a number of other plants. Is identical with *guanosine*, obtained by Levene and Jacobs (Ber. 1909, 42, 2469) by the hydrolysis with water of guanylic acid. M.p. 237°, $[\alpha]_D^{20} = -60.52^\circ$ in alkaline solution. It is hydrolysed by acids to guanine and a pentose, presumably *D*-ribose (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 70, 143).

From the green leaves and berries of the coffee tree a pentoside has been isolated, containing guanine, which is probably identical with *guanosine* obtained by Schulze and Trier from other plants and from 'nucleic acid' by Levene and Jacobs. It is suggested that the

caffeine in the leaves and berries of the coffee tree is derived from *guanosine*, the latter being converted successively into *guanine*, *xanthine*, and *caffeine* by the action of enzymes (T. de A. Camargo, J. Biol. Chem. 1924, 58, 831; J. Soc. Chem. Ind. 1924, 43, B. 312), v. ERGOT.

G. B.

VERONAL. Trade name for diethylmalonylurea $(\text{C}_2\text{H}_5)_2\text{N}[\text{CO}\cdot\text{NH}]_2\text{CO}$, prepared by the condensation of urea and diethyl-malonyl chloride. A white crystalline powder of bitter taste, m.p. 191°. Soluble in water, ether, acetone, acetic ester. Used as a soporific (v. SYNTHETIC DRUGS and PYRIMIDINES). For the chemical detection of veronal poisoning, v. Macadie, Pharm. J. 1913, 90, 134; Richards, Analyst, 1919, 44, 192; van Itallie and van der Veen, Pharm. Weekblad, 1919, 56, 1112; J. Pharm. Chim. 1919, [vii.] 20, 337. Veronal and the malonylureas generally readily condense with xanthidrol to form crystalline dioxanthyl derivatives which may be used for the characterisation and identification of the malonylureas by observation of their melting-points (Fabre, J. Pharm. Chim. 1922, 26, 241). The veronal derivative melts at 245°-246°. Thus, if a solution of 1 grm. of veronal and 2 grms. of xanthidrol in acetic acid is boiled for a few seconds and cooled a crystalline precipitate of a dioxanthylated derivative is formed which can be purified by washing with boiling alcohol and its melting-point determined. In toxicological investigation the veronal has first to be isolated from the viscera. From 100 to 150 grms. of material are digested on a water-bath for 3 hours with a mixture of 95 p.c. alcohol and 5 grms. of tartaric acid, cooled, filtered and concentrated by distillation. The residue is dissolved in 50 c.c. of distilled water, and after being made slightly alkaline, the solution is shaken up several times with ether to eliminate fatty matter. After acidulation with dilute sulphuric acid the liquid is evaporated, and the residue taken up three times with ether which dissolves the veronal. The residue from the extract is purified by dissolving it in water, heating with animal charcoal, filtering and crystallising the filtrate. After several crystallisations the melting-point can be determined. The search for these hypnotic compounds may also be made in the urine, since 60 to 65 p.c. of the veronal absorbed can be found in the urine excreted during the four following days (Analyst, 1922, 47, 523).

VEROPYRIN. Trade name for a mixture of ethylmorphine hydrochloride, veronal-sodium and calcium acetylsalicylate.

VERT DE GUIGNET v. CHROMIUM.

VERVAIN. Cymylacetic aldehyde (1-iso-propyl-4-ethanalbenzene



possesses a strong odour resembling vervain, but not of such delicacy as that of the plant. As it may be easily and economically prepared, it is anticipated that it will be extensively used in synthetic perfumery. It is obtained by condensing magnesium cymyl chloride with ethyl orthoformate, hydrolysing the product with dilute sulphuric acid, and separating the aldehyde by means of its bisulphite compound. It is a pale yellow liquid, b.p. 243°C. (L. Bert,

Comptes rend. 1923, 177, 550-551; J. Soc. Chem. Ind. 1923, 42, 1099 A).

VESALVINE. Syn. for hexamethylenetetramine.

VESIPIRIN. Trade name for phenyl acetosalicylate, v. SALICYLIC ACID and SYNTHETIC DRUGS.

VESTORIEN v. EGYPTIAN BLUE; also ENAMELS.

VESUVIANITE or **IDOCRASE.** A mineral consisting of a complex silicate of calcium and aluminium, together with iron, magnesium, water, fluorine, boron, &c. F. W. Clarke's formula is $R'_4Al_2Ca_2Si_2O_{14}$, where $R'_4 = Ca_2, (AlOH)_2, H_4$, &c. Crystals are tetragonal and usually green or brown in colour; sp.gr. 3.35-3.45; H. 6½. The mineral is of common occurrence in contact-metamorphic rocks, particularly crystalline limestones. Lustrous, brown crystals are common at Monte Somma, Vesuvius (hence the name vesuvianite). Green crystals from Ala in Piedmont are cut as gems at Turin. A compact, massive variety has been found abundantly as blocks and boulders, measuring up to 6 by 3 ft., at several places in California (Siskiyou, Butte, Fresno, and Tulare counties). This has been called *californite* (G. F. Kunz, 1903), and is much used as a gemstone and for larger ornamental objects. It is somewhat translucent, takes a high polish, and ranges from bright green to yellowish-green and white in colour, thus closely resembling jade in appearance (D. B. Sterrett, Min. Res. U.S. Geol. Survey, annual reports for 1909 and 1910.)

L. J. S.

VICINE $C_{10}H_{14}O_2N_4.H_2O$ was discovered by Ritthausen (J. pr. Chem. 1870, [ii.] 1, 336; 1873, [ii.] 7, 374; 1881, [ii.] 24, 202) in the seeds of *Vicia* spp. According to Levene (J. Biol. Chem. 1914, 18, 305; Levene and Senior, *ibid.* 1916, 25, 607) it is a mononucleoside, or glucoside of 2:5-diaminotetrahydropyrimid-4:6-dione (2:5-diamino-uracil) of the following constitution:



It forms needles, m.p. 242°, $[\alpha]_D^{25} -11.7^\circ$. It is hydrolysed by 20 p.c. sulphuric acid at 100° to dextrose and *divicine* (of Ritthausen) = 2:5-diamino-uracil $C_4H_4O_2N_4$. Compare also Johnson, J. Amer. Chem. Soc. 1914, 36, 337; Johnson and Johns, *ibid.* 1914, 36, 545; Fischer, Ber. 1914, 47, 2611; Winterstein, Zeitsch. physiol. Chem. 1919, 105, 258.

Convicine $C_{16}H_{14}O_2N_8.H_2O(?)$ was also found by Ritthausen in vetch seeds and yields on hydrolysis alloxantin, ammonia and a hexose.

G. B.

VICIANIN v. GLUCOSIDES.

VIOLANOSE v. CARBOHYDRATES.

VICTORIA YELLOW. *Gold yellow, Aniline orange, Saffron surrogate.* This colouring matter, introduced by Mottenzwei, under the name of *Victoria yellow* or *aniline orange* (Wag. Jour. 1869, 593), consists of the potassium or ammonium salt of a dinitrocresol (Martius and Wichelhaus, Ber. 2, 206; v. Sommaruga, *ibid.* 2, 579). It is prepared by heating cresol, with three times its weight of sulphuric acid at 100°, until the product is soluble in water. After removing the excess of sulphuric acid by

means of barium carbonate, the cresol-sulphonic acid is converted into potassium salt, which in the dry state is nitrated by introducing it rapidly into about three times its weight of dilute nitric acid (sp.gr.=1.2), and is then poured into water, neutralised with potassium carbonate, and the resulting potassium dinitrocresol crystallised out. Obtained in this way, the colouring matter is a mixture of the potassium salts of dinitro-*o*- and dinitro-*p*-cresol, and varies in colour according to the proportions of these. Thus Victoria yellow is yellowish in colour, and consists chiefly of the potassium salt of dinitro-*o*-cresol (m.p.=86°), which crystallises in yellow needles (Wichelhaus, *ibid.* 7, 176; Piccard, *ibid.* 8, 685), whereas saffron surrogate is distinctly reddish in colour, and consists chiefly (80 p.c. according to Piccard) of the potassium salt of dinitro-*p*-cresol (m.p.=84°), which crystallises in red needles (Armstrong and Field, Chem. News, 27, 318; Hofmann and v. Miller, Ber. 14, 567; Staedel, *ibid.* 14, 900, 906; Nölting and Salis, *ibid.* 14, 986).

Victoria yellow is soluble in water and dyes wool and silk orange, but owing to the fugitive nature of the colour is no longer employed for this purpose. Saffron surrogate is still used to some extent as a colouring matter for butter, margarine, vermicelli, cheese, &c. (Piccard), but this is to be deprecated, since Weyl's experiments show that the compound is poisonous (Ber. 20, 2835; 21, 512). Cf. NITROPHENOLS AND THEIR HOMOLOGUES.

VIENNA BLUE. *Cobalt blue* v. PIGMENTS.

VIENNA GREEN. *Emerald green* v. PIGMENTS.

VIENNA PASTE. A mixture of lime and potash used as a caustic to extirpate malignant growths.

VIFERRAL. A polymerised chloral
($C_2HOC_2H_2$)_x

A white powder, m.p. 153°-155°, sol. in water. Used as a hypnotic.

VIMOPYRIN. Trade name for *p*-phenetidine tartrate.

VINASSE v. SUGAR.

VINE BLACK. *Blue black* v. PIGMENTS.

VINEGAR, AROMATIC. v. ACETIC ACID.

VINEGAR PLANT. v. ACETIC ACID; FERMENTATION.

VINOLINE. A mixture of coal-tar reds, mostly rosaniline salts, used for colouring wines.

VINOPYRIN v. SYNTHETIC DRUGS.

VIOFORM. Trade name for iodochlorohydroxyquinoline. A greyish-green powder used as a bactericide and antiseptic, and as a substitute for iodoform (v. SYNTHETIC DRUGS).

VIOLANE. A variety of the pyroxene (q.v.) group of minerals of a rich violet colour, and occasionally used as an ornamental stone. It is a silicate of calcium, magnesium, aluminium, sodium, iron, and manganese (about 2 p.c. MnO, to which the colour is due). It sometimes forms prismatic crystals of the monoclinic system, but more often compact masses with a lamellar or fibrous structure. It is found, together with other silicates coloured by manganese, in the manganese mines at San Marcel in the Aosta valley, Piedmont. L. J. S.

VIOLANIN v. ANTHOCYANINS.

VIOLANTHRENE v. INDANTHRENE.

VIOLET DE PARIS OR VIOLET DIRECT.

VIOLET DE PARIS or VIOLET DIRECT.
Methyl violet v. TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET 5B, 6B, v. TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET R and RR and 5R. *Hofmann's violet v. TRIPHENYLMETHANE COLOURING MATTERS.*

VIOLIN. An emetic substance contained in the common violet, supposed to be identical with emetine from ipecacuanha root.

VIOLINE or VIOLEIN. A synonym for mauve or aniline purple.

VIOLONES. Coloured anhydro-bases obtained by acting upon pyrylium salts with *p*-hydroxylated phenyl radicles by weak alkalis Dilthey and Burger, Ber. 1921, 54 [B], 825).

VIOLURIC ACID v. PYRIMIDINES.

VIRIDIAN. Hydrated chromium sesquioxide, v. CHROMIUM.

VIRIDINIC ACID v. TANNINS.

VIRIDITE v. THURINGITE.

VISCOSE v. SILK, ARTIFICIAL.

VITAMINS. To deal seriously from a standpoint strictly chemical with substances which have never been isolated in a pure condition is, of course, impossible. The constitution of the peculiar dietary constituents which have been called Accessory Food Factors (Hopkins), or Vitamines (Funk) is as yet entirely unknown. They are not, however, merely hypothetical substances. The evidence for their objective existence is ample enough, but as this evidence is in part, so to speak, of a negative kind, and in any case depends upon studies in which impure preparations have been perforce employed, it calls for critical consideration. The fundamental facts which make necessary a belief in the existence and physiological importance of nutrients differing in kind from those which until lately were alone recognised, can, however, be quite briefly enumerated.

Until fifteen years ago it was generally believed that the efficacy of a diet could be determined by three essential criteria. The first was the obvious one that it should provide enough potential energy for the current dynamic needs of the body. The second was that it should contain a certain minimum of protein, to exercise specific functions which the non-nitrogenous foodstuffs cannot subserve, and the third called for a balanced mineral supply. We now know that these criteria are insufficient. Although data from highly quantitative studies of human and animal nutrition have long existed in great numbers, these data were obtained during the administration of natural food materials. The fats, carbohydrates and proteins contained in these diets were accurately calculated and the effects of their variation evaluated; but that these constituents (with the necessary minerals) were alone responsible for the successful maintenance of the body was an unjustifiable assumption. Quantitatively they account for nearly the whole of the necessary supply, but hundreds of recent experiments and observations have shown that there are other substances in natural foods which, though present in only very small quantities, are yet absolutely essential for proper nutrition. These are the substances which,

pending a knowledge of their nature, it is agreed to call vitamins.

The assumption mentioned in the last paragraph was unjustified, because the food constituents which were thought to cover all needs were never administered in a pure form. It can be shown with the greatest ease that if an animal be supplied with purified protein and pure fats and carbohydrates, together with a salt mixture proved in other associations to be efficient, the food may be well eaten, well digested, and even fully metabolised, yet the animal's nutrition fails, and it finally dies. What, however, endows the phenomena we are considering with their fullest significance is the circumstance that the purified foodstuffs just mentioned become wholly efficient and fully maintain growth, health and activity when material is added to them in amounts so small compared with the whole quantity of food consumed that it would almost be negligible. This material must comprise at least three and probably more vitamins. The extraordinary importance of their nutritional effects and the remarkably small concentration in which these effects are produced are the characteristics which supply the only definition of vitamins at present available.

While, during the first decade of the present century, the facts just mentioned were being established by feeding experiments done mainly upon animals, evidence giving precisely similar indications arose from a new and enlightened study of certain human diseases. It was almost a pure coincidence that these two lines of evidence should have become available contemporaneously. Clear indications showing that the disease, Beri Beri, which mainly—though by no means exclusively—attacks rice-eating populations, is intimately related to diet, was indeed brought forward by Eijkman so far back as 1897. He showed that a condition very similar to the human malady could be induced in fowls by feeding them upon an exclusive diet of polished white rice, while a cure was at once established by adding rice polishings to the diet, or by replacing the polished grain by whole grain. The suggestion given by these experiments was followed up and observations made upon a great number of prisoners in the gaols of Java, and the fact established that Beri Beri is far more frequent among these eating rice deprived of the grain cortex than among those receiving the whole grain. This work was fully confirmed by that of W. Fletcher, published in 1907-8 (Lancet, 1907, 1776). The time was not even then ripe, however, for the simple interpretation of the facts. Only when later studies were published, and in particular those of Frazer and Stanton (Studies from the Inst. for Med. Research, Federated Malay States, No. 12, 1911) did the clear conception arise that the cortex of rice grain, unlike the endosperm, contains a specific substance of unknown nature, but certainly essential to life. It can be supplied in many other foodstuffs besides cereals, but the circumstance that it has a local distribution in grains, together with the one-sided character of Eastern dietaries, conspired to bring the facts to light. The disease scurvy yields even clearer evidence that healthy nutrition calls for a supply of a substance, or substances, not comprised in the ordinary categories of foodstuffs. Its

incidence and cure might, it would seem, have led long ago to a conception of what we should now call a vitamin. Preconceptions and prejudices led, however, to other explanations of the disease. Ultimately, however, though not until about 1912, the convergence of the pathological evidence and that obtained from feeding experiments led to a somewhat sudden emergence of the belief that nutrients must exist with the potent qualities now attributed to vitamins.

Though all attempts to isolate the substances with which we are concerned have so far failed, preparations have been made in a highly concentrated form, and work which, in a limited sense at least, is quantitative, has been done upon them. Certain of the properties of the vitamins are well characterised in a chemical sense, and there is every reason to believe that they will ultimately be isolated. It is as yet impossible, as already admitted, to define them except in terms of their physiological properties. They arise during the growth of the plant. For the animal they are essential, indispensable nutrients. There is clear evidence that at least three distinct members of the class exist and strong suggestions for the existence of a fourth. Each has its own peculiar influence in the body. While we are ignorant of their nature any scheme of nomenclature must be unsatisfactory. It is best to use names without special connotations, and to speak simply of the A-, B- and C-vitamins, respectively, is a justifiable custom.

The B-Vitamin.—Although this substance has received as a prefix the second letter of the alphabet, it will be convenient to deal with it first. It is the so-called 'water soluble vitamin,' or anti-neuritic factor. If it be absent from the diet, a young animal fails to grow, and soon, like the adult animal, develops symptoms which depend upon the occurrence of degenerative changes in the nervous system. In the human individual these symptoms in their more extreme form constitute the picture of Beri Beri. The substance, as its earliest name betokens, is freely soluble in water. It is also soluble in 80 p.c. alcohol, though much less so, if at all, in absolute alcohol. Acidified methyl alcohol extracts it from many tissues containing it. Insoluble in other ordinary organic solvents, it shows a rather remarkable solubility in oleic acid or olive oil (Myers and Voegtlin, *Proc. Nat. Acad. of Sc.* 1920, 6, 3). It is precipitated from aqueous solution by precipitants which throw down organic bases: phosphotungstic acid, for instance, or silver nitrate plus barium hydroxide. This behaviour, together with the fact that very active preparations obtained by the use of these precipitants contained nitrogen, led Funk to believe that the active substance was a base, and, in consequence, he suggested the name *vitamine*, which is now attached to all members of the class. Such precipitation may not be specific, however, but may be due to adsorption. The substance is freely adsorbed, for instance, by fuller's earth, and may be concentrated by its use. This property also allows of its separation from other vitamins (Harden). A silver compound has been prepared with high physiological potency (Seidell, *Pub. Health Reports, Washington*, 1921). The B-vitamin is a relatively stable substance, showing considerable

resistance to destruction by heat. It also resists the effects of acids, but is much more sensitive to alkalis (McCollum and Simmonds, *J. Biol. Chem.* 1918, 33, 55; Daniels and McClurg, *ibid.* 1919, 37, 201). Several attempts to isolate it have been described. Funk obtained, from extracts of rice polishings and yeast, crystalline products capable of curing birds suffering from polyneuritis due to feeding exclusively upon polished rice (*J. Phys. Chem.* 1913, 46, 173). Such results proved, indeed, the potency of almost infinitesimal quantities of the active substance, but unfortunately did not lead to its isolation. Funk believed at first that he had proved it to be a pyrimidine derivative, but when his crystalline preparations were fully purified they were found to be inactive and to consist largely of nicotinic acid, which itself is certainly without the characteristic activity. The purine base adenine has been stated to possess the properties of this vitamin, the remarkable statement being made that this base exists in two forms—one a physiologically active form, which by molecular rearrangement may pass over into a second and inactive form. Certain synthetic α -hydroxy-pyridines have been said to have similar properties (Williams, *J. Biol. Chem.* 1916, 25, 437; Williams and Seidell, *ibid.* 26, 431). These statements have been controverted, however (Harden and Zilva, *Bio-Chem. J.* 1917, 11, 172; Voegtlin and White, *J. of Pharm. and exp. Ther.* 1916, 9, 155). It must be admitted that all attempts to isolate the vitamin or to relate it to known substances have hitherto failed.

The B-vitamin is widely distributed in the tissues of plants, and is stored, though in low concentration, in many animal tissues. In the yeast cell it is especially abundant. As already pointed out, in the grains of cereals it has a local distribution, being present in the germ and pericarp, but not in the endosperm. The relative amounts present in various natural foods have been ascertained by determining on standard lines the minimum quantity of each food which is capable of preventing or curing polyneuritis in birds. The available data will be found in the Report upon Vitamins issued by the Medical Research Council. Such experiments consume much time. Endeavours to use its supposed effects upon the rate of growth of yeast as a measure of its amount have on the whole proved disappointing (*cf.* Funk and Dubin, *J. Biol. Chem.* 1920, 44, 487; McDonald and McCollum, *ibid.* 1921, 46, 525). No chemical means for its estimation are yet available.

Vitamin C.—This is the antiscorbutic substance which, while present in most uncooked foods, is found in exceptionally high concentration in certain fruits and in other vegetable tissues. The very fact that it is an unstable substance—easily destroyed by heat at temperatures not exceptionally high, prone to oxidation, and possibly destroyed under the influence of catalysts present in the tissues themselves—has been in itself the direct cause of much human suffering. Scurvy follows almost automatically when the substance is absent from the diet, and is often a devastating disease in communities cut off from a supply of fresh foods. The tentative efforts which have so far been made to

isolate the antiscorbutic agent, though without success, have served the useful purpose of making it clear that there is a definite substance to look for. We have not to deal with some vague 'property' of fresh foods, nor, as has been thought, with the influence of known constituents such as citrates, malates, or inorganic potassium salts. Because of its great importance to the body and the low concentration in which it is efficient the anti-scorbutic substance must certainly be recognised as a vitamin.

In the endeavour to study its distribution among foodstuffs, and the rate of its destruction by this or that agency, physiological methods have hitherto been perforce employed. For an account of methods whereby highly concentrated preparations of this vitamin are obtained and its main properties demonstrated the papers of Zilva should be consulted (*Bio-Chem. J. passim*). The discovery of even a purely empirical chemical method for estimating the vitamin would certainly be of the utmost practical importance. Determinations of its relative concentrations have been made by observing for each kind of material under study the minimal curative or preventative dose for scurvy in the guinea-pig. This animal reacts in a highly characteristic way when it is deprived of the factor in question, and also when after deprivation a supply is again provided (Axel Holst). Elaborate and careful experiments have been made on these lines (Chick and Hume, 1917, *et al.*). The vitamin is absent from dry cereal foods and from pulses, but appears suddenly in grains, beans, &c., during even the earlier stages of germination. It is present in all fresh vegetables though in varying concentrations. It is usually destroyed when these are dried, though it is stated that very rapid sun drying (an industry in Beluchistan) leaves it largely intact. Its concentration in fruits varies considerably. Those of the genus *Citrus* contain it in relatively large amount—as the long established empirical treatment of scurvy with lime juice would itself suggest. The fact that the concentration differs, however, in the juices of different varieties of citrus has affected the history of anti-scorbutic treatment. On several occasions in the past, and even during the war, 'lime juice' has appeared to fail and faith in its efficacy has consequently wavered. This occurred long ago when in the British Navy the juice of the West Indian lime was substituted for the lemon juice previously used. The explanation came when it was shown that the first-mentioned juice contained no more than one-fourth of the active substance present in the latter. Orange juice, on the other hand, contains about the same proportion as lemon juice (Chick, Hume and Skelton, *Biochem. J.* 12, 131; Davey, *ibid.* 1921, 15, 83). Orange juice retains its activity when wholly freed from its colloids and from citric acid and calcium (Harden and Zilva, *Bio-Chem. J.* 1918, 12, 259; McClendon, *J. Biol. Chem.* 1921, 46, ix.). Orange or lemon juice evaporated to a syrup under reduced pressure at 40°C. or concentrated by rapid methods at higher temperatures, retains its activity (Harden and Robison, *Bio-Chem. J.* 1920, 14, 171). The condition of the vitamin in the tomato is apparently such as to make it exceptionally stable. In all cases a slightly acid reaction in the material makes

for stability. Fresh tomato juice, for instance, boiled for one hour lost 50 p.c. of its activity; boiled for four hours it lost 70 p.c. When the juice was first made slightly alkaline, boiling destroyed it much faster (La Mer, Campbell and Sherman, *Proc. Soc. exp. Biol. and Med.* 1921, 18, 122). In the case of vegetables (cabbage) heating for twenty minutes at 100°C. may destroy 70 p.c. of the anti-scorbutic power (Delf, *Bio-Chem. J.* 1918, 12, 416). Oxidation plays a part in the destruction of this vitamin (Zilva, *Lancet*, 1921, i. 478; Anderson and others, *Science*, 1921, 53, 446). It would seem to be especially rapid in the case of some tissues. Fresh potato has marked anti-scorbutic power, but the juice, unless made acid, quickly loses it even at ordinary temperatures (Berzsonoff, *Compt. rend.* 1921, 173, 417). The anti-scorbutic value of milk, even when fresh, is relatively low, important as the function must be to the infant. The actual concentration of this vitamin (and, indeed, of the other vitamins in cows' milk) depends, however, upon the nature of the food supplied to the cow (Hess and others, *Proc. Soc. exp. Biol. and Med.* 1920, 18, 39; Drummond and others, *Bio-Chem. J.* 1921, 15, 540). The vitamin is largely destroyed by Pasteurisation, and it is becoming well recognised that infants receiving heated milk should be given a ration of fruit juice.

Vitamin A.—The 'Fat soluble' accessory factor. If animals be fed on a synthetic dietary such as that earlier described there may be complete failure of nutrition, even when Vitamins B and C are duly supplied, unless at the same time regard is paid to the nature of the fat comprised in the diet. Most vegetable fats, whether purified or not, prove unable to support nutrition in the circumstances mentioned, while most animal fats are found to be efficient, though in varying degrees. This is of course not due to any differences in the fats as fats. As a source of energy for the animal one type of fat differs but little from any other type. The difference, as abundant evidence proves, is due to the fact that associated with animal fats and not (at least as they appear on the market) with vegetable fats, is a specific substance, not itself a fat or other ester, which is essential to life. While actually made by the plant and present for instance in relative abundance in green leaves, it for some reason does not accompany vegetable oils when these are expressed from plant tissues. When, on the other hand, it is eaten by the animal in its food the substance tends to accumulate in its fatty tissues. It is stored in exceptionally large relative amounts in the livers of fish, but takes its origin from the marine vegetable organisms on which the fish feeds (Hjort, *Proc. Roy. Soc.* 1922, B). As in the case of other vitamins, its relative distribution has been in the main studied by means of standardised feeding experiments, but evidence is accumulating to show that its concentration in a fat is measured by the intensity of a colour reaction produced on the addition of arsenic chloride and certain other reagents (Rosenheim and Drummond, *Bio-Chem. J.* 1925, 19, 753). It is soluble in alcohol, ether, and benzene, and may be extracted, for example, from green leaves by these solvents. The vitamin is stable towards heat, and highly

resistant to the processes involved in saponification. It appears therefore greatly concentrated in the unsaponifiable residue from any fat which contains it. On the other hand, it is easily oxidised, and loses all activity when a fat or oil containing it is thoroughly aerated (Hopkins, *Bio-Chem. J.* 1920, 14, 725). Drummond and his co-workers have shown that when the unsaponifiable material from cod-liver oil is freed as far as possible from cholesterol and distilled in a high vacuum the active vitamin is found in fractions distilling at 184°-220° at pressures of 1 to 2 mm. (*Bio-Chem. J.* 1925, 19, 1047). An ethereal extract of green leaves has been prepared (Osborne and Mendel), of which a daily dose of 30 milligrammes contained enough of the vitamin (doubtless greatly diluted with other substances) to supply the needs of the rat, an animal highly sensitive to deprivation of the substance. Concentrations much greater than this have been obtained from the unsaponifiable residues of cod-liver oil prepared with avoidance of oxidation. Of one such preparation a daily dose of no more than 0.004 mgm. was sufficient to maintain a rat (Paulsen), and very small amounts of such concentrates will serve the purposes of the whole oil in therapeutic practice. The variation in animal fats is great. It has been estimated that cod-liver oil may be 250 times richer in the substance than butter (Zilva and Miura). For the influence of storage and emulsification on the vitamin A in cod-liver oil, see Drummond, Zilva and Coward (*J. Soc. Chem. Ind.* 1924, 43, 236 T).

The following figures have been obtained, representing the relative amount of the fat needed to supply a growing rat with its necessary supply of the vitamin. Crude cod-liver oil 2 mgms., haddock-liver oil 10 to 15 mgms., refined cod-liver oil on sale in this country 10 to 15 mgms., butter 500 mgms. (Zilva and Drummond, *Lancet*, 1921, ii, 753). The effects which follow upon an absence of this vitamin from the food, or a considerable deficiency in the supply, are failure of growth and maintenance, together with a specific form of degenerative changes in the eye, constituting what is known as xerophthalmia. It was for some time believed that the deposition of lime salts in growing cartilage on the lines necessary for the normal formation of bone called for a supply of vitamin A. The work of E. Mellanby has indeed shown clearly that something present in natural animal fats exerts an important influence on this process. When this substance is absent from its food a child becomes prone to develop rickets. It would seem, however, as McCollum and his co-workers were the first to suggest (*J. Biol. Chem.* 1922, 53, 293), that the dietary factor which prevents rickets, while usually associated with vitamin A, is not identical with it. It is a substance less readily oxidised. A fully aerated animal fat will fail to promote growth, but it may efficiently protect the young animal from rickets. It would seem that at least one other vitamin may therefore exist in addition to the three which have been discussed, and it is now usual to speak of this substance as Vitamin D. The remarkable relations between the activity of this food constituent and the effects of light

cannot be here discussed. It is probable that the list of existing vitamins is not exhausted by those discussed. Already there is evidence that a quite specific constituent in the diet is necessary for the maintenance of reproductive functions (Evans and Burr, *Proc. Nat. Acad. Sc.* 1925, 11, 334). F. G. H.

VITELLIN v. PROTEINS.

VITEXIN. The *Vitex littoralis* (A. Cunn.) or 'Puriri' is a large tree, 40-60 feet high, and 3-5 feet in diameter, which grows only in the northern portion of the North Island of New Zealand. The wood affords a very durable timber, and is chiefly used for house blocks, fencing posts, piles for bridges, railway sleepers, &c.

Vitexin, the main colouring matter, is present in the wood in the form of a glucoside which has not yet been isolated. It is prepared by digesting a purified extract of the dyestuff with boiling dilute hydrochloric acid, and by this means separates in the form of a yellow viscous mass. By extracting this crude product with boiling alcohol, a pale yellow crystalline powder remains undissolved, and this, owing to its sparing solubility, is most readily purified by acetylation, and the subsequent hydrolysis of the pure acetyl derivative (Perkin, *Chem. Soc. Trans.* 1898, 74, 1020).

Vitexin consists of minute canary-yellow prismatic or fine hair-like needles, soluble in alkaline solutions with a pale yellow coloration, and from these solutions when boiled it is deposited by acidification in a crystalline condition.

On fusion with alkali vitexin yields *phloroglucinol* and *p-hydroxybenzoic acid*, and when digested with boiling 50 p.c. potassium hydroxide solution *p-hydroxyacetophenone* is also produced. Boiling 15 p.c. nitric acid gives dinitro-*p*-hydroxybenzoic acid, together with a small quantity of *tetranitroapigenin*, m.p. 239°-241°. The formula first assigned to vitexin by Perkin was $C_{15}H_{14}O_7$, and the *acetyl derivative*, colourless prismatic needles, m.p. 251°-256°, was consequently represented as $C_{15}H_{12}O_7(C_2H_3O)_2$. In a later communication in view of its apparent relationship to apigenin, and the difficulty of accounting for the large number of hydroxyl groups which are present, it is suggested by this author (*Chem. Soc. Trans.* 1899, 77, 422) that vitexin is probably a very stable glucoside of apigenin represented by the formula $C_{21}H_{22}O_{10}$. Vitexin is a somewhat feeble colouring matter, and dyes shades similar to those given by apigenin; these, employing woollen cloth mordanted with chromium, aluminium, and tin, are respectively greenish-yellow, pale bright yellow, and pale brown.

In addition to vitexin the wood of the *Vitex littoralis* contains (as glucoside) a small quantity of a second colouring matter, *homovitexin*. It was obtained as a pale yellow powder, m.p. 245°-246°, and is distinguished from vitexin by its ready solubility in alcohol. Fused with alkali it gives phloroglucinol and *p*-hydroxybenzoic acid, and is possessed of feeble dyeing property. The analytical figures approximate to $C_{15}H_{14}O_7$ or $C_{15}H_{12}O_8$.

According to Barger (*Chem. Soc. Trans.* 1906, 89, 1120) the glucoside saponarin, which is present in *Sapindaria officinalis* (Linn.), yields on hydrolysis glucose, saponaretin and a small

VITEXIN.

quantity of vitexin. It is possible that saaponatin and homovitexin are identical. A. G. P.

VITRIFIABLE PIGMENTS v. POTTERY; also **PORCELAIN**

VITRIOL (*vitrum*, 'glass'). An old name for a sulphate, and still frequently applied to the sulphates of certain common metals on account of their vitreous lustre, e.g. white or zinc vitriol $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; blue or copper vitriol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; green or iron vitriol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; red or cobalt vitriol $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. Basic ferric or ferrous-cupric sulphates obtained in the extraction of copper sulphate from ferruginous minerals are known as Admont, Bayreuth, Salzburg vitriols, &c.

VITRIOL, OIL OF. *Vitriolic acid*. Sulphuric acid (*q.v.*).

VITRIOL STONE and COLCOTHAR. Vitriol is the material from which the so-called fuming or Bohemian sulphuric acid was formerly manufactured, and it is obtained from the rock known as vitriol slate ('Vitriolschiefer') in the following manner. Large masses of pyritous slate (which belongs to the Silurian formation, and consists of a quartzose matrix containing pyrites, carbon, and clay) are exposed to the weathering action of the atmosphere for three years. The products of oxidation so formed are ferrous sulphate and sulphuric acid, which latter acts upon the clay, yielding aluminium sulphate and other sulphates. The ferrous sulphate at first formed becomes by oxidation ferric sulphate, which, together with the aluminium sulphate, is the principal product of the weathering of the vitriol slate. Ferrous sulphate remains only in small quantities. The next operation is lixiviation of the mass with water, after which the liquor obtained is concentrated to a density of 40°B., and finally evaporated in pans until, on cooling, a crystalline cake of vitriol stone is obtained. The vitriol stone is now calcined, in order to remove the greater part of its water. The resulting product, when heated to a high temperature in clay retorts, yields sulphur trioxide; and a residue, termed *colcothar*, remains in the retorts. The composition of vitriol stone and colcothar may be seen from the following analyses:—

Vitriol stone.— Fe_2O_3 20.07, Al_2O_3 4.76, FeO 0.64, MnO traces, CaO 0.14, MgO 0.39, K_2O 0.07, Na_2O 0.05, CuO 0.10, SiO_2 0.10, P_2O_5 traces, SO_2 40.51, As traces, H_2O 32.58. Total 99.32; or combining acid oxides and bases: $\text{Fe}_2(\text{SO}_4)_3$ 50.17, $\text{Al}_2(\text{SO}_4)_3$ 11.94, FeSO_4 1.35, MgSO_4 1.17, CaSO_4 0.33, CuSO_4 0.20, K_2SO_4 0.13, Na_2SO_4 0.11, H_2SO_4 1.49, MnO , As , and P_2O_5 traces, SiO_2 0.10, H_2O 3.31—99.29.

Colcothar.— Fe_2O_3 7.62, Al_2O_3 12.53, MgO 3.23, CaO 0.82, SO_2 5.17, SiO_2 1.17, CuO 0.20, H_2O 1.30—99.04 (F. Stolba, B. Königl. Böhm. Gesells. 1885; J. Soc. Chem. Ind. 6, 30).

VIVIANITE. Hydrated ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, crystallised in the monoclinic system. The crystals have a perfect cleavage in one direction, parallel to the plane of symmetry; they are quite soft (H. 1½–2), sectile, and easily bent, being flexible but not elastic. Sp.gr. 2.58–2.68. Crystals from freshly opened rock

cavities are colourless, but on exposure to the air they very soon acquire a greenish-blue tinge, darkening to a characteristic deep indigo-blue. This change in colour is due to a partial oxidation of the iron, which in the black kertschenite $(\text{Fe}, \text{Mn}, \text{Mg})\text{Fe}^{III}(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, from the Kerch peninsula, Crimea, is almost complete. Vivianite is the commonest of the several iron phosphate minerals. The best crystals are found in metalliferous veins, e.g. at Wheal Jane, in Cornwall, with pyrrhotite, and at Leadville in Colorado. Crystals are also found in the interior of fossil shells, e.g. in the iron ores of the Kerch peninsula, Crimea; and also sometimes in bones and horns buried in peat deposits. More often the mineral has the form of a blue earthy powder ('blue iron-earth'), and it is in this form that phosphorus is present in bog iron-ore and other limonitic ores of iron. L. J. S.

VOLBORTHITE. Hydrated basic copper vanadate $(\text{CuOH})_2\text{VO}_4 \cdot 6\text{H}_2\text{O}$, with the copper in part replaced by calcium, barium, and magnesium. It forms olive-green or citron-yellow, pearly scales, which are often aggregated in globular forms. As a dissemination in sandstones of Permian age it occurs over a wide area in Govt. Perm in Russia.

Calciovolborthite is a mineral of very similar appearance and mode of occurrence. It contains, as a rule, rather more calcium and has no water of crystallisation; the composition approximates to the formula $\text{Cu}_2(\text{CuOH})_2(\text{VO}_4)_2$. This is found as golden-yellow or greenish-yellow pearly scales and rosettes on the surfaces of sandstone in Utah, Colorado, and Oregon, and also at Friedrichroda, near Gotha, in Thuringia. On the significance of these occurrences of vanadium and copper minerals in sandstones v. PSITTACINITE. L. J. S.

VOLCANIC GLASS v. OBSIDIAN.

VOLCANIC TUFF v. TUFF.

VOLEMITOL v. CARBOHYDRATES.

VOLUMENOMETER v. SPECIFIC GRAVITY.

VOROBYEVITE v. BERYL.

VRAIC. *Varech*. The French name for kelp, v. IODINE.

VRBAITE. Thallium sulph-arsenite and antimonite $\text{TlAs}_2\text{SbS}_8$ or $\text{Tl}_2\text{S} \cdot 2\text{As}_2\text{S}_3 \cdot \text{Sb}_2\text{S}_3$, containing Tl 32.15 p.c., crystallised in the orthorhombic system. It is greyish-black with metallic lustre, but in thin splinters dark red, and the powder is light red with a yellowish tinge. Sp.gr. 5.3. The small crystals are found embedded in realgar and orpiment, at Alchiar, in Macedonia. Another mineral containing thallium as an essential constituent yielded by this locality is lorandite (*q.v.*). L. J. S.

VULCANISED OILS v. OILS, FIXED, and FATS.

VULCANITE v. RUBBER. Also applied to a nitroglycerin explosive.

VULCAN POWDER v. EXPLOSIVES.

VULPIC or VULPULIC ACID v. LICHENS.

VULPINITE. A variety of anhydrite mixed with silica. That from Vulpino near Bergamo, known as the *Marmo Bardiglio di Bergamo*, takes a fine polish and is used for ornamental purposes.

W

WAD or **BOG-MANGANESE**. A black, earthy mineral consisting mainly of hydrated manganese dioxide, but of variable composition, barium and various other constituents being often present. Many varieties have consequently been distinguished by special names. *Asbolite* or 'earthy cobalt' is a cobaltiferous variety, and *lampadite* contains copper. The mineral may be regarded as an earthy form of psilomelane (*q.v.*); it is so soft and sooty that it soils the fingers, and is sometimes so porous that it floats on water. It has resulted from the weathering and decomposition of other manganese minerals, and is sometimes deposited from solution by springs and in swamps. It is of wide distribution and is mined at many places together with other oxides of manganese. Asbolite is of importance as an ore of cobalt (up to 35 p.c. CoO), as much as 5000 tons per annum having been exported from New Caledonia. L. J. S.

WALNUT HUSKS (*Brous des noix*. Fr.) are employed by the French dyers to give dun colours. The green shells contain *juglone* or *hydroxy-[α]-naphthaquinone*; *v.* NAPHTHALENE.

WALNUT OIL *v.* OILS, FIXED, AND FATS. Walnut oil is obtained from kernels of the walnut tree (*Juglans regia*), which contain from about 65 to 66 p.c. of oil. The best oil is separated by cold expression and from its pale colour is a favourite medium for white paints, and is commonly termed 'nut oil' by artists. It dries more slowly than linseed oil, but yields a more elastic film. In the bromination test it yields from 1.5 to 2 p.c. of an insoluble bromide, which appears to be that of a mixed glyceride.

An oil of similar character is obtained from the seed of the North American walnut, *Juglans niger*. This oil is termed *pecan oil*.

The fruit of *Juglans Siboldiana* gave 26.54 p.c. of kernel, which contained 4.99 p.c. of water, and gave 59.58 p.c. of oil by pressing. The oil has a light yellow colour and no odour, and has the following characters: sp.gr. 0.9332 at 15°; $N_{D^{20}} = 1.4800$; acid value 0.68; Hehner value 92.3; saponification value 191.1; Reichert-Meiss value 0.62; and iodine value (Hübl.) 150.8, and has the properties of a drying oil. C. A. M.

WALSRODE POWDER *v.* EXPLOSIVES.

WARAS, also called 'wars' and 'wurrus', consists of a purplish resinous powder which covers the seed pods of *Flemingia congesta* (Roxb.), an erect woody shrub growing in the thickets and forests of the warmer parts of India. According to Watt (*Dictionary of Economic Products in India*, iii. 482), it is collected also in Africa in the neighbourhood of Harrar, and is sent to Arabia, chiefly to Yemen and Haddramant, where it is used as a dye, as a cosmetic, and as a specific against colds. According to Wardle, waras is distinctly inferior as a dye to kamala, which it closely resembles, and contains only a small amount of colouring matter compared with the yellow vegetable dyes of commerce. It is suitable as a dye for silk rather than for wool, but is quite useless with cotton. It has been

introduced into England from Aden as an adulterant or substitute for kamala (Flückiger and Hanbury's *Pharmacographica*, 1879, 576). Under the microscope waras appears as orange-brown lumps, frequently circular and closely resembling kamala.

Flemingin $C_{12}H_{12}O_4$ (provisional) is a dull orange-red crystalline powder consisting of star-shaped groups of minute prismatic needles, which melt at 171°–172°, and closely resembles the rottlerin of kamala. Solutions of the alkali hydroxides dissolve it with an orange-brown tint, but these solutions when boiled do not deposit resinous matter, as is the case with rottlerin. On fusion with alkali *salicylic acid* and acetic acid are produced.

Silk suspended in a solution of *flemingin* in dilute sodium carbonate, and the whole gradually raised to the boiling temperature, is dyed golden yellow, slightly duller than the shade given by rottlerin; but, on the other hand, *flemingin* possesses much the stronger dyeing power of the two.

In addition to *flemingin* waras contains a trace of a yellow crystalline colouring matter, *homoflemingin*, m.p. 165°–166° ($C=69.97$; $H.=5.75$), together with some quantity of two resinous substances: (a) $C_{12}H_{12}O_3$ (?), m.p. 162°–167°, and (b) $C_{13}H_{14}O_3$ (?), melting below 100°. Fused with alkali these latter gave *salicylic* and *acetic acids*, and appear to be allied to *flemingin*.

Added to a boiling solution of its own weight of sodium carbonate, waras dyes silk golden yellow shades, which are brightened by rinsing in very dilute acetic acid. Contrary to the statement of Wardle, it is to be regarded as a decidedly superior dyestuff to kamala (Perkin, *Chem. Soc. Trans.* 1898, 73, 659). A. G. P.

WASH. The name given to the fermented wort of the distiller.

WATER.**ITS PHYSICAL AND CHEMICAL PROPERTIES.**

Purification.—Because of its solvent action on solids and gases, water is difficult to purify and still more difficult to keep in a pure state. It may be partially freed from dissolved salts by freezing, the ice separating from any unsaturated salt solution containing only the small quantity of the dissolved salt present in the mother liquor included in the ice crystals. The ice separating from, say, sea-water, is fairly free from saline matter. It is not known whether this method of purification eliminates, partially or completely, dissolved gaseous impurities. The method is relatively troublesome and costly, and has not been practically applied.

Water is commonly purified by distillation under atmospheric pressure. When adequate arrangements are made to prevent carrying over of entrained droplets of water formed upon the bursting of steam bubbles, the condensed steam contains only the solid and gaseous impurities it dissolves after condensation. Assuming dust to be excluded, the non-volatile impurities in the distillate will be confined to such traces of

lime, silica, alkalis, tin oxide, etc., as may be derived from condensers and containers, and the volatile impurities, which generally are much the more serious in amount and effect, will comprise volatile organic matter, ammonia, carbon dioxide, oxygen, nitrogen, and the like, originally contained in the raw water and carried over with the steam or dissolved from the atmosphere with which the condensate is in contact.

The proportion of non-volatile impurities may be reduced to insignificance by using suitable material for condensers and containers. Hot, newly condensed water has a much greater solvent action than when cold; therefore a material suitable to contain water for a given purpose may not serve for its condensation. Good resistance glass vessels, which have been freed from superficial soluble matter by blowing steam into them for some hours in such a way that the condensate drains away continuously, after long standing in cold water will yield little impurity to pure water during several weeks. Such glass, so treated, is suitable for the preservation for short periods of cold pure water for all but a few very special purposes. It is unsuitable for condensers, which are usually made of pure block tin or heavily tinned copper. The risk of introducing non-volatile impurity may be reduced by using pure fused silica, or, better, pure tin or silver as the material of condenser and receiver. Occasionally water has been condensed and kept in vessels of gold or platinum, but for all ordinary and most special purposes water condensed in pure tin and kept a short time in steamed resistance glass is quite satisfactory. Water kept in ordinary glass bottles for some weeks or months may dissolve sufficient silica, &c., from the glass to render it unsuitable for ordinary precise analytical work, especially that in which small amounts of silica must be determined.

In the estimation of ammonia in water and for work upon conductivity of dilute solutions, the volatile impurities are much the more serious. Fortunately simple precautions suffice to eliminate them. Organic matter may be destroyed by adding to the raw water in the still a small proportion of potassium permanganate or manganate, with sufficient caustic soda or potash to make the water distinctly alkaline (Stas, *Mém. Acad. Belg.* 1865, 35, 1; *Chem. News*, 1861, 4, 207; 1867, 15, 204). Practically the whole of the carbon dioxide and ammonia will come over with the first 20–30 p.c. of the distillate, and if this be rejected the remaining two-thirds will be pure water.

Many procedures have been described, in which the acidic and basic impurities are retained in the still by added reagents, e.g. aluminium sulphate, potassium hydrogen sulphate or phosphoric acid to retain ammonia, or lime or baryta to retain carbon dioxide (see, e.g. Hulett, *Zeitsch. physikal. Chem.* 1896, 21, 297; Walker and Cormack, *J. Chem. Soc.* 1902, 77, 5; W. R. Bousfield, *ibid.* 1905, 87, 740; 1912, 101, 1443). Some workers have obtained fair conductivity distilled water by redistillation of laboratory distilled water without added reagents (see Bousfield, *l.c.*; Hartley, Campbell and Poole, *J. Chem. Soc.* 1906, 83, 428; Thole, *ibid.* 1912, 101, 207).

In a simpler method for the positive chemical elimination of basic and acidic impurities in one operation, a large glass flask containing an aqueous solution of 10 p.c. potassium dichromate and 5 p.c. sulphuric acid is heated, raw water is run in at a rate equal to the rate of evaporation, and the steam is led through a second flask, also heated, containing saturated baryta solution and then condensed in tin (Moseley and Myer, *J. Amer. Chem. Soc.* 1918, 40, 1409: this method was partially employed by Paul, *Zeitsch. Elektrochem.* 1914, 20, 179).

But still simpler methods are effective. It has long been known that ordinary 'conductivity' water, having a conductivity about 1.0×10^{-6} mho (1 gemmho) is materially improved by contact with an atmosphere freed from carbon dioxide, e.g. by enclosure over lime or even by passing through it clean air from the open, whilst it deteriorates markedly in contact with air contaminated by human breath or by flames (Kohlrausch, *Zeit. physikal. Chem.* 1902, 42, 193).

If a current of purified air be passed through such water heated nearly to its boiling-point in a quartz still, and the water distilling under these conditions be condensed in block tin and collected in quartz, it has a conductivity of $0.05-0.07 \times 10^{-6}$ mho at 18° (Weiland, *J. Amer. Chem. Soc.* 1918, 40, 131). Such water compares favourably with the purest conductivity water prepared by distilling repeatedly *in vacuo* in sealed glass vessels and had a conductivity of 0.043×10^{-6} mhos at 18° (Kohlrausch and Heydweiller, *Zeitsch. physikal. Chem.* 1894, 14, 317; Kohlrausch, *Proc. Roy. Soc.* 1903, 71, 338). This method is applicable only to those cases where carbon dioxide is the sole impurity, but the same principles have been applied in a method, applicable to all types of water, first described by Bourdillon (*J. Chem. Soc.* 1913, 103, 791) and elaborated by Clevenger (*J. Ind. Eng. Chem.* 1919, 11, 964). Raw water containing potassium bisulphate or phosphoric acid is distilled, and the steam is carefully scrubbed and separated from spray and led into a long vertical tube through which a current of purified air passes from the bottom upward. The upper end of this tube is surrounded by a water-jacket maintained nearly at 100°, which, therefore, condenses, but does not cool, the major portion of the steam; the uncondensed steam escapes either to the air or to a second condenser. The hot condensate which flows down the walls of the tube in contact with pure air, is cooled by a cold-water jacket surrounding the lower part of the tube and passes away by a syphon. The apparatus is best constructed wholly of copper heavily tinned and soldered with pure tin. Thus it is not difficult to prepare water having a conductivity about 0.05×10^{-6} mho, but it cannot be preserved save under rigid exclusion of atmospheric carbon dioxide. In contact with clean air its conductivity increases to a limiting value of about 0.75×10^{-6} mho, which is that of a solution of carbonic acid in equilibrium with the $0.035 (\pm 0.004)$ volume p.c. of carbon dioxide present in air (Kendall, *J. Amer. Chem. Soc.* 1916, 38, 1480). Kendall has suggested that as such a solution is permanent it is preferable to use it and correct for its

known conductivity rather than to use water of lower conductivity, the correction for which must be uncertain (Kendall, J. Amer. Chem. Soc. 1916, 38, 2460; *q.v.* also for a full discussion and bibliography of previous work on the preparation of conductivity water).

Pure water has been prepared in other ways. Baker found that pure water prepared by the union of pure and dry hydrogen and oxygen differs in some respects from ordinary pure water. If steam from pure water be passed through a red-hot silica tube and then condensed in silica and Jena glass, the condensate acts upon pure 1 p.c. sodium amalgam much more slowly than do other types of water. This inactivity is independent of the conductivity of the water, and there is evidence that it is due to the absence from such water of traces of hydrogen peroxide which constitute a normal impurity in ordinary pure water (Baker and Parker, J. Chem. Soc. 1913, 103, 2060; Parker, *ibid.* 2071).

Pure water may also be prepared by dehydrating pure hydrates, *e.g.* hydrated barium chloride or telluric acid, H_2TeO_6 , by heat; but the method has usually been applied to obtain very small, accurately known, amounts of water in closed apparatus, and little or nothing is known of the properties of such water.

THE RELATION OF PRESSURE AND TEMPERATURE FOR STEAM, WATER, AND ICE.

The pressure, temperature, volume, and state of aggregation of water are, of course, interdependent, and it is thus difficult to discuss separately the effect of variation of any one or two of these factors. Possibly the simplest method is to discuss first the relations of pressure and temperature for the various states of aggregation, and then consider the effect upon volume of varying temperature and pressure considered separately.

Fig. 1 is the complete pressure-temperature diagram for water, except that to save space the steam-line ΔJ is not continued to the critical point at which it terminates, viz. $374^\circ C.$ and 217 atm. The diagram is defective also in that the line ALM stands for the vapour-pressure curves of both ice and supercooled water, which are in fact distinct but by an amount entirely inappreciable on the scale of pressure necessarily adopted. The line AL represents the vapour pressure of supercooled water, which has been measured down to -16.3° and is given in Table 1; the line AM shows the vapour pressure of ice which has been measured down to about -70° , and is given in Table 2 from -80° to 0° . The maximum difference between the vapour pressures of ice and supercooled water is 0.200 mm. at -11.7° .

The vapour pressure of water has been the subject of much accurate experimental work. The data given in Table 3 from 0° – 100° and in Table 4 from 100° – 370° , and represented on the diagram by the line ΔJ , are the values regarded as most probable.

The area below the line MJ represents the vapour phase, and water as we know it at or near atmospheric pressure, is, on the scale of Fig. 1, represented by little more than the thickness of that line.

For many purposes the changes in the boiling-point of water attending small changes of pressure are of great practical importance. At pressures in the neighbourhood of 1 atm. the value of dt/dp for $dp=1$ mm. of mercury is 0.0376° (Wiebe, *Zeitsch. für Instrumentkunde*, 1893, 13, 329); and the precise values of the boiling-point of water at pressures from 720–800 mm. of mercury are given in a form convenient for reference in Table 5.

Our knowledge of the rest of the PT diagram, covering a range of temperature from -80° to $+80^\circ$ at pressures from 1 to over 20,000 $kgm./cm.^2$, rests upon the work of Tammann as confirmed and extended by Bridgman. The principal numerical data are given in Tables 6 and 7, which show respectively the variations in the melting-points and transition-points of the various forms of ice with variation in pressure; their significance is evident from a consideration of Fig. 1. The line AB represents the equilibrium between water and ordinary ice, Ice I. At pressures above about 2000 $kgm./cm.^2$, whatever the temperature, Ice I cannot exist, but changes into one of the denser forms of ice, II or III, the equilibria between which and Ice I are represented respectively by $K'GB$ and KGB . The line $K'G$ represents stable equilibrium between Ice I and Ice II, whereas KG is the locus of equilibrium between Ice I and Ice III in a metastable condition. Ice III has a stable existence only in the range of temperature and pressure denoted by the area $BCFG$, within which are smaller areas (shown on a larger scale in the upper part of Fig. 1) in which labile modifications of Ice I and Ice III, called respectively Ice I' and Ice III', can exist. The inter-relation of these forms is not as yet well understood.

Two other still denser forms of ice exist at higher pressures. Ice V is in equilibrium with Ice III at about 3500 $kgm./cm.^2$ over a small range of temperature in the neighbourhood of -20° ; its equilibrium with Ice II has been followed over a small range only, the point x being conjectural. The stable equilibrium between Ice V and water, indicated by the line cn , has been traced some distance into the area of Ice III as shown, Ice V being here metastable. Above a pressure of about 6500–8000 $kgm./cm.^2$ Ice V and Ice II are converted into Ice VI, the only form observed at higher pressures. Its equilibrium with liquid water is represented by the line pn , and it is remarkable that at the highest pressures this form is stable at temperatures up to 75° . The existence of metastable Ice VI in equilibrium with liquid water has been traced along the line dp' for a considerable distance in the area of Ice V. The estimated densities of the different forms of ice are:—Ice II 1.03; Ice III 1.04; Ice V 1.06; Ice VI 1.09; as compared with ordinary ice 0.92 and water=1.00.

It must be understood that the evidence for the separate existence of these solids is simply the abrupt change of volume, manifested by a sudden drop of pressure, observed in a mass of water subject to isothermal compression. The conclusion that these are solid forms of water is supported by the fact that Ice III formed at about 2500 $kgm./cm.^2$ and -20° to -30° , if cooled first to -80° and then

WATER.

to -190° , is so stabilised that it is unchanged on release of pressure and can be examined in the open. At temperatures of -120° or higher under atmospheric pressure, the clear trans-

parent Ice III breaks down into a bulky powder of Ice I (Tammann, *Zeitsch. anorg. Chem.* 1909, 63, 285; *Zeitsch. physikal. Chem.* 1910, 72, 609; 1913, 84, 257).

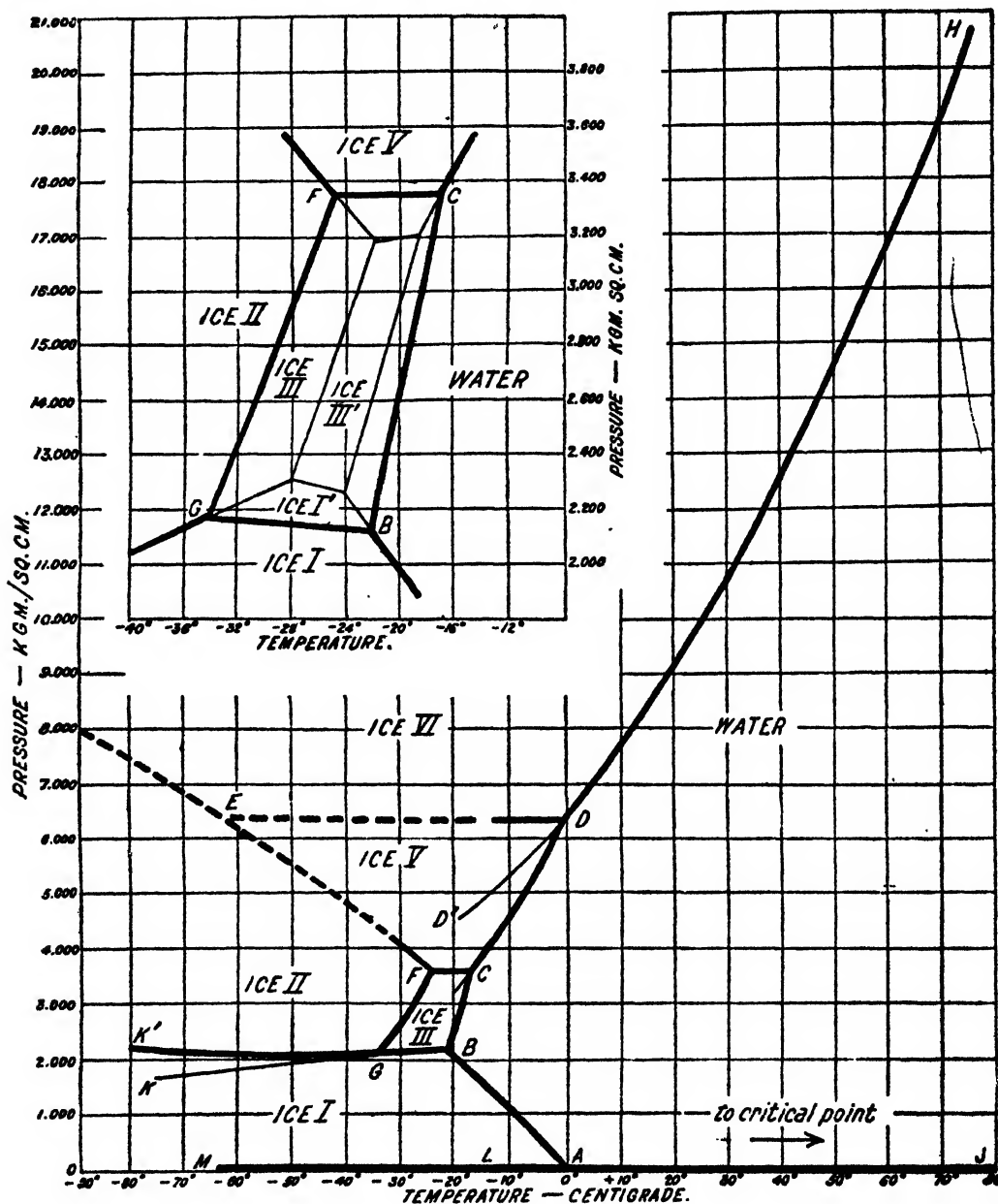


FIG. 1.

The extent and direction of the line DN are of great theoretical interest, inasmuch as they lend no support to the hypotheses which have been formulated (Poynting, *Phil. Mag.* 1881, [5], 12, 32; Ostwald, *Lehrbuch der allgemeinen Chemie*, 1902, 2, ii. 373, 391; Tammann, *Kristallisieren und Schmelzen*, Leipzig, 1903, 29; Planck, *Wied. Ann.* 1882, 15, 446) that the melting-point curve of a solid should, with increase of pressure, terminate at a critical end-point analogous to that of the boiling-point curve, or pass through a maximum.

Critical data for water have been determined as follows:

Authority	Crit. temp.	Crit. press.	Crit. vol.	Crit. density
1	358.1°	—	0.001874	0.429
2	364.3°	194.6 atm.	0.003864	—
3	374.0°	217.0 atm.	—	—

(1) Nadejdine, *J. Russ. Phys. Chem. Soc.* 1885, 9, 721.
 (2) Battelli, *Mem. Torino*, 1890, [ii.] 41.
 (3) Holborn and Baumann, *Ann. Physik.* 1910, 31, 945.

TABLE 1.

VAPOUR PRESSURE OF SUPER-COOLED WATER.

Millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

Temp. degrees	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
—16	—	—	—	—	—	—	—	—	—	1·315
—15	1·326	1·337	1·349	1·360	1·371	1·383	1·394	1·406	1·417	1·429
—14	1·441	1·453	1·465	1·477	1·489	1·501	1·513	1·525	1·538	1·551
—13	1·564	1·577	1·590	1·603	1·616	1·630	1·643	1·657	1·670	1·684
—12	1·698	1·712	1·726	1·740	1·754	1·768	1·783	1·797	1·812	1·826
—11	1·841	1·856	1·871	1·886	1·901	1·917	1·932	1·948	1·963	1·979
—10	1·995	2·001	2·028	2·044	2·060	2·077	2·093	2·109	2·126	2·143
—9	2·160	2·177	2·195	2·212	2·230	2·248	2·266	2·284	2·302	2·320
—8	2·338	2·357	2·375	2·394	2·412	2·431	2·450	2·469	2·489	2·509
—7	2·529	2·549	2·569	2·589	2·609	2·629	2·650	2·670	2·691	2·712
—6	2·733	2·754	2·775	2·797	2·818	2·840	2·862	2·884	2·906	2·928
—5	2·950	2·972	2·994	3·017	3·040	3·063	3·086	3·110	3·134	3·158
—4	3·182	3·206	3·230	3·254	3·278	3·303	3·328	3·353	3·380	3·404
—3	3·429	3·455	3·481	3·508	3·534	3·561	3·588	3·615	3·642	3·669
—2	3·697	3·724	3·752	3·780	3·808	3·836	3·865	3·894	3·923	3·952
—1	3·981	4·011	4·041	4·071	4·101	4·131	4·162	4·193	4·224	4·256
—0	4·287	4·318	4·350	4·382	4·414	4·447	4·480	4·513	4·546	4·579

Scheel and Heuse, Ann. Physik. 1909, [iv.] 29, 723.

TABLE 2.

VAPOUR PRESSURE OF ICE IN MILLIMETRES OF MERCURY.

Measured at 0°C. and at sea-level in latitude 45° over a range of temperatures on the constant volume gas-thermometer (Reichsanstalt scale).

Temp. °C.	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
—60	mm. 0·006	mm. 0·006	mm. 0·006	mm. 0·006	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007
—59	0·007	0·007	0·007	0·008	0·008	0·008	0·008	0·008	0·008	0·008
—58	0·008	0·008	0·009	0·009	0·009	0·009	0·009	0·009	0·009	0·009
—57	0·009	0·010	0·010	0·010	0·010	0·010	0·010	0·011	0·011	0·011
—56	0·011	0·011	0·011	0·012	0·012	0·012	0·012	0·012	0·013	0·013
—55	0·013	0·013	0·013	0·014	0·014	0·014	0·014	0·014	0·015	0·015
—54	0·015	0·015	0·015	0·016	0·016	0·016	0·016	0·017	0·017	0·017
—53	0·017	0·018	0·018	0·018	0·018	0·019	0·019	0·019	0·019	0·019
—52	0·020	0·020	0·020	0·020	0·021	0·021	0·021	0·022	0·022	0·022
—51	0·022	0·023	0·023	0·023	0·024	0·024	0·024	0·025	0·025	0·025
—50	0·026	0·026	0·027	0·027	0·027	0·028	0·028	0·029	0·029	0·029
—49	0·030	0·030	0·030	0·031	0·031	0·031	0·032	0·032	0·032	0·033
—48	0·033	0·034	0·034	0·034	0·035	0·035	0·036	0·036	0·037	0·037
—47	0·038	0·038	0·039	0·039	0·040	0·040	0·041	0·041	0·042	0·042
—46	0·043	0·043	0·044	0·044	0·045	0·045	0·046	0·046	0·047	0·047
—45	0·048	0·048	0·049	0·049	0·050	0·050	0·051	0·051	0·052	0·052

TABLE 2.—VAPOUR PRESSURE OF ICE IN MILLIMETRES OF MERCURY (*continued*)

Temp. °C.	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
—44	0·053	0·053	0·054	0·054	0·055	0·055	0·056	0·057	0·057	0·058
—43	0·059	0·059	0·060	0·061	0·062	0·063	0·064	0·065	0·065	0·066
—42	0·067	0·068	0·068	0·069	0·070	0·071	0·072	0·072	0·073	0·074
—41	0·075	0·076	0·077	0·078	0·079	0·079	0·080	0·081	0·082	0·083
—40	0·084	0·085	0·086	0·087	0·088	0·089	0·090	0·091	0·092	0·093
—39	0·095	0·096	0·097	0·098	0·100	0·101	0·102	0·103	0·104	0·105
—38	0·106	0·107	0·109	0·110	0·112	0·113	0·115	0·116	0·117	0·119
—37	0·120	0·122	0·123	0·125	0·126	0·127	0·129	0·130	0·132	0·134
—36	0·135	0·137	0·138	0·140	0·142	0·144	0·145	0·147	0·148	0·150
—35	0·152	0·153	0·155	0·156	0·158	0·160	0·162	0·163	0·165	0·167
—34	0·169	0·171	0·172	0·174	0·176	0·177	0·179	0·181	0·183	0·185
—33	0·187	0·189	0·191	0·193	0·195	0·197	0·199	0·201	0·203	0·205
—32	0·207	0·209	0·211	0·213	0·215	0·217	0·220	0·222	0·225	0·227
—31	0·229	0·231	0·234	0·236	0·239	0·242	0·244	0·247	0·249	0·252
—30	0·255	0·258	0·260	0·263	0·266	0·269	0·272	0·274	0·277	0·280
—29	0·283	0·286	0·289	0·292	0·295	0·298	0·301	0·305	0·308	0·311
—28	0·314	0·318	0·321	0·325	0·328	0·331	0·335	0·338	0·342	0·345
—27	0·349	0·353	0·356	0·360	0·364	0·368	0·372	0·375	0·379	0·383
—26	0·387	0·391	0·395	0·399	0·403	0·407	0·411	0·416	0·420	0·425
—25	0·429	0·435	0·439	0·443	0·448	0·453	0·457	0·462	0·466	0·471
—24	0·476	0·481	0·485	0·490	0·495	0·500	0·505	0·511	0·516	0·521
—23	0·526	0·532	0·537	0·543	0·548	0·554	0·559	0·565	0·570	0·576
—22	0·582	0·588	0·594	0·600	0·606	0·612	0·618	0·624	0·630	0·636
—21	0·642	0·648	0·652	0·661	0·667	0·674	0·681	0·687	0·694	0·701
—20	0·708	0·715	0·722	0·729	0·736	0·743	0·750	0·758	0·765	0·772
—19	0·780	0·787	0·795	0·802	0·810	0·818	0·826	0·834	0·842	0·850
—18	0·858	0·867	0·875	0·884	0·892	0·901	0·909	0·918	0·926	0·935
—17	0·944	0·953	0·962	0·971	0·980	0·989	0·998	1·008	1·017	1·027
—16	1·037	1·047	1·057	1·067	1·077	1·087	1·097	1·108	1·118	1·128
—15	1·139	1·150	1·160	1·171	1·182	1·193	1·204	1·216	1·227	1·238
—14	1·250	1·261	1·273	1·284	1·296	1·308	1·320	1·333	1·345	1·357
—13	1·369	1·382	1·394	1·407	1·420	1·433	1·446	1·460	1·473	1·486
—12	1·500	1·514	1·527	1·541	1·555	1·569	1·584	1·598	1·613	1·627
—11	1·642	1·657	1·672	1·687	1·702	1·718	1·733	1·749	1·764	1·780
—10	1·796	1·812	1·828	1·845	1·861	1·877	1·894	1·911	1·928	1·946
—9	1·963	1·981	1·999	2·016	2·034	2·052	2·070	2·088	2·106	2·125
—8	2·145	2·164	2·183	2·203	2·222	2·241	2·261	2·281	2·301	2·321
—7	2·342	2·362	2·383	2·404	2·425	2·446	2·467	2·489	2·510	2·532
—6	2·554	2·577	2·599	2·622	2·645	2·668	2·691	2·714	2·738	2·761
—5	2·785	2·809	2·833	2·857	2·881	2·906	2·931	2·956	2·982	3·008
—4	3·034	3·060	3·086	3·112	3·139	3·166	3·193	3·220	3·248	3·276
—3	3·304	3·332	3·361	3·390	3·419	3·448	3·477	3·507	3·536	3·566
—2	3·597	3·627	3·658	3·689	3·720	3·751	3·783	3·815	3·847	3·879
—1	3·912	3·945	3·979	4·012	4·045	4·079	4·113	4·147	4·182	4·216
—0	4·251	4·286	4·322	4·358	4·395	4·431	4·468	4·505	4·542	4·579

TABLE 3.

VAPOUR PRESSURE OF WATER FROM 0° TO 100°.

In millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

(Landolt-Börnstein: *Physikalische-Chemische Tabellen.*)

Temp. degrees	Tenths of a Degree									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	4·579	4·613	4·647	4·681	4·715	4·750	4·785	4·820	4·855	4·890
1	4·926	4·962	4·998	5·034	5·070	5·107	5·144	5·181	5·219	5·256
2	5·294	5·332	5·370	5·408	5·447	5·486	5·525	5·565	5·605	5·645
3	5·685	5·725	5·766	5·807	5·848	5·889	5·931	5·973	6·015	6·058
4	6·101	6·144	6·187	6·230	6·274	6·318	6·363	6·408	6·453	6·498
5	6·543	6·589	6·635	6·681	6·728	6·775	6·822	6·869	6·917	6·965
6	7·013	7·062	7·111	7·160	7·209	7·259	7·309	7·360	7·411	7·462
7	7·513	7·565	7·617	7·669	7·722	7·775	7·828	7·882	7·936	7·990
8	8·045	8·100	8·155	8·211	8·267	8·323	8·380	8·437	8·494	8·551
9	8·609	8·668	8·727	8·786	8·845	8·905	8·965	9·025	9·086	9·147
10	9·209	9·271	9·333	9·395	9·458	9·521	9·585	9·649	9·714	9·779
11	9·844	9·910	9·976	10·042	10·109	10·176	10·244	10·312	10·380	10·449
12	10·518	10·588	10·658	10·728	10·799	10·870	10·941	11·013	11·085	11·158
13	11·231	11·305	11·379	11·453	11·528	11·604	11·680	11·756	11·833	11·910
14	11·987	12·065	12·144	12·223	12·302	12·382	12·462	12·543	12·624	12·706
15	12·788	12·870	12·953	13·037	13·121	13·205	13·290	13·375	13·461	13·547
16	13·634	13·721	13·809	13·898	13·987	14·076	14·166	14·256	14·347	14·438
17	14·530	14·622	14·715	14·809	14·903	14·997	15·092	15·188	15·284	15·380
18	15·477	15·575	15·673	15·772	15·871	15·971	16·071	16·171	16·272	16·374
19	16·477	16·581	16·685	16·789	16·894	16·999	17·105	17·212	17·319	17·427
20	17·535	17·644	17·753	17·863	17·974	18·085	18·197	18·309	18·422	18·536
21	18·650	18·765	18·880	18·996	19·112	19·231	19·349	19·468	19·587	19·707
22	19·827	19·948	20·070	20·193	20·316	20·440	20·565	20·690	20·815	20·941
23	21·068	21·196	21·324	21·453	21·583	21·714	21·845	21·977	22·110	22·243
24	22·377	22·512	22·648	22·785	22·922	23·060	23·198	23·337	23·476	23·616
25	23·766	23·897	24·038	24·182	24·326	24·471	24·617	24·764	24·912	25·060
26	25·209	25·359	25·509	25·660	25·812	25·964	26·117	26·271	26·426	26·582
27	26·739	26·897	27·055	27·214	27·374	27·535	27·696	27·858	28·021	28·185
28	28·349	28·541	28·680	28·847	29·015	29·184	29·354	29·525	29·697	29·870
29	30·043	30·217	30·392	30·568	30·745	30·923	31·102	31·281	31·461	31·642
30	31·824	32·007	32·191	32·376	32·561	32·747	32·934	33·122	33·312	33·503
31	33·695	33·888	34·082	34·276	34·471	34·667	34·864	35·062	35·261	35·461
32	35·663	35·865	36·068	36·272	36·477	36·683	36·891	37·099	37·308	37·518
33	37·729	37·942	38·155	38·369	38·584	38·801	39·018	39·237	39·457	39·677
34	39·898	40·121	40·344	40·569	40·796	41·023	41·251	41·480	41·710	41·942
35	42·175	42·409	42·644	42·880	43·117	43·355	43·595	43·836	44·078	44·320
36	44·563	44·808	45·054	45·301	45·549	45·799	46·050	46·302	46·556	46·811
37	47·067	47·324	47·582	47·841	48·102	48·364	48·627	48·891	49·157	49·424
38	49·692	49·961	50·231	50·502	50·774	51·048	51·323	51·600	51·879	52·160
39	52·442	52·725	53·009	53·294	53·580	53·867	54·156	54·446	54·737	55·030
40	55·32	55·61	55·91	56·21	56·51	56·81	57·11	57·41	57·72	58·03
41	58·34	58·65	58·96	59·27	59·58	59·90	60·22	60·54	60·86	61·18
42	61·50	61·82	62·14	62·47	62·80	63·13	63·46	63·79	64·12	64·46
43	64·80	65·14	65·48	65·82	66·16	66·51	66·86	67·21	67·56	67·91
44	68·26	68·61	68·97	69·33	69·69	70·05	70·41	70·77	71·14	71·51
45	71·88	72·25	72·62	72·99	73·36	73·74	74·12	74·50	74·88	75·26
46	75·65	76·04	76·43	76·82	77·21	77·60	78·00	78·40	78·80	79·20
47	79·60	80·00	80·41	80·82	81·23	81·64	82·05	82·46	82·87	83·29
48	83·71	84·13	84·56	84·99	85·42	85·85	86·28	86·71	87·14	87·58
49	88·02	88·46	88·90	89·34	89·79	90·24	90·69	91·14	91·59	92·05

TABLE 3.—VAPOUR PRESSURE OF WATER FROM 0° TO 100° (continued).

Temp. degrees	Tenths of a Degree									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
50	92·51	92·97	93·43	93·89	94·36	94·82	95·29	95·77	96·24	96·72
51	97·20	97·68	98·16	98·64	99·13	99·62	100·11	100·60	101·10	101·59
52	102·09	102·59	103·10	103·60	104·11	104·62	105·13	105·64	106·16	106·68
53	107·20	107·72	108·24	108·76	109·29	109·82	110·35	110·89	111·43	111·97
54	112·51	113·05	113·59	114·14	114·69	115·24	115·80	116·36	116·92	117·48
55	118·04	118·60	119·16	119·73	120·31	120·89	121·47	122·05	122·63	123·21
56	123·80	124·40	124·99	125·58	126·18	126·78	127·38	127·99	128·60	129·21
57	129·82	130·44	131·06	131·68	132·30	132·92	133·55	134·18	134·81	135·45
58	136·08	136·72	137·36	138·01	138·66	139·31	139·96	140·62	141·28	141·94
59	142·60	143·27	143·94	144·61	145·28	145·96	146·64	147·32	148·00	148·69
60	149·38	150·07	150·77	151·47	152·17	152·87	153·58	154·29	155·00	155·71
61	156·43	157·15	157·87	158·59	159·32	160·06	160·80	161·58	162·28	163·02
62	163·77	164·52	165·27	166·02	166·78	167·54	168·30	169·07	169·84	170·61
63	171·38	172·16	172·94	173·73	174·52	175·31	176·10	176·90	177·70	178·50
64	179·31	180·11	180·92	181·74	182·56	183·38	184·20	185·03	185·86	186·70
65	187·54	188·38	189·22	190·06	190·91	191·77	192·63	193·49	194·35	195·22
66	196·09	196·96	197·84	198·72	199·60	200·48	201·37	202·26	203·16	204·06
67	204·96	205·87	206·78	207·69	208·61	209·53	210·45	211·37	212·30	213·23
68	214·17	215·11	216·06	217·01	217·96	218·91	219·87	220·83	221·79	222·76
69	223·73	224·71	225·69	226·67	227·66	228·65	229·65	230·65	231·65	232·65
70	233·7	234·7	235·7	236·7	237·8	238·8	239·8	240·9	241·9	242·9
71	243·9	245·0	246·0	247·1	248·1	249·2	250·3	251·4	252·4	253·5
72	254·6	255·7	256·8	257·9	259·0	260·1	261·2	262·3	263·5	264·6
73	265·7	266·8	268·0	269·1	270·3	271·4	272·6	273·7	274·9	276·0
74	277·2	278·4	279·5	280·7	281·9	283·1	284·3	285·5	286·7	287·9
75	289·1	290·3	291·5	292·8	294·0	295·2	296·5	297·7	298·9	300·2
76	301·4	302·7	303·9	305·2	306·5	307·7	309·0	310·3	311·6	312·9
77	314·1	315·4	316·7	318·0	319·3	320·7	322·0	323·3	324·7	326·0
78	327·2	328·7	330·0	331·4	332·7	334·1	335·5	336·8	338·2	339·6
79	341·0	342·4	343·8	345·2	346·6	348·0	349·4	350·8	352·2	353·7
80	355·1	356·5	358·0	359·4	360·9	362·4	363·8	365·3	366·8	368·3
81	369·7	371·2	372·7	374·2	376·7	377·3	379·8	380·3	381·8	383·4
82	384·9	386·4	388·0	389·5	391·1	392·7	394·2	395·8	397·4	399·0
83	400·6	402·2	403·8	405·4	407·0	408·6	410·3	411·9	413·5	415·2
84	416·8	418·4	420·1	421·7	423·4	425·1	426·8	428·5	430·2	431·9
85	433·6	435·3	437·0	438·7	440·5	442·2	443·9	445·7	447·4	449·2
86	450·9	452·6	454·4	456·2	458·0	459·7	461·5	463·3	465·1	466·9
87	468·7	470·5	472·3	474·1	476·0	477·8	479·7	481·5	483·4	485·2
88	487·1	489·0	490·9	492·7	494·6	496·5	498·4	500·3	502·3	504·2
89	506·1	508·0	510·0	511·9	513·9	515·9	517·8	519·8	521·8	522·8
90	525·76	527·76	529·77	531·78	533·80	535·82	537·86	539·90	541·95	544·00
91	546·05	548·11	550·18	552·26	554·35	556·44	558·53	560·64	562·75	564·87
92	566·99	569·12	571·23	573·40	575·55	577·71	579·87	582·04	584·22	586·41
93	588·60	590·80	593·00	595·21	597·43	599·66	601·89	604·13	606·38	608·64
94	610·90	613·17	615·44	617·72	620·01	622·31	624·61	626·92	629·24	631·57
95	633·90	636·24	638·59	640·94	643·30	645·67	648·05	650·43	652·82	655·22
96	657·62	660·03	662·45	664·88	667·31	669·75	672·20	674·66	677·12	679·59
97	682·07	684·55	687·04	689·54	692·05	694·57	697·10	699·63	702·17	704·71
98	707·27	709·83	712·40	714·98	717·56	720·15	722·75	725·36	727·98	730·61
99	733·24	735·88	738·53	741·18	743·85	746·52	749·20	751·89	754·58	757·29
100	760·00	762·72	765·45	768·19	770·93	773·68	776·44	779·22	782·00	784·78
101	787·57	790·37	793·18	796·00	798·2	801·66	804·50	807·35	810·21	813·08

Scheel and Heuse, Ann. Physik. 1910, [iv.] 31, 715; Holborn and Henning, *ibid.* 1908, [iv.] 26, 833. Confirmed at 25° by the dynamic method by Derby, Daniels and Gutzke J. Amer. Chem. Soc. 1914, 36, 793; and from 25°–80° by direct weighing by Krasnopski, J. Phys. Chem. 1910, 14, 499.

TABLE 4.

VAPOUR PRESSURE OF WATER FROM 100° TO 370°.

In millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

(Landolt-Börnstein: *Physikalische-Chemische Tabellen*.)

Temp. T _{max} °C.	Units °C.									
	0	1	2	3	4	5	6	7	8	9
100	mm. 760.0	mm. 787.6	mm. 815.9	mm. 845.1	mm. 875.1	mm. 906.1	mm. 937.0	mm. 970.6	mm. 1,004.4	mm. 1,038.9
110	1,074.6	1,111.2	1,148.8	1,187.5	1,227.3	1,268.1	1,310.0	1,353.0	1,397.3	1,442.7
120	1,489.2	1,536.9	1,586.6	1,636.4	1,687.9	1,741.0	1,795.2	1,850.9	1,907.7	1,966.4
130	2,026.3	2,087.6	2,150.6	2,214.8	2,280.9	2,347.4	2,416.5	2,486.3	2,560.8	2,636.0
140	2,710.7	2,788.4	2,867.7	2,949.1	3,032.0	3,116.9	3,203.7	3,292.5	3,383.1	3,475.9
150	3,570.7	3,661.4	3,766.3	3,867.1	3,970	4,076	4,184	4,293	4,405	4,520
160	4,636	4,755	4,877	5,001	5,128	5,257	5,388	5,522	5,659	5,799
170	5,942	6,066	6,234	6,394	6,539	6,695	6,854	7,016	7,181	7,350
180	7,521	7,695	7,873	8,054	8,238	8,425	8,617	8,811	9,008	9,209
190	9,414	9,622	9,833	10,049	10,267	10,490	10,717	10,946	11,181	11,419
200	11,661	11,907	12,157	12,410	12,668	12,931	13,199	13,470	13,745	14,025
210	14,308	14,597	14,891	15,187	15,490	15,795	16,107	16,423	16,744	17,070
220	17,399	17,735	18,076	18,421	18,770	19,126	19,486	19,852	20,223	20,600
230	20,982	21,369	21,761	22,158	22,562	22,972	23,387	23,807	24,234	24,666
240	25,105	25,548	25,999	26,454	26,917	27,387	27,861	28,341	28,829	29,322
250	29,823	30,329	30,843	31,363	31,891	32,424	32,964	33,512	34,066	34,628
260	35,195	35,769	36,351	36,940	37,537	38,141	38,751	39,370	39,995	40,629
270	41,270	41,919	42,575	43,239	43,911	44,591	45,279	45,975	46,680	47,398
280	48,115	48,845	49,582	50,329	51,085	51,850	52,624	53,408	54,200	55,002
290	55,812	56,630	57,460	58,302	59,151	60,007	60,877	61,756	62,642	63,542
300	64,450	65,780	66,290	67,230	68,170	69,130	70,090	71,070	72,060	73,050
310	74,050	75,080	76,100	77,140	78,190	79,250	80,320	81,400	82,490	83,600
320	84,710	85,840	86,900	88,140	89,300	90,470	91,660	92,860	94,080	95,310
330	96,540	97,790	99,050	100,300	101,610	102,910	104,230	105,560	106,900	108,250
340	109,620	111,000	112,390	113,790	115,220	116,650	118,110	119,570	121,060	122,540
350	124,040	125,560	127,090	128,640	130,200	131,780	133,370	134,990	136,620	138,280
360	139,940	141,620	143,320	145,050	146,790	148,570	150,370	152,180	154,020	155,870
370	157,750	159,660	161,670	163,580	165,530	—	—	—	—	—

Holborn and Henning, Ann. Physik. 1908, [iv.] 26, 833; Holborn and Baumann, *ibid.* 1910, v. 31, 945; Crafts, J. Chim. Phys. 1915, 13, 105.

TABLE 5.

BOILING-POINT OF WATER AT VARIOUS BAROMETRIC PRESSURES.

Barometric pressure in mm. of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

Press. mm.	Tenths of a millimeter									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
720	98·494°	497	501	505	509	513	517	520	524	528
721	532	536	540	544	547	551	555	559	563	567
722	571	574	578	582	586	590	593	597	601	605
723	609	613	617	620	624	628	632	636	640	644
724	648	652	655	659	663	667	671	675	678	682
725	98·686°	689	693	697	701	705	709	712	716	720
726	724	728	732	735	739	743	747	751	755	758
727	762	766	770	774	777	781	785	789	793	797
728	801	804	808	812	816	819	823	827	831	835
729	839	843	846	850	854	858	861	865	869	873
730	98·877°	880	884	888	892	896	899	903	907	911
731	915	918	922	926	930	934	937	941	945	949
732	953	956	960	964	968	972	975	979	983	987
733	991	994	998	*002	*006	*010	*013	*017	*021	*025
734	99·029°	032	036	040	044	048	051	055	059	063
735	99·067°	070	074	078	082	085	089	093	097	101
736	105	109	112	116	119	123	127	131	135	138
737	142	146	150	153	157	161	165	169	172	176
738	180	184	187	191	195	199	203	206	210	214
739	218	221	225	229	233	236	240	244	248	252
740	99·255°	259	263	267	270	274	278	282	285	289
741	293	297	300	304	308	312	316	319	323	327
742	331	334	338	342	346	349	353	357	361	364
743	368	372	376	379	383	387	391	394	398	402
744	406	409	413	417	421	424	428	432	436	439
745	99·443°	447	451	454	458	462	466	469	473	477
746	481	484	488	492	495	499	503	507	510	514
747	518	522	525	529	533	537	540	544	548	551
748	555	559	563	566	570	574	578	581	585	589
749	593	596	600	604	607	611	615	619	622	626
750	99·630°	633	637	641	645	648	652	656	659	663
751	667	671	674	678	682	686	689	693	694	700
752	704	708	712	715	719	723	726	730	734	738
753	741	745	749	752	756	760	764	767	771	775
754	778	782	786	790	793	797	801	804	808	812
755	99·815°	819	823	827	830	834	838	841	845	849
756	852	856	860	863	867	871	875	878	882	886
757	889	893	897	900	904	908	911	915	919	923
758	926	930	934	937	941	945	948	952	956	959
759	963	967	970	974	978	982	985	989	993	996

TABLE 5.—BOILING-POINT OF WATER AT VARIOUS BAROMETRIC PRESSURES (*continued*).

Press. mm.	Tenths of a millimetre									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
760	100·000°	004	007	011	015	018	022	026	019	033
761	037	040	044	048	052	055	059	063	066	070
762	073	077	081	085	088	092	096	099	103	107
763	110	114	118	121	125	129	132	136	140	143
764	147	151	154	158	162	165	169	173	176	180
765	100·184°	187	191	195	198	202	206	209	213	216
766	220	224	227	231	235	238	242	246	249	253
767	257	260	264	268	271	275	279	283	286	290
768	293	297	300	304	308	311	315	319	322	326
769	330	333	337	341	344	348	352	355	359	363
770	100·366°	370	373	377	381	384	388	392	395	399
771	402	406	410	414	417	421	424	428	432	435
772	439	442	446	450	453	457	461	464	468	472
773	475	479	483	486	490	493	497	501	504	508
774	511	515	519	522	526	530	533	537	540	544
775	100·547°	551	555	559	562	566	569	573	577	580
776	584	588	591	595	598	602	606	609	613	616
777	620	624	627	631	634	638	642	645	649	653
778	656	660	663	667	671	674	678	681	685	689
779	692	696	699	703	707	710	714	718	721	725
780	100·728	732	735	739	743	746	750	753	757	761
781	764	768	772	775	779	782	786	789	793	797
782	800	804	807	811	815	818	822	825	829	833
783	836	840	843	847	851	854	858	861	865	869
784	872	876	879	883	886	890	894	897	901	904
785	100·908°	912	915	919	922	926	929	933	937	940
786	944	947	951	954	958	962	965	969	972	976
787	980	984	988	991	995	998	*002	*006	*009	*013
788	101·016°	020	023	027	030	034	037	040	044	047
789	051	054	058	062	065	069	072	076	079	083
790	101·087°	090	094	097	101	104	108	112	115	119
791	122	126	129	133	136	140	144	147	151	154
792	158	161	165	168	172	176	179	183	186	190
793	194	197	201	204	208	211	215	218	222	225
794	229	232	236	239	243	246	250	254	257	261
795	101·265°	269	272	276	279	283	287	290	294	297
796	300	303	307	310	314	317	321	324	328	332
797	335	339	342	346	349	353	356	360	363	367
798	371	375	378	382	385	388	392	395	399	402
799	406	409	413	416	420	423	427	430	434	437
800	101·441°	—	—	—	—	—	—	—	—	—

Holborn and Henning, Ann. Physik. 1908, [iv.] 26, 833.

TABLE 6.
MELTING-POINT OF ICE AT HIGH PRESSURE.
(Landolt-Börnstein: *Physikalische-Chemische Tabellen.*)

Solid phases: triple points	Pressure kgm./cm ² .	Melting-point	Reference
Ice I. (AB)	0	0·0°	
	336	-2·5	1
	500	-4·1	3
	615	-5·0	1
	675	-5·53	2
	859	-7·46	2
	890	-7·5	1
	1,000	-8·7	3
	1,099	-9·75	2
	1,141	-10·42	2
	1,155	-10·0	1
	1,353	-12·74	2
	1,410	-12·5	1
	1,500	-14·0	3
	1,597	-15·66	2
	1,625	-15·0	1
	1,835	-17·5	1
	2,000	-20·3	3
	2,042	-20·0	1
	2,200	-22·1	1
Ice I. ; Ice III. (B)	2,115	-22·0	3
	2,200	-22·0	1
Ice III. (BC)	2,115	-22·0	3
	2,510	-20·0	3
Ice III. ; Ice V. (C)	2,910	-18·5	3
	3,530	-17·0	3
Ice V. (CD)	3,140	-20·0	3
	3,800	-15·0	3
	4,510	-10·0	3
	5,540	-5·0	3
Ice V. ; Ice VI. (D)	6,360	0·0	3
	6,380	+0·16	3
	4,500	-18·0	3
	4,790	-15·0	3
	5,280	-10·0	3
	5,810	-5·0	3
	6,360	0·0	3
	6,500	+1·1	3
	7,000	+5·0	3
	7,640	+10·0	3
Ice VI. (DH)	8,000	+12·6	3
	8,310	+15·0	3
	9,000	+20·0	3
	10,590	+30·0	3
	12,390	+40·0	3
	14,430	+50·0	3
	16,690	+60·0	3
	17,840	+64·3	3
	19,670	+72·15	3
	20,670	+76·35	3

1. Tammann, Ann. Physik. 1900, [iv.] 2, 6.
2. Tammann, Zeitsch. physikal. Chem. 1910, 72, 609.
3. Bridgman, Proc. Roy. Acad. 1912, 47, 441.

TABLE 7.
INTER-RELATIONS OF THE STABLE FORMS OF ICE.

Solid phases: triple points	Pressure kgm./cm. ²	Transition points	Reference
Ice I.; Ice III. (BG)	2,103	-20.0°	3
	2,156	-30.8	3
	2,178	-40.0	3
	2,160	-50.0	3
	2,117	-60.0	3
Ice I.; Ice II. Ice III. (G)	2,220	-80.0	1
	2,170	-34.7	3
	2,240	-37.0	1
	2,164	-35.0	3
	2,072	-45.0	
Ice I.; Ice II. (KG)	1,980	-55.0	
	1,886	-65.0	
	1,794	-75.0	
	2,230	-34.0	
Ice II.; Ice III. (FG)	2,530	31.0	
	2,910	-28.0	
	3,370	-25.0	

THE RELATION OF VOLUME AND TEMPERATURE
AT MODERATE PRESSURES FOR STEAM,
WATER, AND ICE.

It is convenient next to consider the relation
of the volume of unit mass of water to tem-

perature at ordinary or moderate pressures,
and the available data are presented in a further
series of tables. Table 8 shows the specific
volume in c.c. per gram of saturated water
vapour corresponding to each degree of temper-
ature from 0°-180°; the specific volume of

TABLE 8.
SPECIFIC VOLUME OF SATURATED WATER VAPOUR.

In cubic centimetres per gram, at temperatures on the constant volume gas-thermometer
(Reichsanstalt) scale.

Tempera- ture. Tens of degrees	Degrees									
	0	1	2	3	4	5	6	7	8	9
0°	205,000	191,400	178,700	167,100	156,300	146,300	137,000	128,300	120,300	112,600
10	105,900	99,400	93,390	87,770	82,550	77,660	73,090	68,850	64,870	61,150
20	57,660	54,400	51,350	48,500	45,820	43,310	40,950	38,740	36,660	34,710
30	32,880	31,160	29,540	28,010	26,570	25,230	23,950	22,750	21,620	20,550
40	19,540	18,590	17,690	16,840	16,040	15,280	14,560	13,880	13,240	12,630
50	12,050	11,500	10,980	10,490	10,030	9,585	9,165	8,766	8,388	8,028
60	7,686	7,360	7,049	6,753	6,472	6,205	5,951	5,710	5,480	5,261
70	5,050	4,850	4,659	4,477	4,303	4,136	3,978	3,826	3,681	3,542
80	3,410	3,284	3,163	3,046	2,935	2,828	2,727	2,629	2,536	2,447
90	2,361	2,279	2,200	2,124	2,051	1,981	1,914	1,850	1,788	1,728
100	1,671.0	1,617.0	1,564.0	1,513.0	1,465.0	1,418.0	1,373.0	1,329.0	1,287.0	1,247.0
110	1,209.0	1,172.0	1,136.0	1,101.0	1,068.0	1,036.0	1,005.0	974.4	945.5	917.5
120	890.7	864.9	839.7	815.5	792.0	769.4	747.5	726.5	706.1	686.4
130	667.3	648.8	631.0	613.8	597.1	581.1	565.5	550.3	535.6	521.4
140	507.7	494.4	481.6	469.1	457.1	445.4	434.0	423.0	412.4	402.1
150	391.1	382.4	372.9	363.8	355.0	346.4	338.0	329.9	321.9	314.3
160	306.8	299.6	292.6	285.9	279.3	272.8	266.6	260.6	254.7	248.9
170	243.3	237.9	232.6	227.5	222.4	217.5	212.8	208.2	203.7	199.3
180	195.1	—	—	—	—	—	—	—	—	—

Calculated by Holborn, Scheel and Henning (Wärmetabellen, 1919) from the results of Holborn and Henning (Ann. Physik. 1906, [iv.] 28, 833) and Henning (ibid. 1906, [iv.] 31, 649; 1909, [iv.] 39, 441). See also J. Southern, Phil. Mag. 1903, 17, 120.

superheated steam is similarly given at 10° intervals of temperature and for pressures from 1-19 kgm./cm.² in Table 9.

The specific volume is given for super-cooled water from -13° to 0° in Table 10, and for stable water from 0°-35° by tenths of a

degree in Table 12, from 30°-100° by degrees in Table 14, and, under pressure of the saturated vapour for ten-degree intervals, from 100°-320° in Table 15. For convenience, the same data in terms of specific gravity are given also in Tables 10, 11, 13 and 15.

TABLE 9.

SPECIFIC VOLUME OF SUPERHEATED STEAM.

Cubic centimetres per gram (M. Jakob, Zeits. Ver. Ing. 1912, 56, 1980).

Temperature	Pressure in kilograms per square centimetre.									
	1	3	5	7	9	11	13	15	17	19
Saturation temperature.	1728.1	618.2	382.6	278.5	219.5	181.3	154.6	134.6	119.3	107.1
110	1781.6	—	—	—	—	—	—	—	—	—
120	1830.2	—	—	—	—	—	—	—	—	—
130	1878.9	—	—	—	—	—	—	—	—	—
140	1927.3	630.5	—	—	—	—	—	—	—	—
150	1975.5	647.6	—	—	—	—	—	—	—	—
160	2023.7	664.6	392.3	—	—	—	—	—	—	—
170	2071.6	681.4	403.0	283.3	—	—	—	—	—	—
180	2119.6	698.1	413.6	291.3	223.2	—	—	—	—	—
190	2167.4	714.6	423.9	299.2	229.6	185.2	—	—	—	—
200	2215.2	731.1	434.2	306.8	235.9	190.6	159.1	135.9	—	—
220	2310.7	763.9	454.4	321.7	247.9	200.9	168.3	144.3	125.9	111.3
240	2406.0	796.4	474.4	336.4	259.7	210.8	177.0	152.0	133.0	118.0
260	2501.1	828.8	494.2	350.9	271.2	220.5	185.3	159.5	139.7	124.2
280	2596.0	861.1	514.0	365.3	282.6	230.0	193.5	166.8	146.3	130.2
300	2690.9	893.2	533.7	379.5	293.9	239.3	201.6	173.9	152.7	135.9
350	2927.9	973.3	582.4	414.7	321.7	262.4	221.4	191.3	168.3	150.1
400	3164.3	1052.9	630.6	449.6	349.1	285.0	240.7	210.9	183.4	163.7
450	3400.6	1132.3	678.6	484.2	376.2	307.4	259.7	224.8	198.1	177.1
500	3636.4	1211.3	726.2	518.4	402.9	329.4	278.5	241.2	212.6	190.1
550	3872.2	1290.2	773.8	556.8	429.5	351.2	297.1	257.3	226.9	202.9

TABLE 10.

SPECIFIC GRAVITY AND SPECIFIC VOLUME OF WATER BELOW 0°.

Temperature	Specific gravity (1)	Specific volume	
		(1)	(2)
-13	—	—	1.00308
-12	—	—	1.00271
-11	—	—	1.00237
-10	0.99815	1.00186	1.00207
-9	0.99843	1.00167	1.00175
-8	0.99869	1.00131	1.00150
-7	0.99892	1.00108	1.00128
-6	0.99912	1.00088	1.00105
-5	0.99930	1.00070	1.00082
-4	0.99945	1.00055	1.00062
-3	0.99958	1.00042	1.00045
-2	0.99970	1.00031	1.00033
-1	0.99979	1.00021	1.00023
0	0.99987	1.00013	1.00013

1. Weidner, Pogg. Ann. 1866, 129, 300; Rosetti, Ann. Chim. 1866, [iv.] 17, 320.
2. Mohler, Phys. Review, 1912, 35, 236.

TABLE 11.

DENSITY OF WATER IN GRAMS PER CUBIC CENTIMETRE.

At temperatures from 0° to 35° on the constant volume gas-thermometer (Reichsanstalt) scale.

(Landolt-Börnstein : *Physikalische-Chemische Tabellen.*)

Degrees.	Tenths of a degree									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.999,868	874	881	887	893	899	905	911	916	922
1	927	932	936	941	945	950	954	957	961	965
2	968	971	974	977	980	982	985	987	989	991
3	992	994	995	996	997	998	999	999	000*	000*
4	1.000,000	000	000	999*	999*	998*	997*	996*	995*	993*
5	0.999,992	990	989	986	984	982	979	977	974	971
6	968	965	962	958	954	951	947	943	938	934
7	929	925	920	915	910	904	899	893	888	882
8	876	870	864	857	851	844	837	830	823	816
9	808	801	793	785	778	769	761	753	744	736
10	727	718	709	700	691	681	672	662	652	642
11	632	622	612	601	591	580	569	558	547	536
12	525	513	502	490	478	466	454	442	429	417
13	404	391	379	366	353	339	326	312	299	285
14	271	257	243	229	215	200	186	171	156	141
15	126	111	096	081	065	050	034	018	002	986*
16	0.998,970	953	937	920	904	887	870	853	836	819
17	801	784	766	749	731	713	695	677	659	640
18	622	603	585	566	547	528	509	490	471	451
19	432	412	392	372	352	332	312	292	272	251
20	230	210	189	168	147	126	105	083	062	040
21	019	997*	975*	953*	931*	909*	887*	864*	842*	819*
22	0.997,797	774	751	728	705	682	659	635	612	588
23	565	541	517	493	469	445	421	396	372	347
24	323	298	273	248	223	198	173	147	122	096
25	071	045	019	994*	968*	941*	915*	889*	863*	836*
26	0.996,810	783	756	730	703	676	648	621	594	567
27	539	512	484	456	428	400	372	344	316	288
28	259	231	202	174	145	116	087	058	029	000
29	0.995,971	941	912	882	853	823	793	763	733	703
30	673	643	613	582	552	521	491	460	429	398
31	367	336	305	273	242	211	179	148	116	084
32	052	020	988*	956*	924*	892*	859*	827*	794*	762*
33	0.994,729	696	663	630	597	564	531	498	464	431
34	398	364	330	296	263	229	195	161	126	092
35	058	023	989*	954*	920*	885*	850*	815*	780*	745*

TABLE 12.

SPECIFIC VOLUME OF WATER IN CUBIC CENTIMETRES PER GRAM.

At temperatures from 0° to 35° on the constant volume gas-thermometer (Reichsanstalt) scale.

Degrees.	Tenths of a Degree									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.000,132	126	119	113	107	101	095	089	084	079
1	073	069	064	059	055	051	047	043	039	035
2	032	029	026	023	020	018	016	013	011	009
3	008	006	005	004	003	002	001	001	000	000
4	000	000	000	001	001	002	003	004	005	007
5	008	010	012	014	016	018	021	023	026	029
6	032	035	039	042	046	050	054	058	062	066
7	071	075	080	085	090	096	101	107	112	118
8	124	130	137	143	149	156	163	170	177	184
9	192	199	207	215	223	231	239	247	256	264
10	273	282	291	300	309	319	328	338	348	358
11	368	378	388	399	409	420	431	442	453	464
12	476	487	499	511	522	534	547	559	571	584
13	596	609	622	635	648	661	675	688	702	715
14	729	743	757	772	786	800	815	830	844	859
15	874	890	905	920	936	951	967	983	999	015*
16	1.001,031	048	064	081	098	114	131	148	165	183
17	200	218	235	253	271	289	307	325	343	361
18	380	399	417	436	455	474	493	513	532	551
19	571	591	610	630	650	671	691	711	732	752
20	773	794	815	836	857	878	899	921	942	964
21	985	007*	029*	051*	073*	096*	118*	140*	163*	186*
22	1.002,208	231	254	277	300	324	347	370	394	418
23	441	465	489	513	538	562	586	611	635	660
24	685	710	735	760	785	810	835	861	886	912
25	938	964	990	016*	042*	068*	094*	121*	147*	174*
26	1.003,201	227	254	281	308	336	363	390	418	445
27	473	501	529	556	585	613	641	669	698	726
28	755	783	812	841	870	899	928	957	987	016*
29	1.004,046	075	105	135	165	194	225	255	285	315
30	346	376	407	437	468	499	530	561	592	623
31	655	686	717	749	781	812	844	876	908	940
32	972	005*	037*	070*	102*	135*	167*	200*	233*	266*
33	0.005,299	332	365	399	432	465	499	533	566	600
34	634	668	702	736	771	805	839	874	908	943
35	978	013*	047*	082*	118*	153*	188*	223*	259*	294*

TABLE 13.
DENSITY OF WATER FROM 30° TO 100°.

Tens of Degrees	Degrees									
	0	1	2	3	4	5	6	7	8	9
30	0.99567	537	505	473	440	406	371	336	299	262
40	224	186	147	107	066	024	*982	*940	*896	*852
50	0.98807	762	715	669	621	573	525	475	425	375
60	324	272	220	167	113	059	005	*950	*894	*838
70	0.97781	723	666	607	548	489	429	368	307	245
80	183	121	057	*994	*930	*865	*800	*734	*668	*601
90	0.96534	467	399	330	261	192	122	051	*981	*909
100	0.95838	765	693	—	—	—	—	—	—	—

TABLE 14.
SPECIFIC VOLUME OF WATER FROM 30° TO 100°.

Tens of Degrees.	Degrees									
	0	1	2	3	4	5	6	7	8	9
30	1.00435	466	497	530	563	598	633	669	706	743
40	782	821	861	901	943	985	*028	*072	*116	*162
50	1.01207	254	301	349	398	448	498	548	600	652
60	705	758	813	867	923	979	*036	*093	*151	*210
70	1.02270	330	390	452	514	576	639	703	768	833
80	899	965	*032	*099	*168	*237	*306	*376	*447	*518
90	1.03590	663	736	810	884	959	*035	*111	*188	*265
100	1.04343	422	501	—	—	—	—	—	—	—

Thiessen, Wiss. Abh. Phys.-Tech. Reichsanstalt, 1904, 4, 1.

TABLE 15.
DENSITY AND SPECIFIC VOLUME OF WATER FROM 100° TO 320°.

Temperature.	Density	Specific Volume
100°	0.9585	1.0433
110	0.9510	1.0515
120	0.9434	1.0601
130	0.9352	1.0693
140	0.9264	1.0794
150	0.9173	1.0902
160	0.9075	1.1019
170	0.8973	1.1145
180	0.8866	1.1279
190	0.8750	1.1429
200	0.8628	1.1590
210	0.850	1.177
220	0.837	1.195
230	0.823	1.215
240	0.809	1.236
250	0.794	1.259
260	0.779	1.283
270	0.765	1.308
280	0.75	1.34
290	0.72	1.38
300	0.70	1.42
310	0.68	1.46
320	0.66	1.51

and Young, Phil. Trans. 1893, 183, 168; Waterston, Phil. Mag. 1893, [iv.] 23, 114; and Hirn, Ann. Chim. 1866, [iv.] 10, 32.

TABLE 16.
DENSITY AND EXPANSIBILITY OF ICE.

Date	Au- thority	Method of experiment	Kind of ice	Natural ice		Artificial ice	
				Density		Density	
1845	1	Weighing in liquid .	Natural .	0.9179	0.0001125		
1845	2	Direct measurement of linear coefficient .	Artificial				0.0001593
1845	3	Dilatometric . .	Not stated		[0.0001050]		[0.0001050]
1852	4	Dilatometric . .	Artificial .			0.91567	0.0001585
1862	5	Neutral equilibrium in liquid (chloroform and petroleum) .	Artificial .				0.9177
1870		Dilatometric . .	Artificial .				0.91674
		(Dilatometric . .	Artificial .				0.91619
			Artificial .				0.91603
1899	7	Weighing in liquid (refined petroleum)	Natural (icicles)	0.91795			
			Natural (new pond ice)	0.91792			
			Natural (pond ice, 1 year old)	0.91623			
		Volume by displace- ment . .	Natural (new pond ice)	0.91760			
		Direct measurement of linear coefficient .	Artificial .				0.0001620
1901	8	Weighing in water .	Natural (old and new)	0.91661			
1902	9	Direct weighing of buoyancy in mercury .	Artificial .			0.9160	0.000152
Means, neglecting results of No. 3				0.9174	0.0001125	0.9165	0.000158

1. Brunner, Pogg. Ann. 1845, 64, 116.
2. Struve, Pogg. Ann. 1845, 66, 298.
3. Marchand, J. prakt. Chem. 1845, 35, 254.
4. Plücker and Geissler, Pogg. Ann. 1852, 86, 265.
5. Dufour, Compt. rend. 1862, 34, 1080.
6. Bunsen, Pogg. Ann. 1870, 141, 1.
7. Nichols, Phys. Review, 1899, 8, 21.
8. Barnes, Phys. Zeit. 1901, 3, 81; Barnes and Cooke, Trans. Roy. Soc. Canada, 1902, 8, (iii.), 143.
9. Vincent, Proc. Roy. Soc., 1902, 69, 422.

A large number of formulæ, for the most part entirely empirical, have been proposed to express the variation of volume of water with temperature, and these are collected, e.g. in Landolt-Börnstein Tabellen, 1921, p. 1231.

As examples the following may be given for water from 0°–40° and from 17°–100° respectively, due to Thiesen, Scheel and Dieselhorst (Wiss. Abh. Phys.-Tech. Reichsanstalt, 1900, 3, 1), and Thiesen (Wiss. Abh. Phys.-Tech. Reichsanstalt, 1903, 4, 1). If s = the density,

$$1 - s = \frac{(t - 3.98)^2}{503570} \times \frac{t + 283}{t + 67.26} \quad (\text{from } 0^\circ - 40^\circ)$$

$$1 - s = \frac{(t - 3.982)^2}{466700} \times \frac{t + 273}{t + 67} \times \frac{350 - t}{365 - t} \quad (\text{from } 17^\circ - 100^\circ)$$

These volume changes may also be considered in terms of the coefficient of cubical expansion α ,

which varies with temperature in the general manner indicated below:

Temp.	20°	40°	60°	100°	140°	180°	200°
$\alpha \times 10^6$	110	217	305	452	584	722	788

(See Meyer, Nernst's Festschrift, Halle a. S., 1912, 278; Hirn, Ann. Chim. 1866, [iv.] 10, 32; Tammann and Zepernik, Zeitsch. physikal. Chem. 1895, 16, 659.)

Despite many investigations our knowledge of the density and expansion of ice is not entirely satisfactory. Table 16 gives an indication of the methods adopted, the kinds of ice used, and the final results obtained in the chief researches on the subject; the papers by Barnes and Cooke and by Vincent, cited in the Table, contain critical reviews of earlier work and should be consulted for more detailed information.

Upon examination it is at once apparent

that these data differ among themselves by amounts much greater than any experimental error to which the actual determination of density can conceivably be subject.

With isolated exceptions the values for natural ice approximate to 0.918, whilst those for artificial ice are near 0.916. The mean values in the Table are respectively less than and greater than these figures, because they each include exceptional data which appear from their magnitude to belong to the other classification. Nichols first drew attention to this apparently systematic difference, and his experiments seem to show firstly, that it is real, and secondly, that the density of natural ice decreases with lapse of time until it approaches that of artificial ice. The experiments of Barnes and Cooke, made with natural ice from the St. Lawrence river, which had been in storage for various periods up to three years, confirm the correctness of the lower value for old natural ice, but it seems probable that none of their samples of ice were as recently formed as those which other observers had found of high density, and their conclusion that age has no effect on the density of ice is open to doubt.

Cooke (Trans. Roy. Soc. Canada, 1902, 8 [iii.] 127), in a discussion of these and earlier results, advances the view that the differences arise from stresses produced in the mass of ice by certain modes of freezing, but it is evident that Nichols' results with icicles discount this hypothesis. Vincent, measuring directly the upward pull exerted by a mass of water or ice completely immersed in mercury, confirmed generally the lower value for artificial ice, but obtained very definite evidence that the same specimen of water can, on different occasions, freeze into specimens of ice having distinctly different densities.

Further investigation is clearly needed on this point, and in the meantime the density of ice may perhaps best be taken at the mean value of 0.917.

Leduc has attempted to show that the observed differences may be due to variation in the content of dissolved air, but this explanation seems inadequate, especially in view of Vincent's results; he finds ice prepared by repeatedly freezing *in vacuo* water previously boiled to expel gases has a density of 0.9176 (Compt rend. 1906, 142, 149).

The difference between the density at 0° of water, 0.99987, and ice, 0.917, nearly 13 p.c.,

is a measure of the great expansion which takes place when water is frozen. Many important practical consequences of this expansion are well known. Freezing water produces disruptive effects in the cells of plant and animal tissues and in pipes and containers of all sorts, and these effects, occurring in the crevices of rocks, stones and buildings, and of the soil, cause progressive superficial disintegration. When water is cooled by contact with cold air, ice is formed, and because of its lower density remains, on the surface; the temperature of the bulk of water does not fall below 4°C., the temperature of maximum density, at which cooling by convection ceases. When water in process of cooling is continuously mixed, as in running streams, and free radiation occurs from the bed-rock to a clear atmosphere through shallow water, the temperature of the bed-rock and the water in contact with it may fall below 0°, when the so-called 'ground,' 'anchor' or 'frazil' ice is formed at the bottom.

Freezing of Water in Capillary Systems.—Much of the water of soils and inorganic gels fails to freeze, even at temperatures as low as -78°, because it is physically adsorbed, chemically combined, or in solid solution. E. A. Fisher (J. Physical Chem. 1924, 28, 360) points out that water present in very fine capillary tubes or pores must be under considerable tension, and so the density may not necessarily be the same as that of water in bulk, but probably less. Hence the expansion on freezing will probably be less, and since the amount of water which fails to freeze is determined by dilatometric measurements, false conclusions may thus be drawn (Chem. Soc. Abstr. 1924, 126, ii, 391).

Temperature of Maximum Density.—The data given in Tables 11 and 12 show the well-known fact that water attains a maximum density at about 4°C. Precise investigation has fixed the temperature as 3.98° at atmospheric pressure (Chappuis, Wied. Ann. 1897, 63, 202; Thiesen, Scheel and Diesselhorst, Wiss. Abh. Phys.-Tech. Reichsanstalt, 1900, 3, 68; de Coppet, Ann. Chim. 1903, [vii.] 28, 145).

At higher pressures the temperature of maximum density of water falls progressively in the manner shown in Table 17, and expressed in the following formula (Lussana, Nuovo Cim. 1910, [v.] 19, 182)

$$t_m = 4.10^\circ - 0.0225(p-1)$$

TABLE 17.
VARIATION OF THE TEMPERATURE OF MAXIMUM DENSITY OF WATER WITH PRESSURE.

Pressure.	Temperature of Maximum Density.	
1 atmo.	4.08°	
1.75 "	4.0	
2.85 "	3.9	
4.06 "	3.8	Grassi, Ann. Chim. 1851,
5.5	3.7	[iii.] 31, 437.
6.9	3.6	
8.6	3.5	
10.5	3.4	
41.6 "	3.3	Amagat, Compt. rend.
93.3 "	2.0	1893, 116, 943.
144.8 "	0.6	

For this reason in specifying water at its temperature of maximum density as the standard of density, it is necessary to stipulate that the pressure must be normal. It is also lowered by the presence of dissolved salts. For a given salt, the lowering is proportional to the concentration of the solute (Law of Despretz, *Ann. Chim.* 1839, [ii.] 70, 49; 1840, [ii.] 73, 296), but it is not connected with the depression of the freezing-point and is not a colligative property (Rosetti, *Ann. Chim.* 1867, [iv.] 10, 461; 1869, [iv.] 17, 370). The molecular lowering of the temperature of maximum density by salts of monovalent ions (e.g. H⁺, Li⁺, Na⁺, K⁺ and NH₄⁺ with Cl⁻, Br⁻, I⁻ and NO₃⁻) does exhibit a regularity in that it can be calculated from the molecular lowering of HCl (the lowest) by adding two numbers, characteristic respectively of the particular base and acid present (Wright, *J. Chem. Soc.* 1919, 115, 119): weak acids, and the salts of divalent acid and basic radicles, show no such regularity (de Coppet, *Ann. Chim.* 1894, [vii.] 3, 246, 268; *Compt. rend.* 1897, 125, 533; 1899, 128, 1559; 1900, 131, 178; 1901, 132, 1218; 1902, 134, 1208).

THE RELATION OF VOLUME AND PRESSURE FOR WATER AND ICE.

The effect of large variations of pressure upon the volume of water or ice is usually expressed in terms of the compressibility coefficient β where

$$\beta = \frac{1}{V_1} \times \frac{V_1 - V_2}{p_2 - p_1}$$

where V_1 = the volume at an initial pressure p_1 ,

and V_2 the volume at a higher pressure p_2 , at the same temperature; β is evidently the fraction by which the original volume is reduced for unit increase of pressure.

Table 18 gives the values of $\beta \times 10^6$ for water according to Amagat for pressures from 1-3000 atmospheres and temperatures from 0°-200°C. Table 19 gives the results, more accurately, but relating to a much smaller range of temperature and pressure, obtained by Richards and Stull and by Tyrer, and, for comparison, those of Bridgman at 0° and 22°.

The same data can, of course, be expressed in terms of specific volume, and Table 20 gives this quantity for water over a range of pressure from 0-12,000 kgm./cm.² and from -20° to +80°C.

Normal liquids show a compressibility which decreases with rise of pressure and increases with rise of temperature. These data show that the compressibility of water is thus affected by rise of pressure, but that increase of temperature up to about 50° lowers the compressibility; at higher temperatures the compressibility of water increases with rise of temperature like that of other liquids. The significance of this fact in relation to current hypotheses of the constitution of water is discussed elsewhere. The relation of the coefficient of expansion of water to pressure and temperature is given in Table 21. Experiments upon the isopiestic expansion of water at higher temperatures and pressures show that the thermal expansibility increases with temperature to a maximum value, which is the less the greater the pressure (Watson, *Proc. Roy. Soc. Edin.* 1911, 31, 456).

TABLE 18.
COEFFICIENT OF COMPRESSIBILITY β FOR WATER.
(Tabulated data are $\beta \times 10^6$).

Temp.	0°	5°	10°	15°	20°	30°	40°	50°	60°	70°	80°	100°	200°
Press. At.													
1-100	51.1	49.3	48.3	47.3	46.8	46.0	44.9	44.9	45.5	46.2	—	47.8	—
100-200	49.2	47.5	46.1	45.1	44.2	43.6	42.9	42.5	42.7	43.0	—	46.8	80.7
200-300	48.0	46.2	45.3	44.3	43.4	42.2	41.4	41.3	41.5	42.5	43.6	45.9	76.9
300-400	46.6	44.9	44.1	43.3	42.4	41.3	40.7	40.2	40.6	41.1	42.2	44.6	73.1
400-500	45.5	44.4	43.0	42.2	41.5	40.6	40.4	39.9	39.4	39.8	40.8	43.4	68.2
500-600	43.8	43.0	41.8	41.1	40.4	39.2	38.0	39.0	38.8	39.1	39.9	41.6	66.0
600-700	42.9	40.9	40.5	39.8	39.4	38.7	38.2	37.7	38.3	38.0	38.7	40.7	62.7
700-800	41.8	40.7	39.8	39.0	38.8	37.5	37.4	37.1	36.9	37.4	37.8	38.9	61.3
800-900	40.6	39.3	38.9	38.0	37.3	36.8	36.2	36.2	36.3	36.6	36.8	38.2	58.9
900-1000	—	—	—	36.8	36.5	36.0	35.3	35.3	36.0	36.1	36.2	37.1	56.5

Temp.	0°	5°	10°	15°	20°	Temperature	0°	5°	10°	15°	20°	50°
Press. At.						Press. atmo.						
1-25	52.5	51.2	50.0	49.5	49.1	1-500	47.5	45.8	44.7	43.8	43.4	61.4
25-50	51.6	49.6	49.2	48.0	47.6	500-1000	41.6	40.6	39.5	39.1	38.0	36.6
50-75	50.9	48.5	47.3	46.5	45.6	1000-1500	35.8	35.5	34.8	34.4	33.8	32.5
75-100	50.2	48.1	47.0	45.7	45.3	1500-2000	32.4	31.8	31.3	31.2	30.9	30.0
100-125	49.4	47.7	46.6	45.4	44.9	2000-2500	29.2	28.9	28.9	28.0	27.8	27.6
125-150	49.1	47.5	46.3	45.4	44.6	2500-3000	26.1	26.4	25.8	26.1	25.7	25.4
150-175	49.1	47.5	46.3	45.1	44.2							
175-200	48.8	47.2	46.0	44.7	43.8							

Amagat, *Ann. Chim.* 1893, [vi.] 29, 68, 505.

TABLE 19.
VARIATION OF THE COEFFICIENT OF COMPRESSIBILITY β FOR
WATER WITH PRESSURE.

Temperature	Pressure range: atmo.	$\beta \times 10^6$	Reference
20°	0—98.7	45.8	1
"	98.7—197.4	44.8	
"	197.4—296	42.4	
"	296—395	41.7	
"	395—494	39.9	
0°	1—2	50.28	2
10°	" "	47.80	
20°	" "	45.90	
60°	" "	44.82	
100°	" "	48.18	
0°	0—484	46.2	3
"	1450—1935	31.2	
"	2900—3390	24.4	
"	4350—4840	20.6	
"	6290—6760	14.2	
22°	0—970	39.6	
"	2900—3870	23.8	
"	5800—6760	16.3	
"	9680—10,620	9.6	

1. Richards and Stull, J. Amer. Chem. Soc. 1904, 26, 399.
2. Tyrer, J. Chem. Soc. 1913, 103, 1675.
3. Bridgman, Proc. Amer. Acad. 1912, 47, 347, 439.

TABLE 20.
SPECIFIC VOLUME OF WATER, C.C. PER GRAM, OVER A RANGE OF TEMPERATURE AND PRESSURE.

Pressure, kgm./cm. ²	Temperature									
	-20°	-10°	0°	+10°	20°	30	40°	50°	60°	80°
0	—	1.0018	1.0001	1.0002	1.0017	1.0042	1.0077	1.0119	1.0169	1.0225
1,000	—	0.9599	0.9579	0.9603	0.9631	0.9664	0.9701	0.9744	0.9792	0.9843
2,000	0.9229	0.9244	0.9261	0.9294	0.9328	0.9365	0.9404	0.9446	0.9490	0.9538
3,000	0.8964	0.8985	0.9016	0.9051	0.9088	0.9106	0.9165	0.9206	0.9248	0.9293
4,000	—	0.8775	0.8808	0.8844	0.8881	0.8898	0.8957	0.8997	0.9038	0.9081
5,000	—	0.8600	0.8633	0.8667	0.8703	0.8720	0.8779	0.8819	0.8859	0.8900
6,000	—	—	0.8481	0.8510	0.8546	0.8565	0.8624	0.8663	0.8703	0.8743
7,000	—	—	—	0.8371	0.8405	0.8426	0.8486	0.8525	0.8565	0.8603
8,000	—	—	—	—	0.8276	0.8301	0.8361	0.8400	0.8439	0.8478
9,000	—	—	—	—	0.8161	0.8209	0.8250	0.8289	0.8328	0.8365
10,000	—	—	—	—	—	0.8190	0.8150	0.8189	0.8227	0.8265
11,000	—	—	—	—	—	—	0.8057	0.8096	0.8134	0.8171
12,000	—	—	—	—	—	—	0.7967	0.8006	0.8044	0.8081

P. W. Bridgman, Proc. Amer. Acad. 1912, 48, 338.

Increase of pressure does not shift the temperature of minimum compressibility, but at high pressures this minimum disappears (Bridgman, *Zeitsch. anorg. Chem.* 1912, 77, 377).

Small as is the compressibility of water it has important practical effects and uses. It has been calculated that were water incompressible the mean sea-level would be 116 feet higher than it actually is, whereby about 4 p.c. of existing

land would be submerged (Tait, Proc. Roy. Soc. Edin. 1884, 12, 46; 1892, 20, 63, 141). Compression waves in water are transmitted with high velocity and are applied in the Constantinesco 'wave-power' system to attain the economical transmission of power, e.g. from a central motor to drilling machines or the like in mines, with an efficiency comparable with that of electrical transmission and with the

TABLE 21.

WATER—COEFFICIENT OF THERMAL EXPANSION AT HIGH PRESSURES.

Temperature	Coefficient of cubical expansion at		
	1 atmo.	500 atmo.	3000 atmo.
0°-10°	0.000012	0.000156	0.000383
0°-30°	0.000138	0.000229	0.000415
0°-50°	0.000238	0.000295	0.000413

Amagat, Compt. rend. 1887, 105, 1120.

convenience and safety characteristic of compressed air.

The compressibility of ice at -7.03° for a range of pressure from 100–500 megabars is 0.0000120 (Richards and Speyers, J. Amer. Chem. Soc. 1914, 36, 491), or about one quarter that of water at 0° ; it does not decrease greatly with increase of pressure. The much higher value calculated by Bridgman (0.000036) probably indicates that the temperature coefficient of increase of compressibility for ice is abnormally high.

In considering the remaining physical properties of water it is convenient to take them in a systematic order for all forms of water, under the main groups, mechanical, thermal, optical and magnetic, and electrical.

MECHANICAL PROPERTIES.

Crystal Form.—Ice crystals, as exemplified by snow, can assume a great variety of forms which are commonly characterised by extreme openness of structure and consequent lightness; they are readily formed by the condensation of water vapour below 0° as hoar frost. Liquid water, if free from dissolved air, freezes to clear transparent ice which may give indications of structure by transmitted light or on melting, but has usually no external crystalline form. Solid, well-defined crystals of ice are extremely rare.

Though liquid water, if perfectly pure and free from dust, can be cooled to about -15° without solidification (Thomson, Trans. Roy. Soc. Edin. 1849, 16, 575; Sorby, Phil. Mag. 1859, [iv.] 18, 105), ice always melts at a definite and fixed temperature at atmospheric pressure,

and its melting-point is therefore used to define the zero point of thermometric scales. The melting-point is lowered by increase of pressure, and this has been adduced in explanation of the phenomenon of *regelation* or welding of separate pieces of ice, and is illustrated by the well-known experiment in which a weighted loop of wire cuts through, but does not sever, a block of ice.

Ice separating from under-cooled water forms hexagonal crystal skeletons or spherulites, according to the degree of under-cooling, and is obtained in feathery forms from very dilute solutions; but inoculation of under-cooled pure water with these forms produces identical forms of ice (Hartmann, Zeitsch. anorg. Chem. 1914, 88, 128).

The crystalline form of ice is hexagonal-bipyramidal with the axial ratio $a : c$ approximately 1 : 1.6 (Nordenskiöld, Öfv. Akad. Förh. Stockholm, 1860, 17, 439; Rinne, Ber. Sachs. Ges. Wiss. 917, 69, 57). Its X-ray spectrum has been investigated (St. John, Proc. Nat. Acad. Sci. 1918, 4, 193; Dennison, Phys. Rev. 1921, 17, 20), and the results are interpreted by Bragg (Proc. Physical Soc. 1922, 34, 98) on the assumption that the molecules are separated into positive and negative ions arranged in a hexagonal lattice in such a manner that each oxygen atom is situated at the centre of gravity of four neighbouring oxygen atoms, from each of which it is separated by a hydrogen ion situated midway between. The extremely open character of the structure is in accordance with the low density of ice.

The velocity of crystallisation of water in long tubes, 12 mm. external and 7 mm. internal diameter, increases with the degree of under-cooling as follows:—

Temp.	-2°	-3.61°	-4.67°	-5.86°	-6.18°	-7.10°	-8.19°	-9.07°
Velocity : } cm./min.	31.6	48.4	71.4	107.1	114.7	266.7	415.2	684.0

(Walton and Judd, J. Phys. Chem. 1914, 18, 722, which see for a useful summary of earlier work), but at any given temperature is retarded by the presence of dissolved acids, salts, dyes, &c. The retardation is not a colligative property of the solute, but appears to depend upon the extent to which the solute is hydrated in solution (Walton and Brann, J. Amer. Chem. Soc. 1916, 38, 317; Brann, *ibid.* 1918, 40, 1188).

Colloidal ice has been obtained by cooling

solutions of water in ether or chloroform, in some cases with the use of fatty acids or rubber as protective colloids (v. Weimarn and Ostwald, Zeitsch. Chem. Ind. Kolloide, 1910, 8, 181; J. Russ. Phys. Chem. Soc. 1910, 42, 226).

Elasticity.—A mass of ice yields steadily to pressure, e.g. a bar of glacier ice supported at the ends and loaded in the middle is slowly deflected, and ice compressed in a cylinder flows steadily, and the flow once started can be maintained by relatively small pressures (Hess,

Ann. Physik, 1902, [iv.] 8, 495). Curiously, the bar of ice when relieved from its load slowly recovers its original form. It has been shown that a bar of ice cut from a single crystal with its length perpendicular to the optic axis is brittle and does not yield to tension or pressure (McConnel, Proc. Roy. Soc. 1891, 49, A. 323), and the behaviour of ordinary ice is therefore

probably attributable to slipping of crystal layers of finite thickness.

The conflicting results of earlier investigators are thus explained, and it is necessary only to record the determinations of modulus of elasticity E and bending moment B in grm. cms. made by Hess (L.c.) upon bars of ice cut from single crystals as tabulated below :

Elasticity of Ice.

Load in gm. on beam 1.2 cm. × 2.5 cm. × 4-16 cm.	Length parallel to crystal axis			Width parallel to crystal axis			Thickness parallel to crystal axis		
	2000	5000	6000	1000	2000	3000	1000	1500	2000
$E \times 10^{-10} =$	0.54	0.70	0.75	3.5	2.9	4.0	1.6	2.0	2.0
$B =$	1350	3400	4000	1500	3000	4450	1600	2350	3100

The recovery of bent ice on removal of stress is much greater than similar effects in other substances, and has not been adequately explained.

The rate of plastic flow of ice is small at low temperatures, but increases rapidly near the melting-point (Tammann, Ann. Physik, 1902, [iv.] 7, 198; Slatowratsky and Tammann, Zeitsch. physikal. Chem. 1905, 53, 341), and a similar variation characterises the hardness of ice. On Mohs' scale the hardness is about 1.5, but as measured by the penetration of a steel rod into a block of ice it is considerably greater at temperatures from -37° to -12° than at about -7° , and at the melting-point ice becomes relatively quite soft (Andrews, Proc. Roy. Soc. 1886, 40, A. 544).

Frictional resistance to motion on the surface of ice is clearly related to the above phenomena; it is greater for small pressures than for large, the respective values of the coefficient of friction being 0.36 and 0.17 (Morphy, Phil. Mag. 1913, [vi.] 25, 133).

Liquid water appears to have, like some other liquids, tensile strength. If a glass tube containing only water and its vapour and nearly filled with the former be warmed until the liquid thus expanded just fills the tube, and then allowed to cool, the water continues to fill the tube even when its volume is thereby greater by about $\frac{1}{100}$ th than that corresponding to its temperature. It is hence calculated that the tensile strength of water is some 700-900 lbs./sq. in. (Berthelot, Ann. Chim. 1850, [iii.] 30, 232; see also Budgett, Proc. Roy. Soc. 1912, 86, A. 25). The rupture of a stream of water flowing through a constriction in a pipe is probably a true tensile rupture, especially as the tensile strength, deduced from the velocity at which rupture occurs, diminishes with rise

of temperature and becomes zero at about 250° (Skinner and Entwistle, Proc. Roy. Soc. 1915, 91, A. 481; Skinner and Burfitt, Proc. Physical Soc. 1919, 31, 131), in accordance with Larmor's calculation from van der Waal's equation that the tensile strength of water could subsist only up to about 265° (Larmor, Proc. London Math. Soc. 1916, [ii.] 15, 191).

The compressibility of water has already been discussed in relation to the attendant volume change, but it must here be noted that it connotes a *bulk elasticity* which is related in the usual manner to the velocity of sound in the medium. Experimental determinations of the velocity have given the following results: At 8.1° , 1435 metres/sec. (Colladen and Sturm, Ann. Chim. 1827, [ii.] 36, 113, 225; Pogg. Ann. 1828, 12, 39, 161); at 3.9° , 1399 m./sec.; at 13.7° , 1437 m./sec.; at 25.2° , 1457 m./sec. (Martini, Wied. Beibl. 1888, 12, 566; Nuovo Cimento, 1909, [v.] 18, 441).

The velocity of sound in water vapour is 401 m./sec. at 0° (Masson, Compt. rend. 1857, 44, 464; Phil. Mag. 1857, [iv.] 13, 533), and about 410 m./sec. at 100° (Jäger, Wied. Ann. 1889, 36, 165).

Viscosity.—The viscosity of water vapour has been determined at about the ordinary temperature by several observers with substantially concordant results as follows:—

At 0° , $\eta = 90.4 \times 10^{-6}$ C.G.S. units; at 16.7° , $\eta = 96.7 \times 10^{-6}$ (Puluj, Sitzungsber. Akad. Wiss. Wien. 1878, 78 (2), 279); at 18.8° , $\eta = 97.5 \times 10^{-6}$ (Kundt and Warburg, Pogg. Ann. 1875, 155, 337, 525); at 28.9° , $\eta = 100.6 \times 10^{-6}$ (H. Vogel, Ann. der Physik, 1914, 43, 1235).

For undercooled water below 0° the most probable values of the viscosity are those given in Table 22; for water from 0° – 100° substantially

TABLE 22.

Temperature	Viscosity η	Temperature	Viscosity η
20.0°	0.01003	-2.10	0.01930
15.0	0.01139	-4.70	0.02121
10.0	0.01307	-6.20	0.02250
5.0	0.01523	-7.23	0.02341
0.00	0.01798	-8.48	0.02458
		-9.30	0.02549

concordant determinations are recorded by a number of observers, and the more important are given in Table 23. The viscosity progressively diminishes with rise of temperature both as these data show and above 100° (becoming 0·00223 at 124° and 0·00181 at 158°: Hosking; Bingham and White; Table 23), but the variation does not follow any simple law and can only be expressed by empirical formulae which it is unnecessary to record.

Water under high pressures of the order of 400 atm. is less viscous than uncompressed water

at temperatures up to about 35°; at higher temperatures the viscosity of water is increased by increase of pressure, just as is that of most other liquids at all temperatures (Hauser, Drude's Ann. 1901, 5, 597).

The viscosity of ice, regarded as a fluid, has been estimated from the movement of glaciers to be of the order of $200\text{--}300 \times 10^{12}$ (Deeley and Parr, Phil. Mag. 1913, [vi.] 26, 85; 1914, [vi.] 27, 153), but measurements on blocks of ice or single crystals give widely divergent results (see e.g. McConnell, Proc. Roy. Soc. 1890, 48, A

TABLE 23.

VISCOSITY OF WATER, η IN C.G.S. UNITS, AND ITS VARIATION WITH TEMPERATURE, ACCORDING TO VARIOUS OBSERVERS.

Temperature	1846 Poiseuille	1876 Sprung	1883 Slotte	1894 Thorpe & Rodger	1909 Hosking	1912 Bingham
0°	0·01716	0·01778	0·01808	0·017800	0·01792	0·01797
5	0·01515	0·01510	0·01524	0·015118	0·01522	0·01525
10	0·01309	0·01301	0·01314	0·013053	0·01305	0·01301
15	0·01146	0·01135	0·01144	0·011366	0·01142	0·01138
20	0·01008	0·01003	0·01008	0·010051	0·01006	0·01006
25	0·00897	0·00896	0·00896	0·008949	0·00892	0·008948
30	0·00803	0·00802	0·00803	0·008019	0·00800	0·007998
35	0·00721	0·00723	0·00724	0·007248	0·00724	0·007229
40	0·00653	0·00657	0·00657	0·006588	0·00657	0·006563
45	0·00595	0·00602	0·00602	0·006029	0·00600	0·005994
50	—	0·00553	0·00553	0·005537	0·00550	0·005500
55	—	—	0·00510	0·005124	0·00508	0·005081
60	—	—	0·00472	0·004752	0·00469	0·004735
65	—	—	0·00438	0·004432	0·00436	0·004369
70	—	—	0·00408	0·004144	0·00406	0·004075
75	—	—	0·00382	0·003885	0·00380	0·003806
80	—	—	0·00358	0·003655	0·00356	0·003570
85	—	—	0·00337	0·003450	0·00335	0·003348
90	—	—	0·00318	0·003260	0·00316	0·003143
95	—	—	0·00301	0·003095	0·00300	0·002993
100	—	—	0·00285	0·002945	0·00284	—

Poiseuille, Mem. Acad. Roy. Sci. Inst. France, 1846, 9, 433.

Sprung, Pogg. Ann. 1876, 159, 1.

Slotte, Wied. Ann. 1883, 20, 257.

Thorpe and Rodger, Phil. Trans. 1894, 185, A. 397.

Hosking, Phil. Mag. 1909, [vi.] 17, 502; 18, 260.

Bingham and White, Zeit. phys. Chem. 1912, 80, 670.

259). Hess found that the apparent value of the viscosity depends upon the direction of flow in relation to the original crystal axis, and varies also with time in the manner indicated by the results given in Table 24. It would appear that even a single crystal of ice may yield by slipping on cleavage surfaces, with consequent recrystallisation similar to that which is familiar in the case of metals yielding to stress.

Surface tension.—Water has a higher surface tension than any other common liquid except mercury. No data are available for its value in undercooled water; Table 25 gives the values of α , the specific cohesion, and of γ , the surface tension in dynes/cm., at 1° intervals of temperature from 0°–90°; the progressive

diminution of γ with rise of temperature may be expressed by $\gamma = 76\cdot09 (1 - 0\cdot002026t)$ (Santia, Journ. de Physique, 1897, [iii.] 6, 183), or better, by $\gamma = \gamma_0 (1 - 0\cdot00190179t - 0\cdot000002499t^2)$. (Forch, Ann. Physik, 1905, 17, 744; see also Reinhold, Ber. 1913, 15, 903). Whilst the relative values of the surface tension at different temperatures are well represented by Table 25, the absolute values may be in error; in very careful measurements of the capillary rise (Richards and Coombs, J. Amer. Chem. Soc. 1915, 37, 1656; Richards and Carver, *ibid.* 1921, 43, 827) and of the 'drop-weight' of water (Harkins and Brown, J. Amer. Chem. Soc. 1919, 41, 499) a number of sources of error incidental to both methods have been discovered and eliminated, and the final results

TABLE 23A.

VISCOSITY OF WATER, γ IN C.G.S. UNITS IN THE NEIGHBOURHOOD OF ITS POINT OF MAXIMUM DENSITY.

Thorpe and Rodger (*loc. cit.*) have determined by the tube method the Viscosity of Water at various Temperatures in the vicinity of its point of maximum density, with the results seen in the annexed table.

Mean temp.	γ		Difference.
	Observed (mean).	Calculated.	
0			
0.37	-01757	-01757	-00000
1.13	-01710	-01712	+00002
1.86	-01670	-01671	+00001
2.41	-01640	-01641	+00001
3.09	-01608	-01605	-00003
3.84	-01568	-01566	-00002
4.47	-01535	-01535	-00000
5.19	-01500	-01500	-00000
5.94	-01464	-01465	+00001
6.67	-01433	-01433	-00000
7.41	-01401	-01401	-00000
8.01	-01377	-01375	-00002

[Note on Table 23a: The viscosity of water at different temperatures has also been determined by the rotating cylinder method by Leroux (Ann. Physique, 1925, [x.] 4, 163), the water being contained between two concentric cylinders, of which the outer is rotated at known velocity and the resulting twisting moment on the inner cylinder measured.

Moritz (Pogg. Ann. 70, 1847), from observations made by the method of Coulomb (oscillating disc), inferred that water had a maximum viscosity in the neighbourhood of 4°. Other observers, and more especially Poiseuille and Sprung, using the tube method, were unable to detect any peculiarity in the rate of change of viscosity at temperatures at about the point of maximum density. The observations of Thorpe and Rodger lend no support to the conclusions of Moritz. It must be borne in mind, however, that the anomalous change in the density of water amounts only to about 1 part in 10,000; hence, since the accuracy attained in these special observations of viscosity probably does not exceed 1 in 5,000, it may be doubted whether any anomalous change in viscosity of the same order of magnitude as that observed in the case of the density would be detected by any of our present experimental methods.]

TABLE 24.

VISCOSITY OF ICE, $\gamma \times 10^{10}$ C.G.S. UNITS, FOR VARIOUS ORIENTATIONS, PRESSURES AND TIMES.

Relation of beam to axis of crystal	Length parallel to axis			Width parallel to axis			Thickness parallel to axis		
	2000	5000	6000	1000	2000	3000	1000	1500	2000
Load: grams.									
Duration of test.									
15 seconds .	6.5	10.5	0.55	3.7	2.4	11.0	7.5	10.0	8.0
60 " .	17.5	11.5	3.6	8.0	6.0	9.0	7.5	11.0	7.0
120 " .	10.0	13.5	3.7	12.0	10.0	—	7.5	9.0	11.0
300 " .	11.0	16.6	3.5	21.0	17.6	—	8.0	12.0	12.0

H. Hess, Ann. Physik. 1902, [iv.] 8, 405.

show respectively $\gamma_{100} = 72.75$ and $\gamma_{100} = 72.800$ respectively. Richards and Carver (*l.c.*) have proved experimentally, by a very ingenious optical method, that the surface of water is actually tangential to a properly wetted glass surface, and thus that the ordinary formula connecting surface tension and capillary rise holds precisely. Minute traces of dust or impurities have a considerable effect on the

surface tension, and precise measurements can only be made in a totally enclosed apparatus; Harkins and Brown have found that the capillary rise is affected by 'steaming' the tubes beforehand with the vapour of the liquid under investigation.

Absorbed or dissolved gases affect the surface tension; Richards and Carver find $\gamma_{100} = 72.73$ in air as compared with 72.75 in *vacuo*; dis-

TABLE 25.

SURFACE TENSION OF WATER.

Expressed in terms of the Specific Cohesion c^2 in mm.² and Surface Tension, (γ), dynes per cm., from 0° to 40° in dry air and from 40° to 80° in air saturated with water vapour.

Temperature	c^2 mm. ²	γ dynes/cm.	Temperature	c^2 mm. ²	γ dynes/cm.
0°	15.406	75.49	40°	14.295	69.54
1	15.375	75.34	41	14.26	69.3
2	15.344	75.20	42	14.23	69.2
3	15.314	75.05	43	14.20	69.0
4	15.283	74.90	44	14.17	68.8
5	15.251	74.75	45	14.14	68.6
6	15.221	74.60	46	14.11	68.5
7	15.192	74.45	47	14.08	68.3
8	15.163	74.30	48	14.05	68.1
9	15.134	74.15	49	14.02	68.0
10	15.105	74.01	50	13.99	67.8
11	15.076	73.86	51	13.96	67.6
12	15.045	73.70	52	13.93	67.4
13	15.017	73.56	53	13.90	67.3
14	14.989	73.41	54	13.87	67.1
15	14.959	73.26	55	13.84	66.9
16	14.933	73.11	56	13.81	66.7
17	14.904	72.96	57	13.78	66.6
18	14.878	72.82	58	13.75	66.4
19	14.849	72.66	59	13.73	66.2
20	14.821	72.53	60	13.70	66.0
21	14.795	72.37	61	13.66	65.8
22	14.768	72.22	62	13.63	65.6
23	14.741	72.08	63	13.60	65.5
24	14.714	71.93	64	13.57	65.3
25	14.686	71.78	65	13.54	65.1
26	14.659	71.63	66	13.51	64.9
27	14.633	71.48	67	13.47	64.7
28	14.607	71.33	68	13.44	64.5
29	14.581	71.18	69	13.41	64.4
30	14.556	71.03	70	13.39	64.2
31	14.527	70.88	71	13.35	64.0
32	14.504	70.74	72	13.31	63.8
33	14.476	70.58	73	13.28	63.6
34	14.447	70.44	74	13.26	63.4
35	14.424	70.29	75	13.24	63.3
36	14.398	70.14	76	13.21	63.1
37	14.373	69.99	77	13.17	62.9
38	14.348	69.85	78	13.14	62.7
39	14.323	69.70	79	13.11	62.5
			80	13.08	62.3

Volkman, Wied. Ann. 1880, 11, 177; 1882, 17, 353; 1895, 56, 457 (0°-40°).

Brunner, Pogg. Ann. 1847, 70, 481 (40°-80°).

solved CO₂, CO, N₂O, H₂S, H₂O, and N₂ similarly cause a small lowering of the surface tension (Quincke, Pogg. Ann. 1870, 139, 1, 89; 1877, 160, 337; Volkman, Wied. Ann. 1880, 11, 177; 1882, 17, 353; 1894, 53, 653; 1895, 56, 457; 1898, 66, 220; Forch, Wied. Ann. 1899, 68, 801; Ann. Physik, 1905, [iv.] 17, 750; Bhatnagar, J. physikal. Chem. 1920, 24, 716).

By measurement of the amplitude of the wave produced when a stream of water emerges under pressure from capillary of elliptical cross-section, evidence has been obtained that the surface tension in a freshly formed surface of

water is about 0.5 dyne/cm. less than in old surfaces (Meyer and Stocker, Zeitsch. Elektrochem. 1916, 22, 5; Stocker, Zeitsch. physikal. Chem. 1920, 94, 149).

From the cooling effect of adiabatic expansion of water, the internal pressure has been calculated to be 2150 atmospheres (Parsons and Cook, Proc. Roy. Soc. 1911, A. 85, 332).

The surface tension in the interface between water and several organic liquids is given in Table 26; it is always less, and usually much less, than in pure water.

The coefficient of diffusion of water vapour

at 760 mm.

(II), and in cm.²/sec. is given in Table 27.

Molecular data have been calculated as follows for water vapour at 0°:

Mean molecular velocity, 58,650 cm./sec.

Mean free path, at 760 mm. press. 4.04×10^{-8} cm.Molecular diameter, about 4.0×10^{-8} .The number of molecules per gram-molecule of liquid water is estimated to be 8.5×10^{23} (Sand, Trans. Faraday Soc. 1919, 15, 94).

TABLE 26.

SURFACE TENSION, DYNES/CM., IN THE INTERFACE BETWEEN WATER AND SOME ORGANIC LIQUIDS.

Organic liquid	Ref.	0°	10°	20°	30°	40°	50°	60°
Benzene	1	—	35.56	34.96	34.34	33.84	—	—
Benzine	2	—	—	48.3	—	—	—	—
Carbon disulphide	3	—	—	38.8	—	—	—	—
Carbon tetrachloride	1	46.97	45.97	45.05	44.04	43.04	—	—
Chloroform	3	—	—	25.8	—	—	—	—
Ethyl capronate	1	21.03	21.42	21.29	21.15	21.02	—	—
Ethylene dibromide	1	—	38.28	37.20	36.08	35.03	—	—
Heptaldehyde	1	10.78	12.51	13.74	14.41	14.82	14.50	12.13
Heptene	1	—	—	28.11	—	—	—	—
Heptylic acid	1	8.34	7.93	7.54	7.13	7.00	—	—
Hexane	1	—	51.25	—	50.66	50.48	—	—
Octane	1	—	51.01	50.81	—	49.58	—	—
n-Octyl-alcohol	1	7.75	—	—	8.97	9.32	—	—
Sec-octyl alcohol	1	8.44	8.80	9.24	9.65	10.04	—	—
Olive oil	3	—	—	18.2	—	—	—	—
Petroleum	2	—	—	48.3	—	—	—	—

1. Harking and Cheng, J. Amer. Chem. Soc. 1921, 43, 35.

2. A. Pockels, Wied. Ann. 1899, 67, 668.

3. Quincke, Pogg. Ann. 1870, 139, 1.

TABLE 27.

COEFFICIENT OF DIFFUSION OF WATER VAPOUR.

Into air (I), carbon dioxide (II), and hydrogen (III), in cm.²/sec. at 760 mm. pressure.

Temperature	I.	II.	III.
0°	0.198	0.132	0.687
49.5°	0.283	0.181	1.000
92.4°	0.345	0.238	1.179

Winkelmann, Wied. Ann. 1884, 22, 1, 152; 1884, 23, 203; 1885, 26, 105; 1888, 33, 445; 1889, 36, 92; Ann. Physik. 1901, 6, 104; 1902, 8, 388.

THERMAL PROPERTIES.

Conductivity.—The principal data for the thermal conductivity of liquid water are given in Table 28; the considerable variation among them is a measure of the difficulty of making a precise measurement of the conductivity, owing to the effects of convection and radiation, but it is clear that it is very small as compared with that of metals, yet greater than that of other non-metallic liquids (e.g. alcohol 0.00055; benzene 0.00033). The conductivity shows a linear increase with temperature and may be represented by conductivity = $0.001326(1 + 0.002954t)$ Cal./cm. sec. degree (Jakob, *loc. cit.*).

The thermal conductivity of solid ice is about four times that of water, the most probable of the recorded values being 0.0057 (Neumann,

Ann. Chim. 1862, [iii.] 66, 183; Phil. — 1863, [iv.] 25, 63), 0.0052 (Straneo, Atti Accad. Lincei, 1897, [v.] 6, (2), 262), and 0.0052 at 0°; 0.0058 at -57°; 0.0052 at -117° (Lees, Phil. Trans. 1898, 191, A. 399; Proc. Roy. Soc. 1905, 74, 337); in all cases gm. calories transmitted per sec. per sq. cm. through a thickness of 1 cm. for 1° temperature drop.

As a matter of common experience the thermal conductivity of snow is much less than that of ice, but it varies considerably with the nature and density of the snow, and attempts to measure it have given widely diverse results. Approximately it is of the order of $\frac{1}{10}$ th to $\frac{1}{15}$ th that of ice (Andrews, Proc. Roy. Soc. 1881, 40, 544; Abels, Rep. Meteorol. Acad. Petrograd, 1892, 16, 53; Hjelström, Oef. Akad. Stockholm, 1889, 46, 669; Jansson, *ibid.* 1901, 53, 207; Okada, J. Meteorol. Soc. Japan, 1906, 341).

TABLE 28.

CONDUCTIVITY FOR HEAT OF LIQUID WATER.

In calories per cm. per second per degree difference of temperature.

Temperature	Conductivity	Reference
4.1°	0.00129	1
7.8°	0.001347	2
11.0°	0.00149	3
12.0°	0.00136	4
20.0°	0.00143	5
23.7°	0.00143	6
24.5°	0.00136	3
28°	0.00150	7
40.8°	0.00155	8
41.4°	0.001492	2
72.4°	0.001610	2

1. Wachsmuth, Wied. Ann. 1893, 48, 158.
2. Jakob, Ann. Physik 1920, [iv.] 63, 537.
3. Lees, Phil. Trans. 1898, 191, 399.
4. H. F. Weber, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1885, 809.
5. Milner and Chattock, Nature, 1898, 58, 532.
6. Weber, Wied. Ann. 1880, 10, 103, 304, 472.
7. Jäger, Sitzungsber. Akad. Wiss. Wien, 1890, 99 [2. a.], 245.
8. Lundquist, Mon. Sci. 1871, 500.

Change of State.—The general relation of the state of aggregation to temperature has been discussed, but reference should be made to the undercooling of the liquid and vapour and the superheating of the liquid.

In the absence of nuclei, water vapour may be cooled much below its saturation temperature without deposition of visible water. Solid nuclei, such as particles of dust, spores, &c., may, and in ordinary air do, cause the condensation of liquid water immediately the saturation temperature is reached. Even less tangible nuclei will suffice. C. T. R. Wilson's simple and ingenious method of rendering the track of α -particles in a gas susceptible to visual observation or photographic record depends upon the fact that gaseous ions (produced by collision between the α -particle and molecules) will act as nuclei for the condensation of super-saturated water vapour.

Similarly, pure water in *vacuo*, in fine capillary tubes, or covered with petroleum, may be cooled some 15° below zero without solidification; even when slightly undercooled, water may be caused to crystallize by mechanical shock or agitation in the absence of nuclei (S. W. Young, J. Amer. Chem. Soc. 1911, 33, 146; Young and Cross, *ibid.* 1911, 33, 1375; Young and van Sicken, *ibid.* 1913, 35, 1067; Hartley and Thomas, J. Chem. Soc. 1906, 89, 1013). There is thus for water no evidence of the so-called 'metastable,' as distinct from 'stable,' condition in which nuclei are essential to crystallisation.

Liquid water is readily superheated; it is indeed difficult to boil water without slight local superheating, and very frequently the superheating is so considerable that when steam bubbles originate they increase in size with explosive violence, producing 'bumping.' In fresh distilled water minute bubbles of dissolved

air expelled on heating serve as nuclei for steam bubbles and minimise the bumping, and the same effect is frequently attained artificially by introducing air-filled porous solids, e.g. broken pottery, or a fine stream of air into the liquid. Without special precautions air-free water can be heated to 130° (see e.g. Donny, Ann. Chim. 1844, [iii.] 16, 167; Gernez, *ibid.* 1875, [v.] 4, 335; Krebs, Pogg. Ann. 1868, 133, 673; 1869, 136, 144; 1869, 138, 489), and if it is suspended in a mixture of olive oil and linseed oil of its own density it may be heated to 178° without boiling (Dufour, Ann. Chim. 1863, [iii.] 66, 370).

Latent Heat.—Heat is absorbed and rendered 'latent' both in the fusion of ice and in the evaporation of ice or water.

Table 29 gives the values of the heat of evaporation of water (frequently and more conveniently called the latent heat of steam) determined by a number of independent investigators at various temperatures from 0°–180°. The value at 100° is an important constant, and for this the most probable round value is 539.0 15° gm. cal. per gram.

Table 30 similarly gives data for the latent heat of fusion of ice, which usefully can be, but commonly is not, called the latent heat of water. Bunsen's value is undoubtedly erroneous, but if corrected for the difference in density between old and new ice (g.c.) becomes 79.67 in good agreement with more recent determinations. The rounded value 79.7 may be used with confidence for most purposes.

There is, of course, a direct relation between the latent heat of steam or water and the effect of dissolved substances upon the boiling-point and freezing-point.

The molecular elevation of the boiling-point is 0.52° (Beckmann, *Zeitsch. physikal. Chem.* 1891, 8, 223; 1908, 63, 177), and the molecular

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point is 1.96° (Rasch, 1903, 63, 441; Zeitsch. Electro-
192, 27, 617; Bedford, 1930, 28, 288; Dickinson and Osborne,
Proc. Roy. Soc. 1910, A, 83, 459; Roth, Zeitsch. J. Franklin Inst. 1915, 179, 489).

TABLE 29.
LATENT HEAT OF STEAM—HEAT OF EVAPORATION OF WATER.
(According to various observers.)

Temperature	Heat of evaporation 15° gm. cal./gm.	Reference	Temperature	Heat of evaporation 15° gm. cal./gm.	Reference
0°	594.8	1	80°	551.6	4
15°	590.9	2	99.96°	538.0	5
20°	585.3	2	100°	540.5	2
25°	581.9	3	100°	539.1	4
30°	578.7	3	100°	538.3	8
30°	579.8	4	100°	539.0	7
40°	574.0	2	100°	538.9	8
40°	574.5	4	120°	525.8	4
49.2°	572.6	3	140°	511.4	4
49.8°	566.5	3	160°	497.0	4
60°	563.4	4	180°	482.7	4

1. Dieterici, Wied. Ann. 1889, 37, 504; Ann. Physik 1905, 16, 912.
2. A. W. Smith, Phys. Review, 1903, 16, 383; 17, 193; 1907, 25, 145; 1911, 33, 173.
3. Griffiths, Phil. Trans. 1895, 186, A, 261.
4. Henning, Ann. Physik, 1906, [iv.] 21, 489; 1909, [iv.] 29, 441; 1919, [iv.] 58, 759.
5. Joly, Phil. Trans. 1905, 186, A, 322.
6. Richards and Mathews, J. Amer. Chem. Soc. 1911, 33, 863.
7. Mathews, J. Phys. Chem. 1917, 21, 536.
8. T. Carlton-Sutton, Proc. Roy. Soc. 1917, 93, 155.

TABLE 30.
LATENT HEAT OF FUSION OF ICE (15° gm. cal./gram.).
(According to various observers.)

Temperature	Latent heat of fusion	Reference
-6.5°	76.03	1
-5.0°	76.60	1
-2.8°	77.71	1
-0.7°	78.26	2
0°	79.25	3
"	79.06	4
"	80.03	5
"	79.24	6
"	79.69	7
"	79.61	8
"	79.2	9
"	79.67	10
"	79.63	11
"	79.74	12

1. Petterson, Oefversigt af Kongl. Vetenskaps. Akad. Förhandlingar, Stockholm, 1878, 35, No. 2, 57.
2. Zakrzewski, Bull. Acad. Cracow, 1892, 153.
3. Person, Ann. Chim. 1847, [iii.] 21, 333; 1848, [iii.] 24, 136, 264; 1849, [iii.] 27, 252.
4. Regnault, Ann. Chim. 1843, [iii.] 8, 27; 1849, [iii.] 26, 278.
5. Bunsen, Pogg. Ann., 1870, 141, 31.
6. Desains, Compt. rend. 1843, 18, 981.
7. A. W. Smith, Phys. Review, 1903, 16, 383; 17, 193.
8. Bogojawlenki, Chem. Zentr. 1905, ii, 945.
9. Leduc, Compt. rend. 1906, 142, 46.
10. Roth, Zeitsch. physikal. Chem. 1906, 63, 441.
11. Dickinson, Harper and Osborne, Bureau of Standards, U.S.A., Bull. 1924, 16, 16, 1913, 178, 453.
12. Dickinson and Osborne, Bureau of Standards, U.S.A., Bull. 1915,

Specific Heat.—The specific heat of steam at the temperature and pressure of saturation and at higher temperatures or lower pressures (when it is unsaturated or 'superheated') is of great theoretical and practical importance in connection with the generation of steam and its use in all types of prime movers. Table 31 gives the values at temperatures from 80°-550° and under pressures from 0.5 to 30 atmospheres. The specific heat of saturated steam increases

with temperature and pressure; that of unsaturated steam at constant pressures less than about 9 atmospheres decreases to a minimum value and then increases progressively with temperature; the minimum of specific heat occurs at temperatures which increase with pressure, and may occur at pressures above 9 atmospheres at higher temperatures than have yet been subject to experiment.

The specific heat of steam at or near

TABLE 31.

SPECIFIC HEAT OF UNSATURATED ("SUPERHEATED") STEAM AT THE TEMPERATURE t° AND UNDER THE CONSTANT PRESSURE p KG./SQUARE CM.

(t_s indicates the saturation temperature under the corresponding pressure.)

$p=0.5$	1	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
$t_s=80.9^{\circ}$	99.1°	119.6°	142.9°	158.1°	169.6°	179.1°	187.1°	194.1°	200.4°	206.1°	211.4°	216.2°	220.8°	225.0°	229.0°	232.8°
t																
110°	0.479	0.486	0.499	0.525	0.551	0.578	0.605	0.633	0.663	0.694	0.726	0.759	0.794	0.829	0.865	0.902
120°	0.470	0.481	—	—	—	—	—	—	—	—	—	—	—	—	—	—
130°	0.468	0.477	0.498	—	—	—	—	—	—	—	—	—	—	—	—	—
140°	0.467	0.475	0.494	—	—	—	—	—	—	—	—	—	—	—	—	—
150°	0.466	0.473	0.489	—	—	—	—	—	—	—	—	—	—	—	—	—
160°	0.465	0.472	0.486	0.519	—	—	—	—	—	—	—	—	—	—	—	—
170°	0.465	0.471	0.483	0.512	0.549	—	—	—	—	—	—	—	—	—	—	—
180°	0.465	0.470	0.481	0.507	0.538	—	—	—	—	—	—	—	—	—	—	—
190°	0.466	0.469	0.479	0.502	0.528	0.561	0.602	—	—	—	—	—	—	—	—	—
200°	0.466	0.469	0.478	0.498	0.522	0.549	0.583	0.625	—	—	—	—	—	—	—	—
210°	0.467	0.470	0.477	0.493	0.515	0.539	0.567	0.601	0.643	—	—	—	—	—	—	—
220°	0.467	0.470	0.477	0.491	0.510	0.531	0.555	0.584	0.616	0.657	0.705	—	—	—	—	—
230°	0.467	0.470	0.477	0.491	0.508	0.524	0.545	0.569	0.595	0.627	0.664	0.709	—	—	—	—
240°	0.468	0.471	0.477	0.489	0.504	0.519	0.537	0.557	0.579	0.604	0.633	0.667	0.706	—	—	—
250°	0.469	0.472	0.477	0.488	0.501	0.515	0.530	0.548	0.568	0.588	0.611	0.638	0.669	0.704	0.743	0.794
260°	0.470	0.473	0.477	0.488	0.499	0.512	0.525	0.540	0.556	0.573	0.594	0.614	0.639	0.665	0.694	0.721
270°	0.471	0.474	0.478	0.487	0.498	0.509	0.521	0.534	0.548	0.563	0.579	0.597	0.617	0.638	0.661	0.687
280°	0.472	0.474	0.478	0.487	0.497	0.507	0.518	0.529	0.541	0.555	0.568	0.583	0.599	0.616	0.635	0.658
290°	0.473	0.475	0.479	0.487	0.496	0.505	0.515	0.525	0.536	0.547	0.559	0.571	0.585	0.599	0.614	0.630
300°	0.474	0.476	0.480	0.487	0.495	0.504	0.513	0.523	0.531	0.541	0.552	0.562	0.574	0.586	0.598	0.611
310°	0.475	0.477	0.481	0.488	0.495	0.503	0.511	0.519	0.527	0.536	0.545	0.555	0.564	0.574	0.585	0.596
320°	0.477	0.478	0.482	0.488	0.495	0.502	0.510	0.518	0.525	0.533	0.540	0.548	0.557	0.566	0.575	0.584
330°	0.478	0.480	0.483	0.489	0.496	0.502	0.509	0.516	0.523	0.530	0.536	0.543	0.550	0.558	0.566	0.574
340°	0.479	0.482	0.484	0.490	0.496	0.502	0.508	0.515	0.520	0.527	0.533	0.539	0.545	0.552	0.559	0.566
350°	0.481	0.483	0.485	0.491	0.496	0.502	0.507	0.513	0.519	0.525	0.530	0.536	0.541	0.547	0.553	0.559
360°	0.482	0.484	0.486	0.492	0.497	0.502	0.507	0.512	0.517	0.523	0.528	0.533	0.537	0.543	0.548	0.554
370°	0.483	0.485	0.487	0.492	0.497	0.502	0.507	0.511	0.516	0.521	0.526	0.530	—	—	—	—
380°	0.485	0.486	0.488	0.493	0.498	0.503	0.507	0.511	0.516	0.520	0.524	0.528	—	—	—	—
390°	0.486	0.488	0.490	0.494	0.498	0.503	0.507	0.511	0.515	0.519	0.523	0.527	—	—	—	—
400°	0.487	0.489	0.491	0.495	0.499	0.503	—	—	—	—	—	—	—	—	—	—
410°	0.489	0.490	0.492	0.496	0.500	0.504	—	—	—	—	—	—	—	—	—	—
420°	0.490	0.492	0.494	0.497	0.501	0.505	—	—	—	—	—	—	—	—	—	—
430°	0.492	0.494	0.496	0.498	0.502	0.506	—	—	—	—	—	—	—	—	—	—
440°	0.494	0.495	0.497	0.500	0.504	0.507	—	—	—	—	—	—	—	—	—	—
450°	0.496	0.497	0.499	0.501	0.505	0.508	—	—	—	—	—	—	—	—	—	—
460°	0.498	0.498	0.500	0.503	0.506	0.509	—	—	—	—	—	—	—	—	—	—
470°	0.499	0.500	0.501	0.505	0.507	0.510	—	—	—	—	—	—	—	—	—	—
480°	0.501	0.502	0.503	0.506	0.508	0.512	—	—	—	—	—	—	—	—	—	—
490°	0.503	0.504	0.505	0.507	0.509	0.513	—	—	—	—	—	—	—	—	—	—
500°	0.505	0.505	0.506	0.509	0.511	0.514	—	—	—	—	—	—	—	—	—	—
510°	0.506	0.506	0.508	0.510	0.512	0.515	—	—	—	—	—	—	—	—	—	—
520°	0.507	0.508	0.510	0.512	0.513	0.516	—	—	—	—	—	—	—	—	—	—
530°	0.509	0.509	0.511	0.513	0.515	0.517	—	—	—	—	—	—	—	—	—	—
540°	0.510	0.511	0.513	0.515	0.516	0.518	—	—	—	—	—	—	—	—	—	—
550°	0.512	0.513	0.515	0.517	0.518	0.520	—	—	—	—	—	—	—	—	—	—
560°	0.514	0.515	0.516	0.518	0.520	0.522	—	—	—	—	—	—	—	—	—	—

Knoblauch and Batsch, Zeitsch. Ver. Ing. 1922, 66, 418; based on previous work by Knoblauch et al.

atmospheric pressure has been measured at still higher temperatures; up to 1400° it is represented by $C_{p, \text{atm}} = 0.4669 - 0.0.168t + 0.0.44t^2$ or $C_{p, \text{atm}} = 0.4644 + 0.006925 \times 10^{-6} t^3$ (Holtz and Henning, Ann. Physik, 1907, [iv.] 23, 309; see also Ann. Physik, 1905, [iv.] 78, 739; Wilm. Abh. Phys.-Tech. Reichsanstalt, 1905, 4, 131; and Lorenz, Phys. Zeit. 1904, 5, 353). The ratio of the specific heats at constant pressure and constant volume is about 1.3 at 103°

1.330 at 110°, 1.313 at 120°, and 1.312 at 130° (Treitz, Bonn. 1903).

The heat capacity of water, usually at 15°, is used as a standard, and its variation with temperature is therefore of great practical importance and has been the subject of many precise investigations. Some of the more important results are given in Table 32 (see also, *inter alia*, Lötlin, Mitt. naturw. Ges. Winterthur, 1906; Dietrich, Ann. der Physik,

1902, [iv.] 16, 592; Barnes, Phil. Trans. 1902, A. 192, 149; Barnes and Cooke, Phys. Review, 1902, 15, 65; Cotty, Ann. Chim. 1911, [viii.] 24, 282).

With rise of temperature from 0°C. the specific heat decreases rapidly to a minimum value and then increases more slowly at a rate which itself increases but slightly with temperature; the measurements of Callendar and of Jaeger and Steinwehr agree in placing the minimum of specific heat at about 35°.

Numerous formulae have been proposed to express the variation of the specific heat of water with temperature, but they have no physical basis; as an example, the formula $C_p = 1.00733 - 0.0007416t + 0.000016845t^2$

$$- 0.000,000,09552t^3$$

where $C_{p,0} = 1$, agrees well from 0°–100° with the best experimental values (Narbutt, Zeitsch. Physik. Chem. 1918, 19, 513).

Below 0° the specific heat of undercooled

water increases very rapidly with fall of temperature, attaining the value 1.0155 at –5° (Barnes, l.c.).

The specific heat of water at 0° is decreased by 0.0001025 if the pressure is increased by one atmosphere.

The specific heat of ice is less well known; it is about half that of water at 0° and becomes quite small at low temperatures. A number of determinations are given in Table 33. It appears to increase very rapidly just below the melting-point (A. W. Smith, Phys. Review, 1903, 17, 193), probably owing to physical inhomogeneity.

Entropy.—The entropy of ice at 0°, calculated from absolute zero, is found to be 9.96 per gram molecule; adding 5.26 the entropy of fusion of ice at 0°, and 1.58 that due to heating water from 0° to 25°, the entropy of water at 25° is 16.8 per gram molecule (Lewis and Gibson, J. Amer. Chem. Soc. 1917, 39, 2575).

TABLE 32.
SPECIFIC HEAT OF WATER.

Temperature	Regnault Air-thermometer	Bousfield: Hydrogen- thermometer	Callendar Kelvin scale	Jaeger and v. Steinwehr Kelvin scale
0°	0.9992	1.0070	1.0093	(1.005)
5°	0.9994	1.0039	1.0047	1.0030
10°	0.9997	1.0016	1.0019	1.0013
15°	1.0000	1.0000	1.0000	1.0000
20°	1.0004	0.9991	0.9980	0.9990
25°	1.0008	0.9989	0.9980	0.9983
30°	1.0012	0.9990	0.9975	0.9979
35°	1.0017	0.9997	0.9973	0.9979
40°	1.0022	1.0006	0.9973	0.9981
45°	1.0028	1.0018	0.9975	0.9987
50°	1.0034	1.0031	0.9978	0.9996
55°	1.0041	1.0045	0.9982	—
60°	1.0048	1.0058	0.9987	—
65°	1.0056	1.0070	0.9993	—
70°	1.0064	1.0080	1.0000	—
75°	1.0072	1.0088	1.0008	—
80°	1.0081	1.0091	1.0017	—
85°	1.0091	—	1.0026	—
90°	1.0101	—	1.0036	—
95°	1.0111	—	1.0046	—
100°	1.0122	—	1.0057	—
120°	1.0169	—	1.0108	—
140°	1.0224	—	1.0167	—
160°	1.0286	—	1.0234	—
180°	1.0355	—	1.0309	—
200°	—	—	1.0392	—

Regnault, Mém. de l'Acad. 1847, 21, 729; Pogg. Anz. 1850, 79, 241.

W. A. and W. E. Bousfield, Phil. Trans. 1911, 211, A. 199.

Callendar, Proc. Roy. Soc. 1912, 86, A. 254; Phil. Trans. 1912, 212, A. 1.

Jaeger and v. Steinwehr, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1915, 424;

TABLE 33.
SPECIFIC HEAT OF ICE.
(According to various observers.)

Temperature	Specific heat	Reference
-250.6°	0.0303	1
-235°	0.086	1
-252° to -188°	0.146	2
-185.9°	0.189	1
-188° to -78°	0.285	2
-189.5° to -81.7°	0.266	3
-100°	0.325	4
-188° to 0°	0.337	5
-185° to 0°	0.345	6
-50°	0.409	4
-78.4° to 0°	0.424	5
-40° to 0°	0.431	7
-76.9° to -2.9°	0.433	3
-78° to 18°	0.463	2
0°	0.505	7

1. Pollitzer, Zeitsch. Elektrochem. 1913, 19, 513.
2. Dewar, Proc. Roy. Soc. 1905, A. 76, 325.
3. Nernst, Koref and Lindemann, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1910, 247.
4. Nernst, *ibid.* 1910, 262.
5. Jackson, J. Amer. Chem. Soc. 1912, 34, 1470.
6. Nordmeyer and Bernoulli, Ber. 1907, 5, 175.
7. Dickinson and Osborne, Bureau of Standards, U.S.A., Bull., 1915, 12, 49.

OPTICAL PROPERTIES.

Crystalloluminescence.—It has been reported that if water be rapidly frozen, bright flashes of luminescence are observed (Trautz, Zeitsch. physikal. Chem. 1905, 53, 9).

Colour: absorption of light.—There is much evidence, irrelevant here, that the bright blue colour often observed in water, notably in that of china-clay settling pits, reservoirs for large scale water-softening, and some lakes, e.g. Lake Geneva, is due to the scattering of light by

WATER VAPOUR—ABSORPTION BANDS IN THE INFRA-RED.

Maxima in μ ($=10^{-3}$ mm. $=10^4$ Å).

0.944*	(4.56)	9.30	19.70
1.128	(4.70)	9.50	20.5
1.157	4.98	9.74*	21.6
1.367	5.04	9.98	22.0
1.411	5.18	10.30*	24.1
1.480	5.24	10.66	27.1
1.843		10.80	29.4
1.870	6.42	10.94*	31.0*
1.904	6.49	11.24	33.1
1.985		11.47	
(2.010)	6.56	11.66*	
	6.61	11.89	
2.898		12.42*	
2.948	7.44	12.82	
2.997	7.58	13.34*	
3.028	7.75	13.62	
3.070	7.88	14.32*	
3.112	8.04	14.98	
3.194*	8.17	15.62*	
3.245	8.23	16.00	
3.295	8.36	(16.80)	
3.340	8.42	17.33*	
3.402	8.51	18.37	
3.463	8.73	19.22	
	8.99		

Hottner, Ann. Physik. 1913, 55, 495.

WATER.

minute suspended particles. But glacier ice and the water produced therefrom, which are undoubtedly very pure, show by transmitted light a distinct greenish-blue colour (H. Davy, Collected Works, 1840, 9, 199; Bunsen, Pogg. Ann. 1851, 83, 197; Rayleigh, Nature, 1910, 83, 48).

Pure distilled water in a tube several metres long and blackened internally is quite definitely greenish-blue by transmitted light.

As ozone is deep blue, liquid oxygen pale slightly greenish-blue, and hydrogen peroxide, methyl alcohol, ethyl alcohol and similar simple hydroxyl compounds are bluish-green, this colour is probably an intrinsic property of pure water. In smaller thicknesses water appears colourless.

The absorption spectrum of water in the visible region accords with its observed colour. In the red from 660-640 μ the absorption coefficient is about 0.3, in the orange at approximately 600 μ it is about 0.15, whence it falls rapidly to about 580 μ , and is less than 0.05 throughout the regions of the spectrum from yellow to violet (von Aufsess, Die Farbe der Seen, München, 1903). The absorption in the ultra-violet has been studied by Kreusler (Ann. der Physik. 1901, [iv.] 6, 412).

Water is opaque to infra-red radiation over a wide range of wave-length. The most recent measurements are given in Table 34 (see also Bode, Ann. Physik. 1909, [iv.] 30, 326; von Bahr, Ber. 1913, 15, 731; and, for the fine structure, Sleator, Astrophys. J. 1918, 48, 125; Wichmann, Physikal. Zeitsch. 1921, 22, 535; Ann. Physik. 1922, [iv.] 66, 501).

Water vapour is more transparent than liquid water to infra-red radiation. The opacity of the atmosphere to such radiation is mainly due to its content of water vapour, and does not extend to wave-lengths shorter than about 11 μ ; the absorption by an equivalent layer, say 2 cm., of liquid water is complete down to 1.2 μ . The difference gave rise to prolonged controversy between Magnus and Tyndall before its nature was established (Magnus, Pogg. Ann. 1861, 112, 497; 114, 635; 1863, 118, 575; 1864, 121, 186; 1866, 127, 613; 1867, 130, 207; Tyndall, Proc. Roy. Soc. 1860, 10, 37; 1861, 11, 558; 1879, 30, 10; 1881, 31, 307, 478; 1883, 35, 21; Phil. Mag. 1861, [iv.] 22, 377; 1862, [iv.] 23, 252; 1863, [iv.] 26, 44; 1866, [iv.] 32, 118; 1867, [iv.] 33, 425).

Water also absorbs X-rays (for details, see Hewlett, Phys. Review, 1921, 17, 284; Richtmyer, *ibid.* 1921, 18, 13).

Refractive Index.—Table 35 gives the refractive index of water for light of various wave-lengths and at temperatures from 0°-80°; these values are substantially confirmed by more recent and very precise determinations, which give, for the iron line E ($\lambda=5270.11$)

$$n_D^{15^\circ} = 1.3356359$$

and, for sodium light, the following values referred to air and *in vacuo*:

Temperature .	20°	25°	30°
n_D in air .	1.33299	1.33248	1.33190
n_D in vacuo .	1.33335	1.33284	1.33225

TABLE 35.

Against air at the same temperature; and its rate of increase with temperature for the temperature ranges and spectral lines specified.

Light		n_D°	$(n_{20^\circ} - n_{20^\circ}) \times 10^6$	n_{20°	$(n_{20^\circ} - n_{20^\circ}) \times 10^6$	n_{20°	$(n_{20^\circ} - n_{20^\circ}) \times 10^6$	n_{20°	$(n_{20^\circ} - n_{20^\circ}) \times 10^6$	n_{20°
Element	λ - Å									
Cd .	2144.5	1.40500	103	1.40397	253	1.40144	382	1.39762	454	1.39308
Cd .	2194.7	1.39987	104	1.39883	252	1.39631	380	1.39521	453	1.38798
Cd .	2265.1	1.39360	103	1.39257	256	1.39001	377	1.38624	455	1.38109
Cd .	2312.9	1.38982	104	1.38878	253	1.38625	378	1.38247	452	1.37795
Au .	2428.1	1.38210	107	1.38103	254	1.37849	374	1.37475	451	1.37024
Ud .	2573.2	1.37447	103	1.37344	251	1.37093	374	1.36719	450	1.36360
Au .	2976.1	1.37007	103	1.36904	248	1.36656	371	1.36285	448	1.35837
Ud .	2748.7	1.36739	102	1.36637	250	1.36387	368	1.36019	446	1.35573
Al .	3082.3	1.35768	97	1.35671	247	1.35424	365	1.35059	441	1.34618
Cd .	3403.6	1.35139	95	1.35044	244	1.34800	364	1.34436	437	1.33999
Cd .	3611.9	1.34834	96	1.34738	241	1.34497	361	1.34136	434	1.33702
Al .	3944.1	1.34457	91	1.34366	242	1.34124	359	1.33765	431	1.33334
Cd .	4415.9	1.34071	90	1.33981	240	1.33741	356	1.33385	429	1.32956
Cd .	4678.3	1.33903	88	1.33815	238	1.33577	352	1.33225	428	1.32797
Cd .	4800.1	1.33834	84	1.33750	234	1.33518	353	1.33163	429	1.32734
Cd .	5338.5	1.33582	83	1.33499	233	1.33266	350	1.32916	423	1.32493
Na .	5893.1	1.33381	81	1.33300	231	1.33069	351	1.32718	418	1.32300

Flatow, Ann. Physik. 1903, [iv.] 12, 85: the values given by Flatow are in substantial agreement with the determinations of other observers cited, e.g. Landolt-Börnstein, Tabellen, 1923, p. 246.

(Gifford, Proc. Roy. Soc. 1906, A, 78, 406; Baxter, Burgess and Daudt, J. Amer. Chem. Soc. 1911, 33, 893).

Temperature	0°	10°	30°	40°	50°	60°	70°
Dispersion equivalent	0.0147	146	148	145	148	147	144
Dispersive power	0.0429	439	445	438	449	448	441

(Gladstone and Dale, Phil. Trans. 1858, 148, 887; 1863, 153, 323).

Measurements with electrical waves, $\lambda=3.5$ – 4.5 cm., show that the refractive index of water increases with the wave-length and that water exhibits anomalous dispersion (Mercury, Bull. Acad. Sci. Cracow, 1911, 123).

Ice exhibits double refraction and is optically positive. The refractive indices for sodium light are for the ordinary ray 1.3091 and for the extraordinary ray 1.3104 (Pulfrich, Wied. Ann. 1888, 34, 336; cf. the values 1.3083 and 1.3133 respectively of Meyer, *ibid.* 1887, 31, 322).

Scattering of Light.—It has been shown that pure water, free from ultra-microscopic suspended particles, scatters light, and that the scattered light is polarised, but the interpretation of the phenomenon is as yet incomplete or lacking (see Einstein, Ann. Physik. 1910, 33, 1275; Cabannes, J. Phys. Chem. 1920, [vi.] 1, 129; Martin, J. Phys. Chem. 1920, 24, 248; 1922, 26, 75; 1923, 27, 558; Rayleigh, Proc. Roy. Soc. 1920, 97 A, 435; Raman, *ibid.* 1922, 102, A, 151; Phil. Mag. 1923, 45, 625).

MAGNETIC AND ELECTRICAL PROPERTIES.

Coefficient of magnetisation.—The coefficient of magnetisation for water referred to unit mass has been determined by several observers to be about -0.72×10^{-6} C.G.S. units at 20° (de Haas

T°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Ω	0.9998	1.0001	1.0008	1.0018	1.0029	1.0041	1.0053	1.0065	1.0074

Electrical conductivity.—Pure water is a very poor conductor of electricity. The purest water ever obtained (see Purification) had a specific conductivity 0.043×10^{-9} reciprocal ohm (mho) at 18°.

It is calculated that the conductivity of

The dispersion equivalent $n_D - n_A$ and the dispersive power $(n_D - n_A)/(n_D - 1)$ are given as follows:

and Drapier, Ann. Physik, 1913, [iv.] 42, 673; Weiss and Piccard, Compt. rend. 1912, 155, 1234; Piccard, Arch. Sci. phys. nat. 1913, [iv.] 35, 458; see also Gray and Birse, J. Chem. Soc. 1914, 105, 2707; Hayes, Phys. Rev. 1914 (2), 3, 295). This coefficient has a temperature coefficient of about $+0.00012$ at 20°.

Ice is said to be diamagnetic (Brunner, Pog Ann. 1850, 79, 173).

Magneto-optic Rotation.—The rotation of the plane of polarisation of light by a given thickness of water in a given magnetic field depends upon the wave-length of light and upon the temperature. The specific rotation (for 1 cm. of liquid in unit magnetic field) for the D line at 18° is $\omega_{18}^D = 0.01309$ minutes of arc (Agerer, Sitzungsber. Akad. Wiss. Wien. 1905, 114, 830), and its variation with temperature is given between 3° and 98° by $\omega_t^D = 0.01311(1 - 0.00305t + 0.000305t^2)$ (Rodger and Watson, Zeitsch. physikal. Chem. 1896, 19, 357).

The molecular magnetic rotation of water at 4°C. is taken as the standard, unity, for fixing that of other liquids, their molecular magnetic rotation being then given by

$$\Omega = \frac{\omega \times \text{mol. weight}}{18}$$

Thus the variation of the molecular magnetic rotation of water is of practical importance and is illustrated by the following data (Rodger and Watson):—

absolutely pure water at 18° should be 0.038×10^{-6} mho. From the same or similar data it is calculated that the *ionisation constant*, $K = [H^+] \times [OH^-]$ for water is 0.73×10^{-14} at 18° (Sorensen, Biochem. Zeitsch. 1909, 21, 191; Sorensen and Palitzsch, *ibid.* 1910, 24, 387);

TABLE 36.

DIELECTRIC CONSTANT OF WATER, ϵ .

Temperature	λ cm.	ϵ	Reference
—	∞	76	1
—	∞	80	2
18°	∞	81.1	3
17°	50	81.0	4
17°	40	80.7	4
17°	30	80.4	4
0	75	88.2	5

1. Cohn and Arons, Wied. Ann. 1886, 28, 454; 1888, 33, 13, 31.

2. Smale, Wied. Ann. 1897, 57, 215.

3. Turner, Zeitsch. physikal. Chem. 1900, 35, 385.

4. Bukop, Diss. Grieswald, 1911.

5. Drude, Wied. Ann. 1896, 59, 17.

It varies very much with temperature (see Noyes, Kato and 1900, 32, 164).

Ice is quite a good insulator; its specific resistance is 4865 megohms at 0° and 33,540 megohms at -17° . Thus, a cable, the insulation of which is defective through moisture, will frequently show a good insulation test when exposed to severe frost.

Dielectric capacity.—The dielectric constant for steam at 145° and 760 mm. is $\epsilon=1.00705$, and its variation with temperature is expressed by $\epsilon_t = \epsilon_0 - \alpha(t_2 - t_1)$ where $\alpha=1.4 \times 10^{-4}$ and $t_1=145^{\circ}$ (Bädeker, Zeitsch. physikal. Chem. 1901, 36, 305).

Table 36 gives a series of values of ϵ for water for different wave-lengths. The dielectric constant varies with pressure from 7-200 atmospheres by about 0.0046 p.c. per atmosphere (Falkenberg, Ann. Physik. 1920, [vi.] 61, 145).

The dielectric constant for ice for $\lambda=5000$ cm. at -18° is 3.1 (Abegg, Wied. Ann. 1898, 65, 229) and for $\lambda=75$ cm. at -190° is 1.76-1.88 (Behn and Kiebitz, Boltzmann's Festschrift, Leipzig, 1904, 610).

The ionising potential for water vapour is calculated to be 8.64 volts (Compton, Phys. Review, 1916, (2), 8, 412).

THE CHEMICAL PROPERTIES OF WATER.

Molecular constitution.—It was formerly supposed that the relatively high density of water vapour in the neighbourhood of the boiling-point and at lower temperatures connoted the presence in it of molecules more complex than H_2O (see e.g. Bose, Zeitsch. Elektrochem. 1908, 14, 269; Oddo, Gazz. chim. ital. 1915, 45, i. 319; 395), but if the experimental values are corrected for the deviation of water vapour from the ideal gas-laws and recalculated by the Clausius-Clapeyron equation the results afford no evidence whatever for any deviation from the simple formula H_2O , and this must, therefore, be assumed to represent correctly the molecular state of water vapour (Kendall, J. Amer. Chem. Soc. 1920, 42, 2477; Menzies, *ibid.* 1921, 43, 851).

On the other hand, experiments with a modified Wilson's expansion apparatus, interpreted in accordance with Lenard's theory, indicate the presence of about 1.9×10^{-11} p.c. of uncharged nuclei of relatively large dimensions which are most probably polymerised molecules of the type $(H_2O)_n$ or $(H_2O)_m$ (Andrén, Ann. Physik. 1917, [iv.] 52, 1).

With regard to liquid water, there is a great body of evidence pointing to the presence of complex molecules. It is now fairly generally held that the abnormality of water as compared with other liquids in so many physical properties is due to polymerisation. This explanation was first advanced by Whiting (A New Theory of Cohesion Applied to the Thermodynamics of Liquids and Solids, Harvard University, Cambridge, Mass. 1884, p. 70), who pointed out that water at 0° may contain 15-25 p.c. and at 100° 17-26 p.c. of dissolved ice, and that the observed expansion of 4 p.c. by volume in this interval is the resultant of a normal expansion of some 8-10 p.c. by volume and a contraction due to the melting of the

dissolved ice. Eight years later, Röntgen (Wied. Ann. 1892, [5] 45, 91) independently suggested that water consists of 'ice molecules' and 'water molecules,' the former being more complex but less dense than the latter.

Later, Sutherland elaborated the hypothesis still further and, possibly influenced by Traube's theory that normal liquids consist of 'liquidogenic' and 'gasogenic' molecules, supposed water to consist of single, double and triple molecules, to which he gave the names *hydrol* (H_2O), *dihydrol* (H_4O_2), and *trihydrol* (H_6O_3).

In liquid water we then have the equilibria: $2H_2O \rightleftharpoons 3H_4O_2 \rightleftharpoons 6H_6O_3$. Steam is hydrol; ice is supposed to consist chiefly or wholly of trihydrol. Because of the lower density of ice it seems probable that trihydrol is less dense than dihydrol; and our present knowledge of the crystal structure of ice (*q.v.*) accords well with the view. Whiting's theory, originally propounded simply to explain the anomalous expansion of water, has been applied successively to the other physical properties of water, and has been found to accord so well with the observed facts that its substantial truth seems clear (see e.g. Walden, Guye, Bonsfield and Lowry, Sutherland and Nernst, Trans. Faraday Soc. 1910, 6, 71-123). It is of interest to consider some examples.

The melting of ice is attended by considerable absorption of heat and decrease of volume; *ex hypothesi* then, these phenomena characterise the conversion of trihydrol to dihydrol. Therefore, in accordance with Le Chatelier's theorem, either rise of temperature or increase of pressure will tend to dissociate trihydrol and so reduce the proportion present in water. If the volume change of water on heating is the resultant of (a) contraction due to depolymerisation of trihydrol and (b) the normal expansion of dihydrol, the preponderance of (a) up to 4° (owing to the relatively higher proportion of trihydrol then present) can explain the observed net contraction between 0° and 4° . Similarly, the diminution of the proportion of trihydrol by pressure explains the lowering of the temperature of maximum density by increase of pressure.

The minimum of compressibility of water about 50° is best accounted for by Bonsfield and Lowry's extension of the hypothesis (Trans. Faraday Soc. 1910, 6, 85); they assume that monohydrol, like trihydrol, is less dense than dihydrol, and constitutes an important proportion of water above 50° . The increased proportion of a less dense and therefore more compressible constituent both above and below that temperature then accords with the observed greater compressibility (see also Richards and Palitzsch, J. Amer. Chem. Soc. 1919, 41, 63, for a discussion of this matter, and Pagliani, Gazz. chim. ital. 1920, 50, i. 186).

Similarly convincing explanations have been elaborated for the observed variations with temperature and pressure of the viscosity (Pagliani, *loc. cit.*), specific heat (Nernst, J. Chem. Soc. 1910, A. ii. 844), index of refraction (Chéneveau, Compt. rend. 1913, 156, 1972), magnetisation (Piccard, *ibid.* 1913, 155, 1497), dielectric constant (Falkenberg, Ann. Physik. 1920, [iv.] 61, 145), &c.

Measurements of the molecular weight of water by the cryoscopic and ebullioscopic

WATER.

methods in supposedly neutral solvents give no evidence of association, but in fact water does react (*vide infra*) with such solvents in a manner which renders the method untrustworthy. More reliable conclusions may be drawn from measurements upon dilute solutions in such definitely reactive solvents as phosphorus oxychloride or nitrogen tetroxide, and these give concordant values for the molecular weight approximating closely to 36, indicating the formula H_2O , (Oddo, *Gazz. chim. ital.* 1916, 46, i. 172; see also Bruni and Amadori, *Gazz. chim. ital.* 1910, 40, ii. 1). Attempts to calculate the complexity of ice molecules in solution from the variation of expansibility, compressibility and specific heat on the assumption that ice (H_2O)_n in solution in water retains its normal density lead to values for *n* around 12 (Duclaux, *Compt. rend.* 1911, 152, 1387), but this assumption is probably incorrect.

Many attempts have been made by extrapolation to calculate the properties of pure monohydrol and dihydrol, but in the present state of knowledge these are premature (see e.g. Sutherland, *J. Chem. Soc.* 1910, A. ii. 843; Oddo, *Gazz. chim. ital.* 1916, 46, i. 188).

Observations upon the formation and liquefaction of ice crystals (Skworzoff, *J. Chem. Soc.* 1911, A. ii. 970) and the phenomena of scattering of light by water suggest the presence in water of molecules of definite structure, which is intelligible on the assumption that water is actually not a simple liquid, but, at low temperatures, a solution of ice molecules in water (dihydrol). From this standpoint, the freezing-point of water is simply to be regarded as the temperature at which the concentration of trihydrol, increasing with fall of temperature, becomes equal to the solubility of trihydrol in water which, it is assumed, decreases with fall of temperature. Regulation of ice under slight pressure may conceivably occur through local

liquefaction of the ice and its resolidification on release of pressure. But neither pressure nor capillary action (alleged by Thomson, *Proc. Roy. Soc.* 1857, 8, 455; 1859, 9, 198; 1862, 11, 473; *Phil. Mag.* 1862, [iv.] 23, 497; 24, 395) are necessary, because regelation can occur under water without pressure (Faraday, *Proc. Roy. Soc.* 1860, 10, 440). On the ice solution hypothesis it is easy to understand how two blocks of ice under water may grow together by a process of solution and recrystallisation.

In addition to the evidence indicated very briefly above there is a mass of experimental work on solution which can best be explained on the foregoing hypothesis.

It is, perhaps, important to observe that if this hypothesis of the constitution of water be correct, the melting of ice, the expansion of water (at least at low temperatures), the generation of steam, &c., commonly regarded as types of simple physical change, are in fact changes of precisely the same kind as, say, the dissociation of nitrogen tetroxide or phosphorus pentachloride or the polymerisation of aldehydes, cyanogen chloride, &c., the essentially chemical character of which is never questioned. It is unnecessary to elaborate the obvious conclusion as to the validity of the distinction so frequently drawn between chemical and physical change.

CHEMICAL REACTIONS.

Dissociation and synthesis.—Water is a fairly stable compound, and is dissociated only to a small extent at about 3000°, the temperature of the oxyhydrogen flame.

In the oxyacetylene flame, which is considerably hotter, steam is largely dissociated, and the wide applicability of this flame to the welding of metals is in fact due to the consequent presence in it of free hydrogen. The following table shows the percentage dissociation of water vapour at high temperatures:—

Temperature	1124°	1207°	1290°	1432°	1510°	1590°	1695°	1984°	2370°	2488°	2561°	2656°
P.c. dissociated	0.008	0.019	0.034	0.102	0.182	0.354	0.518	1.79	4.3	6.6	9.8	11.1

The data from 1984° upwards, obtained by an explosion method, are less trustworthy than those at lower temperatures, but probably represent well enough the general trend of the reaction (Löwenstein, *Zeitsch. physikal. Chem.* 1906, 54, 715; Langmuir, *J. Amer. Chem. Soc.* 1906, 18, 1357; v. Wartenburg, *Zeitsch. physikal. Chem.* 1906, 56, 513; Bjerrum, *ibid.* 1912, 79, 513; but see Holt, *Phil. Mag.* 1907, [vi.] 12, 630).

In agreement with these facts, gaseous hydrogen and oxygen readily combine to form water when heated, when exposed to the electric spark or to a silent electric discharge, when subjected to the radiations of radioactive elements, or when exposed to ultra-violet light.

There is no evidence, though the assumption has frequently been made, that oxygen and hydrogen combine at all at ordinary temperatures in the dark, though they do so very slowly in sunlight (Baker, *Proc. Chem. Soc.* 1902, 12, 40). Isothermal increase of pressure to 50 atmospheres has no effect in promoting union (de la Roche, *Schweigger's Journ.* 1811, 1, 172; see also Degen, *Pogg. Ann.* 1836, 38, 645).

At 100° no combination can be detected in 218 days, but at 300° the formation of water is just appreciable in 65 days (Meyer and Raum, *Ber.* 1895, 28, 2904). At 400° the velocity of reaction is such that the formation of water may be recognised within a week (Bone, *J. Chem. Soc.* 1902, 81, 535; 1904, 85, 694), and thereafter the velocity of the reaction increases rapidly with temperature until at about 510°–560° explosive combination occurs. The precise value of the ignition temperature depends on the composition of the explosive mixture (being lowest, 507°, when the ratio $H_2 : O_2 = 1 : 4$) and falls with increase of pressure (Dixon and Coward, *J. Chem. Soc.* 1906, 95, 514; Dixon, *ibid.* 1910, 97, 661), but depends also upon the method of experiment and the material of the containing vessels. A small proportion of water vapour is essential to combination by normal combustion (Baker) or through the catalytic action of platinum (French, *Chem. News* 1900, 81, 292); oxygen and hydrogen dried with phosphorus pentoxide do not react on platinum black, and only combine slowly in contact with a platinum wire at about 800°; but the explosion flame, once started, is similar in both cases and

and dried gases (Dixon and Bradshaw, *Proc. Roy. Soc.* 1907, A, 79, 224).

Ignition of detonating gas by an electric spark is frequently a purely thermal effect, but this cannot be true of the slow combination brought about by the silent discharge (Berthelot, *Ann. Chim.* 1879, [v.] 17, 142; Deherain and Maquenne, *Compt. rend.* 1881, 93, 895, 963, 1021; Mixter, *Amer. Journ. Sci.* 1898, [iv.] 4, 51; Kirby, *Phil. Mag.* 1904, [vi.] 7, 223). A general examination of the effects indicates that the cathode column is the region of greatest chemical activity (Kirby, *Phil. Mag.* 1907, [vi.] 13, 269), and it seems probable that reaction proceeds by the ionisation of both gases, though short wave-length radiations akin to ultra-violet light may contribute to the effect.

Kernbaum has found (*Compt. rend.* 1910, 151, 319) that H_2O_2 and H_2 are produced by the silent discharge in oxygen and hydrogen mixtures, and concludes that the action of the discharge is analogous to that of ultra-violet light.

Ultra-violet light causes combination of hydrogen and oxygen and decomposes water, the reaction in either case tending to the same point of equilibrium which, for example, at 150° is that corresponding to thermal equilibrium at 1250° (Coehn, *Ber.* 1910, 43, 880; Coehn and Grote, *Nernst's Festschrift*, 1912, 136; Andréeff, *J. Russ. Phys. Chem. Soc.* 1911, 43, 1342). Water in a quartz vessel is decomposed thus even by sunlight (Kernbaum, *Compt. rend.* 1909, 149, 273; *Bull. Acad. Sci. Cracow*, 1911, A, 583).

The action of ultra-violet light in decomposing water is chiefly due to the radiation of very short wave-length ($\lambda=1900$), and is best observed, therefore, by the use of low-tension or new high-tension quartz mercury vapour lamps, which emit radiation relatively rich in rays of short wave-length (Tian, *J. Chem. Soc.* 1915, A, ii, 828; Obolewsky, *Ann. Physik*, 1912 [iv.] 39, 961).

In this decomposition pure hydrogen is at first the only gaseous product; later oxygen also is produced and accumulates until the composition of the mixture is that of detonating gas. This is best explained on the assumption that the primary action is an auto-oxidation producing hydrogen and hydrogen peroxide, $2H_2O \rightarrow H_2 + H_2O_2$, oxygen being formed by a secondary decomposition of the latter,



which can result from the action of moderately short wave-length radiation (λ 2500–3000) (Tian, *Compt. rend.* 1911, 152, 1012). In support of this theory, there is evidence that hydrogen peroxide formed from water-vapour in air by the action of ultra-violet rays in sunlight forms active nuclei for the condensation of moisture (Bleher, *Ann. Physik*, 1912, [iv.] 39, 1313). Contrary to suggestions which have been made, it would seem that the amount of hydrogen peroxide produced by ultra-violet light is much too small to account for the bactericidal action of the latter (see Courmont, Nogier and Rochat, *Compt. rend.* 1910, 150, 1453).

The fact that changes of potential occur at polished inert electrodes immersed in solutions of photo-sensitive colouring matters and exposed

to light may be explained on the assumption of a photochemical decomposition of the water by visible light; but there is no other evidence in support of this hypothesis (Baur and Rebmann, *Helv. Chim. Acta.* 1923, 4, 256).

The synthesis and decomposition of water by α -radiation is well established (Davis and Edwards, *J. Soc. Chem. Ind.* 1905, 24, 266; Pickel, *Zeitsch. anorg. Chem.* 1904, 38, 307; Lind, *J. Amer. Chem. Soc.* 1919, 41, 531, 551; Duane and Scheurer, *Compt. rend.* 1913, 156, 466). In a given spherical or cylindrical vessel the velocity of reaction depends only on the quantity of emanation present and the gas pressure, but the velocity diminishes with increase in the volume of the vessel and depends upon the hydrogen:oxygen ratio. There is reason to suppose that combination is preceded by collision-ionisation of both gases, but the mechanism of reaction is not well understood.

Catalytic action in the synthesis of water was first observed by Davy (*Phil. Trans.* 1817; 97, 45, 77) in the case of platinum, and has been the subject of so many investigations that its adequate discussion here would be impossible, and properly belongs to the general consideration of catalytic action.

The energy change involved in these reactions is expressed by the heat of formation of water for which the chief data are given below.



$x=68,310$. Ice calorimeter; const. pressure, $t=0^\circ$ (Schuller and Wartha, *Wied. Ann.* 1877, 2, 381).

68,390. Burning at const. pressure, $t=18^\circ$ in 15° calories (Thomsen, *Thermochem. Untersuch.* 2, 45).

68,400. Burnt in bomb; calc. to const. pressure at $t=17^\circ$ in 15° cal. (Mixter, *Silliman's J.* 1903, (4), 16, 214).

68,380. Mean result of critical recalculation of foregoing, at 18° and const. pressure, in 15° cal. (Roth, *Zeitsch. f. Elektrochem.* 1920, 26, 1, 288).

Water is decomposed by the passage of an electric current, but owing to its very low conductivity the extent of the decomposition is very small with pure water. In practice, the electrolytic decomposition of water so-called, is effected by the electrolysis of aqueous solutions of electrolytes, and according to the ionic hypothesis the production of one at least of the constituent gases at the electrodes is due to a secondary action of the discharged ions.

It has long been known that the passage of an electrical discharge through steam produces both decomposition and a sorting of the products apparently akin to electrolysis (Farrot, *Compt. rend.* 1858, 46, 180; 47, 359; *Ann. Chim.* 1861, [iii.] 61, 161; J. J. Thomson, *Recent Researches in Electricity and Magnetism*, Cambridge, 1893, 559). But both oxygen and hydrogen may appear at either or both electrodes according to the size and form of the discharge vessel, and it seems probable that the separation observed is due to effects of diffusion and gaseous flow and not to true electrolysis (Chapman and Lidbury, *J. Chem. Soc.* 1902, 81, 130; Holt and Hopkinson, *Phil. Mag.* 1908, [vi.] 16, 82).

Oxidising and reducing action.—It is common

knowledge that water acts on many metals, usually forming a basic oxide and hydrogen. The alkali and alkaline earth metals react with cold water; glucinum (beryllium), magnesium, and many rare-earth metals react with water below its boiling-point; zinc, cadmium, tin, iron, cobalt, nickel, and chromium decompose steam at a red heat, and some other metals, *e.g.* copper and lead, react only at a white heat. Mercury, silver, gold, platinum, iridium, &c., do not react at all with water.

Whilst this is broadly true for ordinary distilled water and ordinary metals, some qualification is necessary.

The very detailed and critical study which has been made of the interaction of water and air upon iron shows clearly how greatly such actions are influenced by minute traces of impurity in either water or metal, and it has been proved that water has no action on magnesium below 100° if free from air (Roberts and Brown, *J. Amer. Chem. Soc.* 1903, 25, 801), and acts extremely slowly at ordinary temperatures with sodium amalgam if free from traces of hydrogen peroxide (Baker and Parker, *J. Chem. Soc.* 1913, 103, 2060). Therefore caution must be used in regarding the observed reactions with metals, especially at low temperatures, as those of pure water. It is known that in the wet oxidation of some metals, *e.g.* zinc, hydrogen peroxide is produced and appears to take part in the reaction (*see e.g.* Smith, *J. Chem. Soc.* 1906, 89, 479).

Water can also oxidise many non-metals. Silicon is attacked by water in glass vessels at 100°, but the action is probably due to dissolved alkali (Moissan and Siemens, *J. Chem. Soc.* 1904, A. ii. 398) and occurs with pure water only at a higher temperature. Reaction of steam with carbon begins at about 850° (Farup, *Zeitsch. anorg. Chem.* 1906, 50, 276), and at higher temperatures proceeds according to the equations $C + H_2O \rightarrow CO + H_2$; $C + 2H_2O \rightarrow CO_2 + 2H_2$, with a reversible secondary reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ (*see* Gautier, *Compt. rend.* 1906, 142, 1382). It is of great importance in the manufacture of producer-gas and water-gas (*q.v.*). Boron at a red heat similarly yields with steam boric oxide and hydrogen. At 2000° even nitrogen is oxidised by steam with the production of nitric oxide and hydrogen, $N_2 + 2H_2O \rightleftharpoons 2NO + H_2$, the mixture at equilibrium containing about 0.5 p.c. by volume of NO (Tower, *J. Amer. Chem. Soc.* 1905, 27, 1209).

Some of the lower oxides of metals, *e.g.* MnO, UO_2 , CrO , or compounds derived therefrom, *e.g.* potassium cobaltocyanide $K_3Co(CN)_6$ and molybdenous chloride Mo_2Cl_4 , are oxidised by water with liberation of hydrogen.

Thus the oxidising action of water is pronounced at high temperatures and occurs at low temperatures with powerful reducing

Towards some non-metals, notably the halogens, water acts as a reducing agent, forming the non-metallic hydride and free oxygen. This action occurs with sulphur and phosphorus, but the oxygen simultaneously forms the non-metallic oxide. Thus with sulphur above 100° the reaction

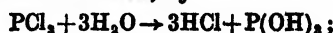
$2H_2O + S \rightleftharpoons 2H_2 + SO_2$ is induced by the equation

though, of course,

equilibrium is reached at low concentrations of H_2S and SO_2 .

Hydrolysis.—Under this heading are included many of the most important and characteristic reactions of water.

The typical case is the hydrolysis of non-metallic chlorides, *e.g.* PCl_3 , PCl_5 , BCl_3 , $SiCl_4$, &c., to form hydrogen chloride and the hydroxy acid of the non-metal, *e.g.*



$BCl_3 + 3H_2O \rightarrow 3HCl + B(OH)_3$. Similar reactions occur with the corresponding bromides and iodides, and their irreversible character constitutes an important distinguishing characteristic of non-metallic elements. The outstanding exception to this rule is the case of the halides of carbon, *e.g.* CCl_4 , CBr_4 , CH_2Br_2 , &c., which are not hydrolysed water to any appreciable extent at ordinary temperatures.

A similar, but reversible hydrolysis occurs to a greater or less extent with many metallic halides. The chlorides of bismuth and antimony are extensively hydrolysed in cold dilute aqueous solution, insoluble oxychlorides being precipitated: $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$; $SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$, and the higher chlorides of lead, tin, titanium, &c., $PbCl_4$, $SnCl_4$, $TiCl_4$, are hydrolysed with the formation of the corresponding hydroxides, which in some cases remain in solution. Many other metallic salts, *e.g.* $MgCl_2$, $ZnCl_2$, $CuSO_4$, &c., are appreciably hydrolysed in their aqueous solutions, which thereby acquire an acid reaction. It is indeed only in the case of relatively few salts, those of strong bases such as the alkalis, with strong acids such as the halogen hydrides, nitric acid, sulphuric acid, perchloric acid, &c., that hydrolysis in solution is inappreciable. Just as the hydrolysis of the salts of weak bases with strong acids, *e.g.* $Al_2(SO_4)_3$, gives acid solutions, so that of salts of strong bases with weak acids, *e.g.* Na_2CO_3 , Na_2S , &c., causes their solution to have an alkaline reaction. It is frequently assumed that the neutral character of a solution of, say, potassium chloride, indicates an absence of hydrolysis, but this is by no means necessarily so. The neutrality of such a solution is quite compatible with extensive hydrolysis to yield equivalent amounts of acidic and basic solutes of the same type which, by the preponderance of one or other sort, give the basic or acidic character to solutions in which hydrolysis obviously occurs. This point is of importance to the theory of solutions (Vol. vi. p. 286).

The hydrolytic action of water increases with temperature, so that at a red-heat most metallic salts are completely hydrolysed by steam, *e.g.* $MgCl_2 + H_2O \rightarrow MgO + 2HCl$ (Moldenhauer, *Zeitsch. anorg. Chem.* 1906, 51, 369), and many, *e.g.* $NaCl$, which show no sign of hydrolysis in the cold, are partly decomposed.

Many binary compounds of metals with non-metals are readily and completely hydrolysed by water at ordinary temperatures, to produce the metallic hydroxide and the non-metallic hydride. The sulphides, selenides, nitrides, phosphides, and silicides of magnesium, glucinum, and aluminium are thus decomposed, and the hydrolysis of aluminium phosphide

of silicide is a convenient method for the preparation of phosphine or silicon hydride. Hydrolysis of the carbides is of special interest; some, e.g. aluminium or glucinum carbide, yield pure methane; others give various mixtures of hydrocarbons and hydrogen. The hydrolysis of calcium carbide to produce acetylene is the basis of a great industry, and that of nitrides, e.g. AlN , to produce ammonia has been employed in some processes for the fixation of atmospheric nitrogen.

Some binary compounds of non-metals, e.g. boron nitride, and the sulphides and selenides of boron and silicon, are similarly hydrolysable.

Hydrolysis of many metallic hydrides, e.g. LiH , CaH_2 , &c., yields the metallic hydroxide and hydrogen.

In organic chemistry innumerable hydrolytic reactions of importance are known, e.g. of organo-metallic compounds $Zn(CH_3)_2$, halides, esters, cyanides, etc.

Addition.—The direct addition reactions of water with basic and acidic oxides to form bases and acids occupy an intermediate position between hydrolytic action of the foregoing type and the so-called simple hydration discussed below.

Anhydrides of strong acids and bases, *e.g.* SO_3 , P_2O_5 , N_2O_5 , or Na_2O , CaO , Li_2O , &c., combine very readily with water; those of weaker acids and bases, *e.g.* B_2O_3 , SiO_2 , or ZnO , MgO , &c., react slowly or at higher temperatures. Data for the heat of hydration of typical basic oxides are given in Table 37.

TABLE 37.
HEATS OF HYDRATION OF OXIDES.

Typical examples of the heat of hydration of basic oxides, hydroxides and peroxides are given in the following table: the values given are in 16° gram-calories.

Heats of hydration	15° gram-calories	Reference
$\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH}$	14,400	1
$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$	35,440	1
$\text{K}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{KOH}$	35,620	4
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$	42,100	1
	15,100	1
	15,540	4
$\text{SrO} + \text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2$	17,100	1
	17,700	4
$\text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2$	17,600	1
	22,260	4
$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$	5,400	1
$\text{ZnO} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2$	-2,750	4
$\text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{TiOH}$	3,230	4
$\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaOH} \cdot \text{H}_2\text{O}$	3,250	1
$\text{KOH} + \text{H}_2\text{O} \rightarrow \text{KOH} \cdot \text{H}_2\text{O}$	8,900	1
$\text{KOH} + 2\text{H}_2\text{O} \rightarrow \text{KOH} \cdot 2\text{H}_2\text{O}$	15,400	1
$\text{Sr}(\text{OH})_2 + 8\text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	26,280	4
	24,700	1
$\text{Ba}(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$	3,580	4, 2
$\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	27,470	4
" "	24,400	1
$\text{SrO}_2 + 9\text{H}_2\text{O} \rightarrow \text{SrO}_2 \cdot 9\text{H}_2\text{O}$	20,480	3
$\text{BaO}_2 + \text{H}_2\text{O} \rightarrow \text{BaO}_2 \cdot \text{H}_2\text{O}$	2,800	1
$\text{BaO}_2 + 10\text{H}_2\text{O} \rightarrow \text{BaO}_2 \cdot 10\text{H}_2\text{O}$	18,200	3

1. Berthelot, *Thermochimie*, II. 1897.
2. de Forcrand, *Compt. rend.* 1888, 103, 60.
3. de Forcrand, *Compt. rend.* 1901, 130, 1017.
4. Thomsen, *Thermochem. Untersuch.* III. 1883.

This type of hydration leads to a profound change in the properties of the compound, and it is generally held that the water loses its character as such and enters into the constitution of the product in the form of hydroxyl groups. Such addition, therefore, resembles hydrolysis, save that one product only results.

Hydration.—The union of water with substances to form *hydrates*, as distinct from *ice*, is characterized by the slightness of its effect upon the physical and chemical

properties of the original substance. This is especially well seen where a compound forms a series of hydrates, e.g. FeCl_3 , Na_2CO_3 , CuSO_4 , as these differ from each other only slightly in colour, solubility, &c., and not at all in chemical properties.

It is the practice to confine the term *hydrate* to compounds in which water is present in fixed and simple molecular proportions; this, however, is an arbitrary rule. We have practically no evidence as to the manner in which

water of hydration (water of crystallisation) is held in the molecule. We know simply that water is evolved from hydrates, usually at comparatively low temperatures, that it is not directly and necessarily concerned in the most characteristic reactions of the hydrated substance, and that it can frequently be replaced molecule for molecule by other solvents, *e.g.* ether or alcohol, with a minimal change in the character of the hydrate.

The ease with which water is expelled from hydrates is illustrated by its liberation by simple grinding (Gillette, Chem. News, 1911, 104, 313), and in one recorded case by the action of light (McKee and Berkheiser, Amer. Chem. J. 1908, 40, 303). It has been suggested that hydrates may retain some water in solid solution (Richards, J. Amer. Chem. Soc. 1911, 33, 888).

Water of crystallisation has many of the properties of free water. It acts like free water upon calcium carbide (Masson, J. Chem. Soc. 1910, 97, 851) and upon some metals, *e.g.* magnesium (Michailenko and Mushinsky, J. Russ. Phys. Chem. Soc. 1912, 44, 181). It exhibits the same infra-red absorption bands as water (Schaefer and Scherbert, Ann. Physik. 1916, [iv], 50, 339).

Water can pass through solid plates of crystalline hydrates (Baker and Adams, J. Chem. Soc. 1911, 99, 567) by a process apparently resembling its diffusion through solutions.

Hydrated salts are curiously akin to the solutions from which they form. Where the colour of an anhydrous salt differs from that of its solution, *e.g.* CuSO_4 , CoCl_2 , CuBr_2 , CuCl_2 , &c., the colour of the crystalline hydrate is usually that of the solution. Hydrates exhibit a definite vapour tension of water; hence, on the kinetic theory, water molecules must pass freely in and out of the crystal space lattice as they do in and out of a solution. If the pressure of water vapour above the hydrate is less than its vapour tension, the hydrate loses water and *effloresces*. Conversely, it absorbs water and may *deliquesce*.

When a salt, capable of forming several hydrates (typically $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which yields $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and CuSO_4) is in equilibrium with its vapour in a closed space, and water is slowly but continually removed, the pressure of aqueous vapour over the hydrate remains constant until the whole is converted to the next lower hydrate, when the vapour pressure *suddenly* drops to that characteristic of the second hydrate and maintains that

TABLE 38.

VAPOUR PRESSURES OF HYDRATED SALTS.

Equilibrium	<i>p</i> .	Reference
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{aq. vap.}$	18.2 mm.	1
	19.22 "	2
	19.20 "	3
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + \text{aq. vap.}$	18.0 "	1
	19.13 "	2
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + \text{aq. vap.}$	12.4 "	1
	14.51 "	2
$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 + \text{aq. vap.}$	8.9 "	1
$\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{CO}_3 + \text{aq. vap.}$	1.1 "	1
$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{CaO} + \text{aq. vap.}$	0.8 "	1
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{aq. vap.}$	4.8 "	1
	5.26 "	4
	5.8 "	2
$\text{BaCl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 + \text{aq. vap.}$	2.5 "	1
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + \text{aq. vap.}$	7.0 "	1
	7.68 "	4
	7.80 "	2
	7.77 "	5
$\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O} + \text{aq. vap.}$	4.7 "	1
$\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{aq. vap.}$	0.8 "	1

1. Foote and Scholes, J. Amer. Chem. Soc. 1911, 33, 1809.

2. Wilson, J. Amer. Chem. Soc. 1921, 43, 704.

3. Baxter and Lansing, J. Amer. Chem. Soc. 1920, 42, 419.

4. Partington, J. Chem. Soc. 1911, 99, 468.

5. Menzies, J. Amer. Chem. Soc. 1920, 42, 1951.

value until conversion to the third hydrate is complete. This step by step transformation, readily interpreted in terms of the phase-rule, affords a means of detecting the existence of hydrates.

If during dehydration the vapour pressure be plotted against the percentage of water in the residual solid, the existence of a hydrate will be evidenced by a flat 'platform' on the curve; a continuous curve indicates the absence of definite hydrates.

Care must be exercised in applying this method, because there is frequently a delay, or period of induction, in the rise of the vapour pressure to the value characteristic of the temperature (Cumming, *Trans. Chem. Soc.* 1910, 97, 593; Partington, *ibid.* 1911, 99, 466; Ephraim and Millmann, *Ber.* 1917, 50, 529; Ephraim and Wagner, *Ber.* 1917, 50, 1088).

Indeed, Faraday showed (Pogg. Ann. 1834, 33, 186) that whereas hydrated sodium carbonate, sodium hydrogen phosphate, and sodium sulphate readily effloresce in air, perfect crystals of these salts may be kept in air for years without change. Inoculation with the lower hydrate at once causes the vapour pressure to assume its normal value. The period of induction in dehydration receives a rational explanation if we consider that the minute particles of the second phase formed at first by dehydration have, like small drops of water, an abnormally high vapour pressure (Rae, *J. Chem. Soc.* 1916, 109, 1229; see Pavlov, *J. Russ. Phys. Chem. Soc.* 1909, 41, 679).

Table 37 contains data for the thermal effect of several typical hydration reactions. Table 38 gives the equilibrium pressure of water vapour, in mm. of mercury, at 25° over a few of the more important crystalline hydrated salts, when in equilibrium with a lower hydrate or the anhydrous salt.

Solution and ionisation.—Water is, *par excellence*, the solvent. It has been argued that all substances are soluble in water, but this is not proven. Most salts and compounds usually classed as insoluble, e.g. silver chloride, glass, silica, are well known to have a small, but definite, solubility in water. The great majority of solids and liquids, and all known gases, are distinctly soluble, and some very soluble, in it.

There is much reason to believe that the solvent power of water and its pre-eminence as an ionising solvent are both due to chemical action between solvent and solute of the kind considered under hydrolysis and hydration.

An overwhelming mass of real evidence exists that substances dissolved in water are intimately associated, one had better say combined, with water or 'solvated' (see, for a list of references, Dhar, *Zeitsch. Elektrochem.* 1914, 20, 57; and for a critical review of earlier work, Washburn, *Hydrates in Solution*, *Tech. Quart.* 1908, 21, 360; as examples of more recent evidence, see e.g. Schaeffer, Paulus and H. G. Jones, *Phys. Zeitsch.* 1914, 15, 447; Philip and Bramley, *J. Chem. Soc.* 1915, 107, 571, 1935; Kornfeld, *Monatsh.* 1915, 36, 865; Porter, *Trans. Faraday Soc.* 1917, 13, 123; Smith, Lands and Bowman, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, 23, 969, and

chemists have preferred to interpret all solution phenomena in terms of such compounds, even going so far as to regard the whole of the solvent as being combined with the solute (Kahlenberg, *Trans. Faraday Soc.* 1905, 1, 42).

On the other hand, much work adduced as evidence for solvation is unconvincing and contradictory. Kendall has remarked: "In the system $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$, for instance, as many as '02 different hydrates have been 'discovered,' ing in composition from $36\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4\cdot 4950\text{H}_2\text{O}$. Few of these have been encountered twice by independent investigators, the opportunity for originality being almost unlimited." Thus many chemists have supported the original view of Ostwald and van't Hoff, which regards the solvent simply as a dispersive medium, enabling the solute to behave as if alone and in a gaseous state (see *Brit. Association Report*, 1890, 60, 311-338).

But the 'solvate' theory, rejecting the conception of ionisation altogether (see e.g. Armstrong and Worley, *Proc. Roy. Soc.* 1912, 87 A, 604), fails to explain in any satisfactory manner the mechanism of conduction in electrolytes, whilst the strict ionic theory equally fails to explain why and how ionic dissociation occurs.

It has been generally recognised by those who admit the existence of ions, that the ions in solution are hydrated (see Arrhenius, *Theories of Solutions*, pp. 184-195), and it has been pointed out that the rival 'solvate' and 'ionic' theories are in reality not irreconcilable but supplementary (Walker, *Brit. Association Report*, 1911, 81, 356).

There is, in fact, an intimate and general connection between ionisation and compound formation in solutions, and Kendall and Booge have strongly advocated the hypothesis that ionisation is preceded by, and is a consequence of, the formation of such compounds (Kendall and Booge, *J. Amer. Chem. Soc.* 1917, 39, 2323; this paper contains a detailed discussion of the hypothesis and numerous references to the literature, and should be consulted; the same idea had been indicated by others, to whom reference is made in the above paper, and was formulated with some precision by Bogorodski, *J. Russ. Phys. Chem. Soc.* 1914, 46, 1716).

Experiments with tetraethyl-ammonium iodide in a large number of solvents have shown that conductivity of solutions is fundamentally related to the dielectric constant and to the state of unsaturation of the simple molecules of the solvent (Walden, *Zeitsch. physikal. Chem.* 1903, 46, 103; 1906, 54, 129; H. G. Jones, *Amer. Chem. J.* 1901, 25, 232). These properties, as might be anticipated from their general parallelism, have a causal relationship (Thomson, *Phil. Mag.* 1914, [vi.] 27, 757; Lewis, *J. Amer. Chem. Soc.* 1913, 35, 1448; 1916, 38, 762).

Unsaturation implies the presence in the molecule of electrons which are free to move under the influence of an electric field. The simple water molecule (H_2O) contains two doublets, as in the formula $\text{H}^+-\text{O}^--\text{H}^+$; and the six free electrons of the oxygen atom will move into such positions as enable them to exert a maximum attractive force upon the

positive parts of these doublets, so that an unequal distribution of electric charges will result. By proximity of two such molecules this unequal distribution is accentuated and may lead to the formation of associated molecules, possessing a still larger electrostatic moment, in which the constraints are correspondingly weakened. Further association can occur with enhancement of these effects.

Great attractive forces are exerted by such associated molecules upon any solute RX ; these forces are cumulative as the molecules come into closer proximity, and can evidently lead to the formation of complexes of the type $R(H_2O)_n-X$, in which the constraints upon the electrons are still further weakened. Such complexes are much less stable than the simple component molecules and dissociable at any point, and it is thus possible to see how hydration may cause ionisation.

The essential probability of this theory is illustrated by the case of aqueous hydrochloric acid. Both hydrogen chloride and water when pure are almost non-conductors (Kohlrausch and Heydweiller, *Zeitsch. physikal. Chem.* 1894, 14, 326; Steele, McIntosh and Archibald, *ibid.* 1906, 55, 148); both contain unsaturated atoms in the simple molecule and are in consequence associated; both have high dielectric constants. When mixed they constitute a good electrolyte.

In contrast with the older ionic hypothesis, Kendall's theory permits us to regard the ionisation and conductivity as due to both constituents of the solution. Complex molecules $(H_2O)_n \cdot (HCl)_m$ are formed and dissociate to yield positively and negatively charged radicals. Taking the simplest case these would be either $(Cl \cdot H_2O)^-$ and $(H \cdot H_2O)^+$ or $(HCl \cdot OH)^-$ and $(HCl \cdot H)^+$, and on inspection these two alternatives are seen to be the same thing. The complex $(H_2OCl)^-$ may be regarded either as a hydrated chloride ion or a solvated hydroxyl ion.

The following table shows the degree of dissociation of pure water at various temperatures from 0° – 50° ; α being the weight in grms. of hydrogen ion in 1 c.c. of water at the stated temperature.

Temp.	$\alpha \times 10^{10}$
0°	0.36
2°	0.40
10°	0.57
18°	0.80
26°	1.10
34°	1.45
42°	1.91
50°	2.44

(Kohlrausch and Heydweiller, *Wied. Ann.* 1894, 53, 234; *Zeitsch. physikal. Chem.* 1894, 14, 330; the numbers are in substantial agreement with the indirect measurements of Arrhenius, *Zeitsch. physikal. Chem.* 1893, 11, 823; Nernst, *ibid.* 1894, 14, 155; Lorenz and Behl, *ibid.* 1909, 66, 748; Noyes and Kato, *ibid.* 1910, 73, 20; Dolezalek, *Zeitsch. Elektrochem.* 1899, 5, 536; Kanolt, *J. Amer. Chem. Soc.* 1907, 29, 1414; Lewis, Brighton and Sebastian, *ibid.* 1917, 39, 2260; Lunden, *J. Chem. Phys.* 1907, 5, 589; Heydweiller, *Ann. Physik.* 1909, [iv.] 28, 511).

The heat of formation of water from its ions is +14,700 gm. cal. per gm. mol. at $0^\circ C$, the value at other temperatures t , being given by +14,700–50 t . This is the most probable value derived from a number of researches by different methods, as follows:

1. From the heat of neutralisation of strong acids by strong bases (Wärmann, *Ann. Physik.* 1905, [iv.] 18, 793; Heydweiller, *Ann. Physik.* 1909, [iv.] 28, 503; Thomsen, *Thermochem. Untersuch.* 1882; Muller, *Bull. Soc. chim.* 1918, [iv.] 23, 8; Müller and Bauer, *J. Chim. Phys.* 1904, 2, 457).

2. From the change of conductivity of pure water with change of temperature; calculated by van 't Hoff from the data of Kohlrausch and Heydweiller.

3. From the variation with temperature of degree of hydrolysis of salts (Lunden, *J. Chem. Phys.* 1907, 5, 145, 574; 1908, 6, 6, 81; Noyes, *Carnegie Inst. Publ.* 1907, No. 63).
H. V. A. B.

Water in its Economic and Sanitary Relations. Drinking Water.

Water for Domestic Supply.

Water is absolutely indispensable to both animal and vegetable life; it is the cause of many of the most striking phenomena in nature, and is employed for countless purposes by man. Its distribution is as wide as that of the air itself whilst its amount on the earth is enormously greater. In an absolutely pure state it is never met with in nature. The impurities in natural water are derived from the materials—solid, liquid, or gaseous—with which it comes in contact, and they may be present either in suspension or in solution or in both. Inasmuch, therefore, as the interest attaching to different waters depends upon the impurities they contain, and these are dependent upon the matters with which they have been in contact, it is most convenient to classify waters according to their origin.

1. *Rain-water, snow, hail, dew, and hoar-frost.* All these forms of water are obtained by the condensation of the aqueous vapour which is invariably present in the air. The amount of aqueous vapour which can be contained in a given volume of air is solely dependent upon the temperature. If the atmosphere has become saturated with aqueous vapour at any given temperature and is cooled below that temperature, the excess of aqueous vapour will condense, according to circumstances, as rain, hail, snow, mist, dew, or hoar-frost. This condensation is promoted by the presence of dust and electrically charged particles. All these forms of water having been only in contact with the air and not with the earth are characterized by the small proportion of solid matter which they contain, although the amount found, especially in the vicinity of towns, is often considerably greater than would be anticipated, and the rain-water falling in the neighbourhood of the sea is often mixed to a considerable extent with sea-spray, which with favourable winds is carried many miles inland. In the following table are recorded the maximum, minimum, and average proportions of several in of rain-water collected at
where, expressed in parts per 100,000—

WATER.

	Total solid impurity	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum	0.62	0.021	0.003	0.005	0	0	0
Maximum	8.58	0.372	0.121	0.155	0.044	1.65	1.7
Average	3.42	0.095	0.021	0.049	0.007	0.33	0.5
Rain-water collected at Land's End, Cornwall, Jan. 2, 1873	42.80	0.131	0.034	0	0.020	21.8	10.0
Rain-water collected near Hyde Park, London, Nov. 8, 1873	2.76	0.383	0.040	0.210	0.008	0.5	1.1

It is thus seen that the composition of rain-water, even in the open country, is able to great fluctuations, and that the amount of impurity, both mineral and organic, occasionally surprisingly large. The amount

of organic impurity in dew and hoar-frost is still greater owing to these forms of water being condensed out of the lowest and most-contaminated couches of the atmosphere. Thus—

SEVEN SAMPLES OF DEW AND HOAR-FROST, ROTHAMSTED, 1869 AND 1870.

(Results of Analysis expressed in parts per 100,000.)

	Total solids	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum	2.64	0.195	0.026	0.130	0	0.35	1.3
Maximum	8.00	0.450	0.196	0.280	0.050	0.80	2.5
Average	4.87	0.264	0.076	0.198	0.023	0.53	1.9

Two other impurities, not referred to above, which are generally present in the rain-water and snow of towns are sulphurous and sulphuric acids derived from the combustion of coal. Angus Smith found in the rain-water of London 2.05, of Liverpool 3.96, in that of Manchester 4.48, and in that of Glasgow 7.02 parts of sulphuric acid per 100,000, to a considerable extent in the free state. Sendtner found freshly-fallen snow in Munich to contain 0.7 part sulphuric acid (SO_3) per 100,000, on the following day 1.76 parts, after 10 days 6.22 parts, and after 16 days 9.18 parts. The presence of this free acid in the rain-water of towns is, of course, not only detrimental to vegetation, but also to sculptures and buildings in which marble or limestone are employed. The proportion of ammonia increases in the snow after lying on the ground (Wagner, *Technologie*, 305).

2. *Upland surface water* most nearly approaches in composition to that of the atmospheric waters dealt with in the last section. It is, in fact, rain-water which has undergone minimum contact with the earth, although in consequence of its solvent action even this contact is sufficient to impart to the water in many cases such proportions of dissolved matter as are never found in rain-water. The amount and nature of these ingredients depend, of course, mainly upon the kind of soil over which the water has travelled, and consequently it becomes convenient to sub-divide this class according to the geological character of the ground from which the upland surface water has been obtained.

In the tables on p. 370 are recorded the maximum, minimum, and average amounts of impurity found in the examination of a large series of samples of waters principally derived from land not under cultivation, so as to represent the characters naturally acquired by water passing over the various geological formations.

The tables (I. and II.) show that upland surface waters generally contain a considerable amount of dissolved matters only when they are derived from calcareous strata. The organic matter is subject to great variation, but in every case contains only a very small proportion of nitrogen in comparison with the carbon, indicating that the organic substances present are of vegetable origin, which is further attested by the almost entire absence of ammonia, nitrates, and nitrites, all of which, when present in amount beyond that in which they occur in rain-water, are nearly exclusively derived from the decomposition of animal matters. The chlorine is also low, the gathering grounds being generally beyond the reach of sea-spray and not receiving the liquid excrements of animals, which are particularly rich in chlorides, whilst from their mere surface contact with the soil they have not extracted any considerable quantities of the salts present in the latter, as is the case with spring- and well-water.

3. *Surface water derived from cultivated land.*—This includes the great body of stream-waters, inasmuch as practically all streams flow through and receive accessions from land under cultivation before reaching the sea. The nature

I.—WATERS FROM NON-CALCAREOUS STRATA.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Upland surface water from Igneous rocks. ¹										
Maximum . . .	12.70	0.582	0.071	0.004	0.029	0.073	2.10	0.4	5.7	5.9
Minimum . . .	1.52	0.074	0.013	0	0	0.014	0.35	0	0.8	0.8
Average (18 samples)	5.15	0.278	0.033	0.001	0.002	0.035	1.13	0.1	2.0	2.1
(b) Upland surface water from Metamorphic, Cambrian, Silurian, and Devonian rocks. ²										
Maximum . . .	12.48	1.059	0.076	0.008	0.043	0.110	3.35	1.8	6.9	6.9
Minimum . . .	2.14	0.042	0.001	0	0	0.002	0.52	0	0.3	0.4
Average (81 samples)	5.12	0.293	0.024	0.002	0.006	0.031	0.92	0.3	2.5	2.5
(c) Upland surface water from Yoredale and millstone grits and non-calcareous portions of the Coal Measures. ³										
Maximum . . .	15.00	1.457	0.103	0.024	0.042	0.116	1.59	3.7	8.1	8.7
Minimum . . .	4.58	0.033	0	0	0	0.012	0.65	0	0.9	0.9
Average (47 samples)	8.75	0.377	0.033	0.003	0.010	0.050	1.05	0.4	4.3	4.7
(d) Upland surface water from Lower London Tertiaries and Bagshot beds.										
Maximum . . .	13.14	0.439	0.056	0.012	0.020	0.086	2.60	0.9	5.6	5.6
Minimum . . .	5.92	0.282	0.039	0	0	0.039	1.24	0	1.8	1.8
Average (3 samples)	8.40	0.379	0.048	0.004	0.007	0.058	2.06	0.3	3.5	3.8

¹ All soft and peaty. Generally turbid, and of a yellowish or even brownish colour.

² This water is also generally peaty, and often turbid and coloured. Owing to the large area of these rocks exposed they form some of the most important gathering grounds, especially in Scotland.

³ Soft, but generally turbid, peaty, and of a yellow or brownish colour.

II.—WATERS FROM CALCAREOUS STRATA.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			
								Temporary	Permanent	Total	
(a) Upland surface water from Silurian and Devonian rocks. ¹											
Maximum . . .	14.46	0.475	0.046	0	0.055	0.080	1.62	3.5	9.6	9.6	
Minimum . . .	12.26	0.103	0.008	0	0	0.016	0.83	0	5.2	7.5	
Average (3 samples, all from Scotland)	13.71	0.301	0.026	0	0.021	0.047	1.20	1.2	7.4	8.6	
(b) Upland surface water from Mountain Limestone. ²											
Maximum . . .	23.40	0.812	0.097	0.002	0.042	0.097	1.59	9.3	10.6	14.6	
Minimum . . .	12.45	0.218	0.023	0	0	0.024	0.92	1.7	4.3	9.8	
Average (7 samples)	17.07	0.370	0.047	0.001	0.011	0.059	1.24	5.7	7.0	12.7	
(c) Upland surface water from calcareous portion of Coal Measures. ³											
Maximum . . .	77.36	0.856	0.089	0.010	0.061	0.122	4.85	11.6	13.6	25.0	
Minimum . . .	10.20	0.082	0.001	0	0	0.014	0.84	0	3.0	6.2	
Average (26 samples)	22.79	0.346	0.037	0.003	0.016	0.056	1.52	4.0	8.3	12.3	
(d) Upland surface water from Lias, New Red, and Conglomerate Sandstone.											
Maximum . . .	26.32	0.506	0.075	0.008	0.034	0.100	2.00	16.0	12.9	24.8	
Minimum . . .	11.08	0.186	0.020	0	0	0.022	0.99	2.9	3.1	6.0	
Average (8 samples)	18.92	0.300	0.042	0.002	0.012	0.056	1.50	7.8	6.3	14.0	
(e) Upland surface water from Magnesian Limestone. ⁴											
Ripon, the Kex Beck, 8 miles from source, Jan. 27, 1874 . . .	17.84	0.172	0.036	0.001	0	0.037	1.40	6.4	8.3	14.7	
(f) Upland surface water from Oolites. ⁵											
The Frome, above Woodlands Mill, Somersetshire, March 10, 1870 . . .	17.46	0.326	0.025	0.004	0.042	0.070	1.55	6.6	5.8	12.4	

¹ Owing to the compact nature of the limestone in these old formations, the hardness is very moderate.

² Hardness not excessive, but large amount of organic matter (peaty), rendering the waters coloured and unpalatable.

³ Of very variable character; generally of only moderate hardness, but containing much peaty matter, and hence coloured and unpalatable.

⁴ Slightly turbid.

⁵ Slightly turbid. Owing to the porous nature of Oolite formation, surface water is very rare.

position of such waters is very varied, depending upon local circumstances, and being liable to great fluctuations at different seasons of the year. This group may be conveniently divided into two sub-groups, according as the water

is derived from calcareous or non-calcareous districts. The following results of analyses of British waters of this description are compiled from the Sixth Report of the Rivers Commission, 1874:—

SURFACE WATERS FROM CULTIVATED LAND.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Water from non-calcareous districts. ¹										
Maximum . . .	18.10	1.124	0.112	0.056	0.258	0.393	2.80	4.6	8.0	10.1
Minimum . . .	5.26	0.125	0 ²	0	0	0.017	0.70	0	1.8	2.1
Average (31 samples)	9.52	0.276	0.034	0.007	0.089	0.128	1.49	0.6	4.3	4.9
(b) Water from calcareous districts. ²										
Maximum . . .	110.40	1.338	0.307	0.030	1.005	1.096	12.75	26.3	42.1	67.3
Minimum . . .	13.22	0.069	0.009	0	0	0.033	0.54	0	2.1	7.8
Average (144 samples)	30.08	0.268	0.053	0.005	0.257	0.314	2.24	12.4	8.2	20.6

¹ Usually turbid, organic matter generally moderate in amount, but partially of animal origin.

² This result is extremely improbable, more especially as the particular water in question (a sample of the water supplied to Bury and Radcliffe, Lancashire) contained 0.229 organic carbon, 0.032 ammonia, and 0.066 nitrogen as nitrates and nitrites.

³ Generally turbid, the organic matter is much the same in amount as in the water from non-calcareous districts, but generally more nitrogenous, in consequence of calcareous soils being usually under higher cultivation than non-calcareous ones. The total combined nitrogen is also for the same reason considerably greater, and the hardness is, of course, very much higher.

In connection with the effect of cultivated land upon the water with which it comes in contact, it is instructive to note the nature of the water which drains from such land, as this throws light upon the composition of subterranean waters (from springs and wells), which will be considered below.

In the following table is recorded the composition of the water obtained from drain-pipes placed from 18 ins. to 5 ft. below a plot of land at Rothamsted which had remained both unmanured and uncropped for a period of 11-15 years:—

COMPOSITION OF WATER FROM LAND UNMANURED AND UNCROPPED FOR ELEVEN TO FIFTEEN YEARS.¹ (6th Rep. Riv. Com. p. 62.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	63.28	0.235	0.116	0.026	4.936	4.981	3.80	7.2	11.9	16.6
Minimum . . .	18.00	0.096	0.026	0	0.607	0.654	0.60	0.3	3.2	3.5
Average (15 samples distributed over four years) . . .	32.06	0.154	0.053	0.006	2.195	2.253	1.65	4.1	8.5	12.6

¹ The samples varied from clear to turbid.

It will be seen that the conversion of the original nitrogenous organic matter in the soil into mineral products is a very slow process, large quantities of nitrates being still present in the drainage waters after the lapse of so many years.

It is interesting to compare with the above the composition of the water draining from a plot of land unmanured for 16-21 years, but continuously bearing an annual wheat crop during that time:—

COMPOSITION OF WATER FROM LAND UNMANURED FOR SIXTEEN TO TWENTY-ONE YEARS, BUT CONTINUOUSLY BEARING WHEAT CROPS. (6th Rep. Riv. Com. p. 80.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	48.40	0.242	0.058	0.006	2.268	—	3.80	14.1	22.4	32.7
Minimum . . .	13.80	0.099	0.010	0	0	—	0.80	8.9	3.9	13.5
Average (11 samples distributed over five years) . . .	24.96	0.170	0.034	0.002	0.645	—	1.37	10.8	8.4	19.2

As might have been anticipated, the proportions of ammonia and nitrates finding their way into the drainage water in this case were much less, and in the summer months during the growth of the crop the amount of this mineral nitrogen found in the drainage water was practically *nil*.

We will, in the next place, compare with the above the composition of the drainage water from land which had been manured annually with 14 tons of farmyard manure per acre over a period of 24–29 years, and bearing wheat continuously during that time:—

COMPOSITION OF DRAINAGE WATER FROM LAND MANURED WITH 14 TONS FARMYARD MANURE PER ACRE FOR TWENTY-FOUR TO TWENTY-NINE YEARS. (6th Rep. Riv. Com. p. 58.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	51.20	1.243	0.335	0.052	2.592	2.754	3.35	12.1	20.6	32.1
Minimum . . .	14.00	0.181	0.036	0	0.082	0.130	0.60	1.4	5.4	8.7
Average (13 samples over five years) . . .	25.90	0.519	0.115	0.009	0.528	0.665	1.30	6.8	8.6	15.4

Thus the difference between the drainage waters from the unmanured and manured land is not nearly so great as might have been expected, being principally confined to the larger proportion of organic matter found in the latter.

The above results may be compared with

those obtained in the analysis of a number of samples of the drainage water from sewage farms, in all of which the town sewage is, or was, applied to land, with the double object of purifying the sewage and deriving a profit out of the crops raised. Thus:—

COMPOSITION OF DRAINAGE WATER FROM SEWAGE FARMS. (6th Rep. Riv. Com. pp. 55–57.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	103.00	2.160	0.517	1.366	6.499	6.833	13.40	36.9	39.3	56.6
Minimum . . .	18.60	0.108	0.034	0.005	0	0.069	2.15	0	3.9	3.9
Average (72 samples)	64.02	0.982	0.191	0.388	0.756	1.266	6.36	17.6	15.4	23.0

It will be seen that the drainage water from sewage farms is generally richer in organic and inorganic impurities than the water draining from manured or unmanured land, the passage of the water through the ground being in the latter case a much slower one, and thus allowing time for more perfect purification by soil and

plants. Occasionally, as indicated by the above minimum results, the drainage water from sewage farms is remarkably free from impurities. A much purer drainage water is often yielded in the intermittent downward filtration of sewage through suitable land.

thus gained of the compos-

SHALLOW WELL WATERS.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Gneiss and Silurian rocks ¹ (8th Rep. Riv. Com. p. 69).										
Maximum	100.20	0.362	0.110	0.625	2.465	3.090	17.00	22.3	19.2	41.5
Minimum	6.32	0.027	0.003	0	0.033	0.040	0.90	0	3.3	3.4
From Devonian rocks ² (29 samples analysed).										
Maximum	105.20	0.794	0.172	0.630	4.197	4.261	17.00	18.3	47.8	55.7
Minimum	12.16	0.004	0.003	0	0.033	0.039	1.60	0	3.2	5.0
From Yoredale and Millstone grits ³ (20 samples analysed).										
Maximum	133.60	0.859	0.216	0.010	5.100	5.200	13.90	37.2	65.1	90.0
Minimum	5.92	0.039	0.007	0	0.006	0.013	0.65	0	2.9	2.9
From Coal Measures ⁴ (44 samples analysed).										
Maximum	220.92	1.200	0.169	0.170	10.102	10.262	29.00	28.2	112.6	140.8
Minimum	9.40	0.024	0.007	0	0	0.015	0.99	0	1.4	3.4
From Mountain Limestone and Magnesian Limestone ⁵ (9 samples analysed).										
Maximum	108.88	0.190	0.070	0.002	4.812	4.884	13.35	40.1	48.5	88.6
Minimum	45.84	0.037	0.010	0	0.527	0.549	2.40	18.3	21.8	40.7
From New Red Sandstone ⁶ (87 samples analysed).										
Maximum	240.20	2.349 ⁷	0.346 ⁷	0.620	14.717	15.333	39.00	52.0	99.6	127.1
Minimum	20.64	0.029	0.009	0	0	0.027	1.40	0	3.8	17.1
From Lias ⁸ (38 samples analysed).										
Maximum	306.85	1.792	0.298	0.152	19.858	20.123	40.50	40.1	111.0	116.9
Minimum	49.48	0.052	0.023	0	0	0.033	1.75	0	2.1	2.7
From Oolites ⁹ (25 samples analysed).										
Maximum	269.60	2.662	0.531	0.240	12.220	12.508	44.50	42.6	55.9	78.9
Minimum	31.00	0.041	0.008	0	0	0.178	1.23	10.8	3.1	23.0
From Upper and Lower Greensand and Wealden ¹⁰ (21 samples analysed).										
Maximum	381.10	0.485	0.196	0.160	6.722	6.735	82.50	35.8	44.7	80.5
Minimum	10.52	0.014	0.006	0	0	0.012	2.10	0	3.8	3.8
From Chalk ¹¹ (33 samples analysed).										
Maximum	159.16	0.772	0.340	1.700	6.345	7.779	28.50	39.7	47.1	71.5
Minimum	32.48	0.014	0.007	0	0.613	0.628	1.79	12.0	5.6	23.6
From gravel on the London Clay ¹² (49 samples analysed, 37 from London itself).										
Maximum	396.50	1.006	0.604	2.750	25.840	25.927	34.60	49.2	164.3	191.0
Minimum	31.80	0.040	0.012	0	0	0.013	1.90	0	5.7	14.3
From Bagshot beds ¹³ (8 samples analysed).										
Maximum	286.80	1.295	0.154	0.630	17.940	—	31.15	21.5	111.9	131.7
Minimum	23.18	0.078	0.027	0.001	0.	0.087	2.48	5.4	5.6	13.1
From Fluvio-marine series ¹⁴ (13 samples analysed).										
Maximum	66.12	0.429	0.093	0.016	3.640	3.734	7.20	12.1	29.3	36.4
Minimum	8.16	0.063	0.010	0	0	0.010	2.40	0	4.6	4.6
From Alluvium and gravel ¹⁵ (29 samples analysed).										
Maximum	320.72	0.931	0.940	3.050	11.265	14.300	36.25	36.4	118.6	152.4
Minimum	28.58	0.015	0.010	0	0	0.074	1.70	2.7	1.9	4.6

¹ In almost all cases clear and palatable. ² Generally clear and palatable. ³ Almost all clear and palatable.

⁴ In many cases clear and palatable; but in others turbid, and even very turbid.

⁵ All clear or slightly turbid and palatable.

⁶ Generally clear, or only slightly turbid and palatable. In a few cases saline taste.

⁷ Even this water clear and palatable.

⁸ In nearly all cases clear, or slightly turbid and palatable.

⁹ Varying from clear and palatable to very turbid. In some cases saline taste.

¹⁰ Mostly more or less turbid. Palatable.

¹¹ Clear to very turbid. Palatable, or occasionally slight saline taste.

¹² Generally more or less turbid and palatable. Occasionally slight saline taste.

¹³ Generally more or less turbid and palatable.

¹⁴ More or less turbid and palatable.

¹⁵ Generally clear or only slightly turbid and palatable. Occasionally slight saline taste.

tion of waters draining from cultivated land becomes of special value in studying the nature of the next group of waters (shallow well water).

4. *Shallow well water*.—It has been estimated that about twelve millions of the inhabitants of Great Britain are supplied with water for domestic purposes from shallow wells. This class of water is very liable to serious contamination with sewage and refuse animal matters, inasmuch as such wells are almost invariably sunk in the vicinity of human dwellings, and frequently within a few feet of the cesspool receiving their drainage. It is these waters which have most frequently caused serious outbreaks of typhoid fever. In consequence of the great practical interest attaching to these waters, their composition will be considered in connection with the principal geological formations upon which such shallow wells may be sunk.

The results recorded in the previous table serve to show the general composition of shallow well waters as met with in Great Britain. The composition of these waters varies within very wide limits, even when derived from one and the same geological formation, which is due to their being not generally an aqueous extract of a soil in its natural condition, but of ground which is often saturated with sewage and other animal refuse. In consequence of the oxidising power of soil, the organic matter of this refuse is not unfrequently almost entirely destroyed before reaching the wells, and even the ammonia, which is one of the first products of its decomposition, has often disappeared, having generally become converted into nitrates and nitrites. Of nitrates and nitrites these shallow well waters generally contain some, and often a large amount, which thus, together with the ammonia,

DEEP WELL WATERS. (6th Rep. Riv. Com. p. 89.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Devonian rocks.										
Maximum . . .	45.30	0.083	0.016	0.001	0.696	0.713	4.20	26.2	16.4	32.5
Minimum . . .	8.94	0.021	0.005	0	0.044	0.049	1.40	0.5	3.1	3.6
Average (5 samples)	29.41	0.047	0.012	0	0.400	0.412	2.96	8.9	9.4	18.3
Polluted well at Bromyard . . .	85.12	0.177	0.048	0	2.279	2.327	11.25	25.0	16.2	41.2
Polluted well at Dundee . . .	27.50	0.119	0.027	0.025	0.532	0.580	3.05	9.6	8.5	18.1
From Millstone Grit.										
Well at Bradford, Yorks . . .	55.40	0.150	0.005	0.028	0.038	0.066	3.23	6.8	7.3	14.1
Well at Glossop, Derby . . .	26.32	0.092	0.020	0.003	0.019	0.042	0.89	9.8	5.9	15.7
From Coal Measures.										
Maximum . . .	144.88	0.198	0.064	0.170	1.468	1.494	59.85	28.2	48.5	75.0
Minimum . . .	33.42	0.045	0.014	0	0	0.029	1.29	5.7	1.2	9.9
Average (9 samples)	83.10	0.119	0.034	0.044	0.207	0.278	18.05	15.1	20.6	35.7
Polluted well at Holyrood, Edinburgh . . .	92.54	0.326	0.175	0.056	0.950	1.171	7.95	27.9	8.3	36.2
From Magnesian Limestone. ¹										
Mansfield, Woodhouse . . .	54.32	0.139	0.039	0	1.188	1.227	3.20	23.4	26.0	49.4
Pontefract, Yorks . . .	84.92	0.054	0.021	0	2.673	2.694	5.55	26.5	40.8	67.3

¹ The following is a more recent analysis made by the writer of water derived from deep wells in the Magnesian Limestone:—

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total Combined nitrogen	Chlorine	Hardness	Remarks
Sunderland and South Shields Water Supply, March 2, 1906.	45.52	0.029	0.005	Trace	0.328	0.335	2.65	25.0	(Alkalinity = 28.4 CaCO ₃ Total Hardness (CaCO ₃) = 16.5 " Magnesia (MgCO ₃) = 0.30

DEEP WELL WATERS (continued).

Description	Total solid matters	Organic carbon	Organic nitro- gen	Am- monia	Nitro- gen as nitrates and nitrites	Total com- bined nitro- gen	Chlor- ine	Hardness		Total
								Temp- orary	Perma- nent	
From New Red Sandstone.										
Maximum . . .	62.84	0.091	0.038	0.039	3.508	3.528	7.51	19.4	20.0	35.6
Minimum . . .	14.20	0	0	0	0	0.009	1.30	0	4.9	5.7
Average (28 samples)	30.63	0.036	0.014	0.003	0.717	0.734	2.94	7.4	10.5	17.9
Polluted well at Lich- field . . .	32.06	0.163	0.038	0.003	0.489	0.529	2.20	9.3	9.0	18.3
Polluted well at Liverpool . . .	86.70	0.135	0.038	0.005	8.678	8.721	12.61	11.5	24.0	35.5
Polluted well at Ox- ton . . .	27.80	0.249	0.034	0.001	0.376	0.411	3.52	5.6	8.5	14.1
From Lias.										
Well at Northampton	57.76	0.168	0.024	0.003	0	0.026	5.15	8.6	1.7	10.3
Well at Somerton, Somerset . . .	84.20	0.124	0.030	0	0.778	0.808	3.70	35.3	14.7	50.0
Polluted well at Trow- bridge, Wilts . .	144.34	0.236	0.057	0.002	0.550	0.609	36.70	27.4	29.7	57.1
From Oolites.										
Maximum . . .	41.90	0.054	0.018	0.110	1.898	1.907	3.70	18.0	10.6	23.0
Minimum . . .	26.60	0.023	0.005	0	0	0.099	1.35	8.3	3.6	18.9
Average (5 samples) .	33.60	0.037	0.010	0.022	0.625	0.654	2.69	13.8	6.8	20.6
Polluted (maximum of 3 wells) . . .	71.04	0.217	0.053	0.002	0.778	0.800	7.80	26.4	12.9	39.3
Polluted (minimum of 3 wells) . . .	27.48	0.106	0.020	0	0	0.047	2.10	12.6	8.6	21.2
From Hastings Sand, Lower and Upper Greensand, and Wealden.										
Maximum . . .	79.20	0.120	0.021	0.074	1.074	1.085	10.00	27.8	26.0	44.3
Minimum . . .	28.24	0.028	0.003	0	0	0.007	1.60	1.1	1.2	3.6
Average (20 samples)	45.20	0.068	0.014	0.016	0.196	0.223	5.38	16.8	10.5	27.3
Polluted well in Lower Greensand at Sevenoaks . .	38.76	0.447	0.072		0.252	0.324	5.90	7.2	13.4	20.6
From Chalk.										
Maximum . . .	66.34	0.131	0.064	0.029	2.277	2.319	11.10	38.6	13.8	50.0
Minimum . . .	23.30	0	0	0	trace	0.014	1.00	10.8	2.7	19.1
Average (66 samples)	36.88	0.050	0.017	0.001	0.610	0.628	2.76	21.2	6.5	27.7
Polluted wells, maxi- mum . . .	216.40	0.821	0.186	0.150	3.401	3.484	106.0	36.1	34.3	51.5
Polluted wells, mini- mum . . .	32.16	0.107	0.028	0	0	0.204	1.83	13.9	5.3	23.9
From Chalk beneath London Clay.										
Maximum . . .	106.70	0.195	0.067	0.118	0.645	0.681	38.80	29.5	25.4	48.5
Minimum . . .	33.38	0.055	0.005	0	0	0.053	2.38	0	0.9	0.9
Average (13 samples)	78.09	0.093	0.028	0.048	0.068	0.135	15.02	9.7	8.7	18.4
Polluted wells at Col- chester . . .	96.20	0.174	0.030	0.021	2.582	2.629	21.00	12.7	13.0	25.7
Polluted wells at Hounslow . . .	82.40	0.273	0.042	0.001	0.846	0.889	9.05	26.2	8.1	34.3
From Thanet Sand and Drift.										
Maximum . . .	61.10	0.133	0.021	0.190	0.438	0.457	9.10	23.7	12.0	34.0
Minimum . . .	45.96	0.074	0.019	0	0	0.019	5.20	4.5	3.6	8.1
Average (4 samples)	53.34	0.113	0.020	0.072	0.116	0.202	6.32	14.4	7.6	22.0

testify to the water having previously been in contact with nitrogenous organic matter which has subsequently undergone destruction. In shallow well waters, even when the organic matter is only small in amount, it is generally highly nitrogenous, pointing to its probable animal origin, and in some exceptional cases the organic nitrogen found is actually in excess of the carbon. These waters, which are generally suspicious from the presence of mineral nitrogen, become in the highest degree dangerous when the proportion of organic matter is large.

5. *Deep well waters.*—It is convenient to distinguish for sanitary purposes between waters which are obtained from comparatively shallow wells and those which are derived from wells, say, upwards of 100 ft. in depth, and sometimes reaching to the distance of more than 1000 ft. below the surface of the earth. The presumption is that waters obtained from such a depth have undergone perfect filtration through porous strata, and consequently it is not usual to view the evidence of previous contact with animal matters afforded by the presence of mineral nitrogen with so much suspicion as in the case of the waters from the shallower wells. The great efficiency of the filtration which most of these deep well waters have undergone is attested both by their freedom from organic matter, and from every kind of suspended material, whether organic or inorganic. In consequence of the excellent water obtainable from such deep wells, they have been multiplied greatly during past years, so that at the present time not only are many towns (including a part of London) and villages supplied from this source, but also nearly all larger breweries and many private establishments. In some cases these deep wells are of the kind known as 'Artesian' (from Artois, in France, where they were probably first employed); that is to say, on reaching the water-bearing stratum the water rises to the level or even considerably above the level of the ground, due to the underground water being confined under pressure beneath an impervious stratum of clay or the like, and through the outcrop of the water-bearing stratum being at a considerably higher altitude than the point at which the boring has been made. Thus, in the London basin, 'Artesian wells' are obtained by sinking through the London clay into the chalk beneath, which has its outcrop at considerable altitudes in the chalk hills on the north and south of the Thames valley. Owing to the large abstraction from such water-bearing strata, the water of many wells which formerly rose to the surface has now to be pumped. In the majority of deep wells the water does not rise nearly to the surface, and the pumps have often to be placed at considerable depths in the shaft. It is usual to line these wells with closely-fitting iron cylinders, in order to exclude surface water, as unless this is done the deep wells may become as objectionable and dangerous as shallow ones.

The preceding tables afford a survey of the general character of the deep well waters obtained in Great Britain. In nearly all the samples of which the maximum, minimum, and average results are given, it may be taken that the wells are unpolluted by surface water, but for the sake of comparison there are appended

to most of the sections analyses of deep well waters from the same strata in which pollution by surface or imperfectly-filtered water is highly probable.

These results demonstrate the great superiority from a chemical point of view of the subterranean waters obtained at great depths to those derived from shallow wells. Indeed, these deep well waters are, as regards organic matter, amongst the purest to be found in nature, and hence, unless extremely hard, are of the best quality for drinking purposes.

Closely associated with these deep well waters is the next group of spring waters.

6. *Spring water.*—In the following table is given the composition of, presumably unpolluted, British spring waters arranged according to the geological nature of the ground from which they are derived, whilst for the sake of comparison the composition of probably polluted waters from the same geological source is in many cases appended.

7. *Mineral spring waters.*—Many springs possess marked medicinal properties in consequence of the materials they hold in solution. Until the discovery of radium it was generally supposed by chemists that the therapeutic value of such waters containing only an insignificant amount of mineral matter must be imaginary, but it is now known that some of these, such as the waters of Bath and Buxton, are pronouncedly radioactive, and it is generally accepted at the present time that the old-established efficacy of these waters in the treatment of gout and rheumatism is due to their content of radioactive material (*see Nature*, 1911, 86, 157). Indeed, radium-salt is now much employed for the artificial production of radioactive water for medicinal purposes. An immense number of mineral waters are in use, and have been submitted to careful analysis; a very extensive collection of such analyses is to be found in Raspe's *Heilquellen Analysen*, Dresden, 1885.

These mineral waters are conveniently classified by Hermann Weber (*Quain's Dictionary of Medicine*), according to the ingredients which characterise them, into—(1) Simple thermal waters; (2) common salt or muriated saline waters; (3) alkaline waters; (4) sulphated saline waters; (5) iron or chalybeate waters; (6) sulphur waters; (7) earthy and calcareous waters.

(1) *The simple thermal waters*, whilst containing only a moderate proportion of dissolved solids, are characterised by a high temperature, from 27°–65°, and sometimes by the presence of an unusually large proportion of nitrogen, which is now known to be mixed with appreciable quantities of helium. Doubtless the medicinal reputation of most, if not all, of these waters depends on their radioactivity. The principal springs of this class are: Panticoos, Leukerbad, Bormio, Gastein, Pfäfers, Johannisbad, Ragatz, Wildbad, Plombières, Buxton, Bath, Looe, Teplitz, Schlangenbad, &c.

(2) *Common salt or muriated saline waters* contain sodium chloride as the principal constituent, although this also occurs often in large quantity in many of the other classes of mineral waters. These salt waters or brines are very common in almost all countries. Some of the

SPRING WATER. (6th Rep. Riv. Com. p. 107.)

100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Granite and Gneiss.										
Maximum	9.44	0.119	0.019	0.002	0.204	0.210	3.10	1.2	5.3	5.6
Minimum	1.40	0	0	0	0	0.013	0.55	0	1.2	1.2
Average (8 samples)	5.94	0.042	0.008	0.001	0.106	0.115	1.69	0.4	2.6	3.0
From Silurian Rocks.										
Maximum	27.10	0.096	0.042	0.005	0.659	0.674	3.70	6.9	9.3	15.6
Minimum	3.04	0.011	0.002	0	0	0.011	0.90	0	1.5	1.5
Average (15 samples)	12.33	0.051	0.014	0.001	0.178	0.192	1.84	1.5	5.3	6.8
From Devonian and Old Red Sandstone.										
Maximum	66.90	0.124	0.034	0.006	4.104	4.128	13.80	22.4	12.4	29.9
Minimum	5.50	0.009	0.001	0	0.013	0.028	1.30	0	1.9	2.2
Average (22 samples)	25.06	0.054	0.012	0.001	0.764	0.777	3.85	4.8	7.2	12.0
From Mountain Limestone.										
Maximum	98.50	0.286	0.023	0.006	1.022	1.036	32.00	20.9	29.5	48.5
Minimum	15.70	0.011	0	0	0	0.001	0.70	2.1	3.3	11.0
Average (13 samples)	32.06	0.087	0.010	0.001	0.224	0.235	4.63	10.9	8.9	19.8
From Yoredale and Millstone Grits.										
Maximum	40.80	0.109	0.028	0.006	0.617	0.650	3.45	21.4	11.5	26.4
Minimum	3.32	0.017	0.004	0	0	0.005	0.95	0	2.7	2.7
Average (8 samples)	17.73	0.042	0.011	0.001	0.169	0.181	1.73	6.6	5.7	12.3
From Coal Measures.										
Maximum	39.60	0.120	0.027	0.008	1.813	1.860	3.35	14.5	17.1	25.7
Minimum	6.84	0.029	0.004	0	0	0.010	0.95	0	2.3	2.6
Average (22 samples from millstone grit and coal measures)	21.91	0.050	0.014	0.001	0.393	0.408	1.85	5.2	7.9	13.1
From Magnesian Limestone.										
Pontefract, Yorks	66.52	0.058	0.038	0.002	1.686	1.726	3.40	24.9	34.8	59.7
From New Red Sandstone.										
Maximum	74.26	0.118	0.069	0.014	1.256	1.275	7.00	19.8	25.0	35.7
Minimum	12.90	0.027	0	0	0	0.006	1.30	0	4.2	8.0
Average (15 samples)	28.69	0.065	0.017	0.001	0.330	0.349	2.19	8.1	10.7	18.8
From Lias.										
Maximum	58.12	0.131	0.036	0.009	1.332	1.353	4.80	32.3	17.4	45.7
Minimum	21.22	0.024	0.006	0	0	0.035	1.35	9.1	5.3	15.1
Average (7 samples)	36.41	0.073	0.019	0.001	0.467	0.487	2.48	21.3	8.6	30.1
From Oolites.										
Maximum	52.16	0.140	0.021	0.014	1.157	1.168	3.30	30.0	13.5	38.7
Minimum	22.30	0.009	0.003	0	0	0.014	0.97	11.3	3.5	16.9
Average (35 samples)	30.33	0.043	0.011	0.001	0.402	0.414	1.55	18.2	6.2	24.5
From Lower Greensand, Hastings Sand, and Upper Greensand.										
Maximum	68.40	0.135	0.028	0.003	1.116	1.129	7.10	25.0	22.1	40.2
Minimum	4.55	0.002	0.002	0	0.034	0.045	1.10	0	0.7	0.7
Average (19 samples)	30.05	0.053	0.012	0	0.326	0.338	2.98	13.6	6.6	20.2
From Chalk.										
Maximum	39.30	0.097	0.023	0.006	0.663	0.674	7.40	25.3	8.1	33.2
Minimum	25.36	0.008	0.003	0	0	0.009	1.05	6.9	3.6	12.4
Average (30 samples)	29.84	0.044	0.010	0.001	0.382	0.392	2.45	18.1	5.8	23.6
From Fluvio Marine, Red Crag, Drift, and Gravel.										
Maximum	225.24	0.164	0.043	0.007	1.277	1.293	4.27	32.2	94.3	126.5
Minimum	24.62	0.004	0.006	0	0.004	0.034	2.10	0.7	6.1	12.8
Average (19 samples)	61.33	0.086	0.019	0.001	0.354	0.374	2.76	16.0	19.6	37.6

* Water supply of Western-super-Mare; these exceptionally high results doubtless due to access of sea water.

principal ones in England are: Droitwich, Nantwich, Middlewich, Woodhall, and Harrogate; Leamington and Cheltenham along with sodium sulphate. In Germany: Kissingen, Homburg, Nauheim, Krensnach, Soden, Pyrmont, Wiesbaden, Ischl, Kreuth, Baden-Baden, &c. In France: Bourbonne-les-Bains, Lamotte-les-Bains, Balaruc, Salins. In Italy: Castellamare, Ischia, Monte Catini, La Porretta. In Switzerland: Bex.

(3) *Alkaline waters* are characterised by the presence of sodium carbonate, almost always with more or less free carbon dioxide, and sometimes with a large quantity also of sodium chloride. Of the simply alkaline waters, there are—(a) *Hot*: Vichy, Neuenahr, Mont-Dore, Chaudesaignes, Nérès; (b) *Cold*: Apollinaris, Vals, Salzbrunn, Bilin, Wilhelmsquelle, Taunus, Marco; whilst the chief muriated alkaline waters are: (a) *Hot*: Ems, Royat, La Bourboule; and (b) *Cold*: Luhatschowitz, Selters, Gleichenberg, Rosbach, Vic-sur-Cère. Several of these, but especially La Bourboule and Mont-Dore, contain a marked proportion of arsenic.

(4) *Sulphated waters* contain either sodium or magnesium sulphate, or both, as the prominent ingredients, in some cases also associated with sodium carbonate and chloride. They are often called '*bitter waters*.' The chief simple sulphated waters are: Galthof, Pullna, Said-schutz, Sedlitz, Birmensdorf, Ivanda, Hunyadi Janos, Epsom, Aranjuez, Friedrichshall, Mergentheim; the two latter are also rich in chlorides. Weaker springs of the same kind are found at Leamington, Cheltenham, Scarborough, and at Purton Spa. Of alkaline sulphated waters there are: Carlsbad, Marienbad, Tarasp-Schuls, Franzensbad, Elster, and Bertrich.

(5) *Iron or chalybeate waters* are those in which an unusual proportion of this element is present, either in otherwise comparatively pure water or associated with other mineral matters. Thus, of comparatively pure chalybeate waters, there are those of Schwalbach, Spa, Brückenau, Schandau, Liebwert, Flinsberg, Freienwalde, Reccaro, Königswarth, Liebenstein, Altwasser, Alexishad, Muskau, Tunbridge Wells, and some of the springs at Harrogate; whilst of waters in which the iron is associated with a considerable quantity of other salts, there are those of Aratapak, Orezza, Pyrmont, Driburg, Rippoldsau, Griesbach, Antogost, Petersthal, Bocklet, St. Moritz, Reinerz, Godesberg, Cudowa, Imnan, and Santa Catarina.

(6) *Sulphur waters* are those containing appreciable quantities of either sulphuretted hydrogen or the sulphides of sodium, potassium, calcium, or magnesium. Some of the more important thermal sulphur waters are those of Eaux Chaudes, Cautelets, Saint Sauveur, Bagnès, Bagnères-de-Luchon, Ax, Escaldes, Le Vernet, Amélie-les-Bains, Uriège, Allevard, Aix-les-Bains, Aix-la-Chapelle, Baden (Austria), Baden (Switzerland), Lavey, Schinznach, Battaglia, and Abano in the Euganean Mountains, Panticosa, Mehadia, Helouan, near Cairo; whilst of cold sulphur springs there are those of Hilsen, Neundorf, Langenbrücken, Weilbach, Meisberg, Reutlingen, Engheim, Challes, Stachelberg, Hemstich, Gurnigel, some of the Harrogate springs, Llandrindod, Bulth, Moffat, Strathpeffer, Llandudnew.

(7) *Earthy and calcareous waters* are characterised by the presence of large proportions of calcium carbonate and sulphate, and magnesium carbonate. Some of the more important are found at Wildungen, Lipp Springs, Weissenburg, Contrexéville, Bagnères-de-Bigorre, St. Arnaud, Crausac, whilst the table waters of Couzan, St. Galmier, and Taunus are of the same character.

8. *Sea water*.—The ocean is a great evaporating-basin, which is constantly receiving waters, more or less impure, in the shape of rivers, whilst at the same time it is constantly losing pure water in the form of vapour, the impurities remaining behind and imparting to the sea its well-known saline character. This also distinguishes all lakes which are devoid of outlet, like the Dead Sea, Caspian, Aral, Great Salt Lake Utah, &c., in which the same process of concentration by evaporation is going on. As will be seen from the table on the next page, the composition of the ocean varies considerably in different places and at different depths, whilst land-locked seas, like the Mediterranean, Black Sea, and Baltic, present even still greater differences.

Thus in the vicinity of the poles the proportion of salt is less than near the equator; similarly, land-locked seas, such as the Black Sea and Baltic, which receive large rivers are salt; whilst the Mediterranean in most places is more salt than the great oceans. Of salt lakes the Dead Sea is far more and the Caspian far less salt than the oceans. In addition to sodium chloride, the principal substances present in sea water are the sulphates and carbonates of calcium and magnesium, and salts of potassium, whilst in very minute quantities there are found also a number of others, amongst which may be mentioned bromides, iodides and fluorides, silica, phosphoric and nitric acids, iron, silver, gold, copper, lead, arsenic, zinc, cobalt, nickel, lithium, rubidium, and caesium.

The volume of gas dissolved in sea water is, according to Hunter (Chem. Soc. Trans. 1870, 20), only from 2·2 to 3·5 vols. in 100 vols. of water.

	CO ₂	O	N
	cent.	per cent.	per cent.
2·2 vols. consisted of	28·62	21·94	49·44
3·5 " "	48·28	17·22	34·50

A very extensive examination of the composition of sea water was made in connection with the voyage of H.M.S. *Challenger*, and the elaborate report prepared thereon by Dittmar should be consulted for detailed information on this subject. From 77 complete analyses, the following numbers for the average composition of ocean-water salts are calculated:—

Average composition of ocean-water salts, in parts per 100 of total salts (Dittmar).

Chlorine	55·232
Bromine	0·1834
Sulphuric acid (SO ₃)	6·410
Carbonic acid (CO ₂)	0·152
Lime (CaO)	1·076
Magnesia (MgO)	6·200
Potash (K ₂ O)	1·333
Soda (Na ₂ O)	41·334
(Basic oxygen equivalent to gms)	12·100

550·000

(Results of Analysis expressed in parts per 1000.)

Sea	Point of collection of sample	Na	Cl	Mg	Ca	K	SO ₄	Br	CO ₂	Fe	Fired residue	Authors
Atlantic Ocean	0° 47' S.—33° 20' W.	11.081	19.460	0.9568	0.4567	0.7604	2.577	0.4069	—	—	35.700	
"	20° 54' N.—40° 44' W.	10.464	19.012	1.2735	0.4684	0.7252	2.446	0.3102	—	—	34.700	
"	41° 18' N.—36° 28' W.	11.719	20.840	1.1981	0.5568	0.6682	3.029	0.3878	—	—	38.400	Bibra, Annalen, 77, 90.
"	Cape Horn	10.457	18.841	1.1763	0.5289	0.5916	2.878	0.3271	—	—	34.800	
North Sea	"	10.117	18.954	1.3141	0.4782	0.6811	2.563	0.2924	—	—	34.400	
"	Between Belgium and England	10.206	18.168	1.1582	0.3244	0.3536	2.590	(?)	—	—	32.800	Bischof, C. Geolog., 1, 98.
Straits of Dover	Some miles from Havre	10.142	17.794	1.2305	0.4093	0.0425	2.882	0.1046	0.078	traces	32.700	Figuiet et Mialhe, J. Pharm. [iii.] 13, 406.
Mediterranean	Marseilles	10.688	21.090	3.0037	0.048	0.0041	5.716	(?)	0.142	—	40.700	Laurent, J. Pharm. 21, 93, [ii.] 92, 172.
"	At 3500 metres from the coast of Cettie.	11.706	20.527	1.3104	0.4411	0.2643	2.943	0.434	0.0679	0.0028	37.700	Usiglio, Ann. Chim. Calamai, 1847.
"	The Lagunes of Venice	8.779	15.882	1.1646	0.1769	0.4356	2.662	(?)	—	—	29.100	
Pacific Ocean	3.5 metres below the surface	10.262	18.950	1.3151	0.4719	0.6038	2.786	0.3102	—	—	34.700	Bibra, l.c.
"	140 metres below the surface	10.233	19.321	1.4714	0.4752	0.6336	2.827	0.2394	—	—	35.200	Pfaff, Schweigger's Journ. 22, 271.
Baltic	"	5.894	10.386	1.6115	0.0363	—	0.719	—	—	—	17.710	
Black Sea	Coast south of the Crimea	5.512	9.574	0.6622	0.1305	0.0975	1.2505	0.005	0.2475	0.1271	17.605	Göbel, P. Suppl. 1, 187.
Sea of Azof	Between Kertch and Mariapol	3.997	6.585	0.4010	0.0908	0.0670	0.8045	0.004	0.0695	0.0358	11.900	Ibid.
Caspian Sea	South-west of Pischnoi	1.144	2.737	0.4098	0.1916	0.1397	1.337	(?)	0.0773	0.0401	6.296	Ibid.
Dead Sea	From the surface	0.885	17.628	4.177	2.150	0.474	0.2424	0.167	traces	traces	27.078	Terreil, Compt. rend. 62, 1329. (Wurtz, Dictionnaire de Chimie.)
"	From 300 metres below the surface	14.300	174.985	41.428	17.269	4.386	0.6276	7.093	traces	traces	278.135	

To these may be added the following analysis of the water of the Irish Channel in the winter of 1870 (Thorpe and Morton, Chem. Soc. Trans. 1871, 506).

(Results of Analysis expressed in parts per 1000.)

NaCl	26.43918	MgSO ₄	2.06608	CaSO ₄	0.00044	Sp. gr at 0°C. = 1.02721
KCl	0.74619	MgCO ₃	Trace	CaCO ₃	0.00603	" 15°C. = 1.02484
MgCl ₂	3.15083	Mg(NO ₃) ₂	0.00207	LiCl	Trace	Total = 33.85946
MgBr ₂	0.07025					

The salinity of the ocean, expressed in parts of total salts per 1000 parts of sea-water, was found to vary between the following limits: Minimum (from the southern part of the Indian Ocean, south of 66° lat.), 33.01; maximum (from the middle of the North Atlantic, at about 23° lat.), 37.37.

As regards the carbon dioxide in sea water, Dittmar comes to the following conclusions:

(1) Free carbonic acid in sea water is the exception; as a rule, the carbonic acid is less than the proportion corresponding to bicarbonate. (2) In surface waters the proportion of carbonic acid increases when the temperature falls, and vice versa. (3) Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean.

Drinking Water. It has long been known that the palate is by no means a safe guide in the choice of drinking water, for although unpalatable waters are obviously unsuitable for drinking, palatable waters may contain materials capable of doing serious injury. It is now established beyond question that the diseases termed 'zymotic' are due to minute forms of life known as micro-organisms, and in a number of cases the specific forms responsible for such diseases have been discovered, identified, and studied. Of zymotic diseases there are two—Asiatic Cholera and Typhoid Fever—which are with certainty known to be propagated by drinking water, and in the case of these two diseases authorities are agreed as to the particular organisms to which they are due. The propagation unquestionably takes place through the excreta of persons suffering from these diseases gaining access to water which is afterwards used for drinking, whilst water contaminated with the sewage of healthy persons is generally believed to be capable of producing diarrhoea and other minor disturbances in those drinking it.

In selecting water for drinking purposes it is necessary, therefore, in the first instance, to make a careful inquiry as to the possibility of the water having been in contact with refuse animal matters, and if possible all waters open to such suspicion should be discarded. For the same reason it is of the first importance in the examination of water to discover what evidence, if any, there is of the water having been in contact with such refuse substances. In the present state of knowledge this is a difficult matter, as, although the results of chemical analysis frequently point to such contamination when on a sufficiently large scale, it is occasionally and indeed generally impossible to prove the negative. The bacteriological examination, on the other hand, is of extreme delicacy, but, inasmuch as we have at present no means of ascertaining whether the bacteria indicative of faecal contamination are derived from man or from the lower animals, the results obtained by this means, also, are often of restricted value from a hygienic point of view. It becomes, therefore, of the greater importance to make a thorough inspection of the source and to trace out the further history of the water, for unless this be done the results of the scientific examination may often receive an erroneous interpretation. As, however, it is comparatively rarely

that natural waters are to be met with which are absolutely above suspicion of any contamination with refuse animal matters, it is generally necessary to be satisfied with relative purity, and thus the examination, chemical and biological, of drinking waters becomes a matter of the highest importance and utility. The natural waters which can lay claim to the greatest degree of safety for drinking purposes are of two kinds.

1. Unpolluted surface waters (generally upland waters).

2. Naturally filtered waters (spring and deep well waters).

In the first case the waters, both by inspection and analysis, must bear no evidence of animal contamination, and this is generally possible in the case of waters which are fit at altitudes above that of human habitations. A number of our large towns are supplied with water of this kind, although the gathering grounds do in most cases contain some houses so that absolute freedom from sewage contamination cannot generally be guaranteed. In the table on p. 381 the chemical composition of some of these upland surface water supplies is recorded.

The majority of upland surface waters are either very soft or of only very moderate hardness, and as in many of these towns extensive manufactures are carried on, these supplies are not only valued because of their safety for drinking, but also on account of their fitness for industrial purposes. It should always be remembered, however, that these surface waters may at times receive more or less sewage contamination, and that the ova of animal parasites derived from the cattle grazing on the gathering grounds may also be present, and that, therefore, to reduce these sources of danger to a minimum, it is highly desirable that such waters should be subjected to prolonged storage in reservoirs, followed by careful filtration through sand before delivery to the consumer.

In the second class of water its original purity is a matter of secondary consequence, the guarantee of safety resting upon the exhaustive process of filtration which the water has undergone in passing through porous strata of the earth's crust. This filtration effects, on the one hand, the more or less complete chemical purification of the water from organic substances, and, on the other hand, the mechanical removal of organised matters, such as bacteria and animal parasites. The most perfectly filtered waters of this kind are those obtained from springs and from deep wells, and, again, many of our towns are supplied with water of this kind—more especially from the Chalk, Greensand, Oolite, and New Red Sandstone formations, which constitute efficient filter beds. In the table on p. 382 is recorded the chemical composition of the water supplied to some of our towns from such sources.

Of other forms of drinking water we have river waters and shallow-well waters, upon both of which a very large portion of the population is dependent for domestic supply. Both of these classes of water are open to grave objections, and nearly all the best authenticated cases of the propagation of cholera and typhoid through drinking water have been traced to

UPLAND SURFACE WATER SUPPLIES.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness			Remarks
							Temporary	Permanent	Total	
Heywood and Middleton supply, Sept., 1908	8.96	0.044	0.010	0	0.037	0.047	0.4	2.2	2.6	Almost clear.
Terquay supply, April, 1903	6.84	0.141	0.018	Trace	0.118	0.136	0.3	2.2	2.5	Very slightly turbid.
Paisley supply, Sept., 1898	8.68	0.487	0.064	0.002	0.035	0.101	0.1	3.8	3.9	Clear.
Pontypriidd supply, Nov., 1907	5.28	0.183	0.025	0	0.032	0.057	—	—	2.3	Very slightly turbid.
Cardiff supply, Dec., 1908	6.28	0.100	0.016	0	0.024	0.040	0.3	3.0	3.3	Almost clear.
Aberdeen supply, intake from River Dee, March, 1910	4.76	0.193	0.026	0	0.010	0.036	0.2	1.6	1.8	Very slightly turbid.
Aberdeen, proposed supply from River Avon, March, 1910	2.60	0.091	0.015	0	0.008	0.023	0	0.5	0.5	Very slightly turbid.
Glasgow, L. Katrine water, Nov., 1891	2.80	0.149	0.025	0	0.004	0.029	—	—	0.6	Slightly turbid.
Liverpool, Rivington Water, Average for 1903	9.82	0.153	0.025	0.002	0.005	0.032	—	—	4.1	
" Vyrnwy Water	4.67	0.211	0.027	0.002	0	0.029	—	—	1.5	
Birmingham, Elean Valley Water, Jan., 1911	6.44	0.171	0.019	0	0.016	0.035	0.2	2.5	2.7	Almost clear.
" " " June, "	4.92	0.089	0.015	Trace	0.016	0.031	0.3	2.6	2.9	Almost clear.
Dewsbury supply, Dec., 1910	7.52	0.226	0.025	0.002	0.053	0.080	0.2	2.7	2.9	Slightly turbid and opalescent.
" " July, 1911	6.24	0.067	0.005	Trace	0.035	0.040	0.2	2.5	2.7	Slightly turbid.
Belfast, Woodburn supply, Jan., 1910	14.40	0.325	0.022	Trace	0.032	0.054	5.5	3.6	9.1	Almost clear.
" " " June, "	15.32	0.155	0.019	Trace	0.027	0.046	5.6	3.4	9.0	Almost clear.
" Stonyford supply, Jan., 1910	13.68	0.427	0.036	0	0.026	0.062	4.4	3.5	7.9	Almost clear.
" " " June, "	12.16	0.265	0.031	Trace	0.016	0.047	4.2	3.4	7.6	Almost clear.
" Mourne Mountains supply, Jan., 1910	9.28	0.195	0.015	0	0.041	0.056	0.2	3.4	3.6	Very slightly turbid.
" " " June, "	7.00	0.171	0.018	Trace	0.027	0.045	0.5	2.2	2.7	Slightly turbid.

WATER SUPPLIES FROM DEEP WELLS AND SPRINGS.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		Remarks	
								Temporary	Permanent		Total
Portsmouth supply: from chalk springs, August, 1905	29.80	0.032	0.009	Trace	0.326	0.335	1.65	19.0	5.3	24.3	Very slightly turbid.
Nottingham: borehole 500 ft. deep in New Red Sandstone, Dec., 1910	19.80	0.020	0.005	0	0.020	0.025	1.25	9.6	7.8	17.4	Almost clear.
Liverpool: Dudlow Lane well in New Red Sandstone, 1903	18.43	0.024	0.007	0	0.677	0.684	3.01	—	—	7.8	
" Green Lane well "	32.79	0.028	0.007	0	0.625	0.632	3.33	—	—	19.1	
" Windsor well "	41.20	0.019	0.006	0	0.786	0.792	4.38	—	—	26.5	
Long Eaton supply: well in New Red Sandstone, Sept., 1911	48.32	0.038	0.008	0.002	0.295	0.305	2.50	22.3	13.4	35.7	Very slightly turbid.
Eastbourne supply: well in chalk, August, 1911	28.56	0.028	0.004	0	0.378	0.382	3.63	15.1	3.8	18.9	Clear.
Lancaster: well 200 ft. deep in Grey Sandstone, Sept., 1901	22.00	0.016	0.004	Trace	Trace	0.004	2.20	9.8	5.9	15.7	Very slightly turbid.
Mansfield: well in New Red Sandstone, May, 1907	14.92	0.034	0.006	Trace	0.373	0.379	1.30	0.6	8.0	8.6	Almost clear.
E. Worcestershire Waterworks: Burroft well in New Red Sandstone, Oct., 1908	17.72	0.028	0.006	Trace	0.314	0.320	1.20	2.1	7.0	9.1	Almost clear.
Shanklin: springs in Upper Greensand, June, 1908	34.88	0.036	0.009	0	0.276	0.285	3.40	18.6	5.3	23.9	Almost clear.
Exmouth: borehole 338 ft. deep in New Red Sandstone, June, 1909	23.60	0.025	0.006	0	0.386	0.392	2.60	9.1	4.6	13.7	Almost clear.
Great Grimsby: well in chalk at Healing, April, 1911	30.00	0.010	0.005	0	0.386	0.391	1.80	18.6	3.6	22.2	Almost clear.
" " at Cleethorpes, April, 1911	31.00	0.011	0.004	0	0.149	0.153	2.88	19.4	3.5	22.9	Almost clear.

shallow wells. There are, however, many potent influences tending to remove bacteria from water which, on a *priori* reasoning, would have been regarded as almost, if not wholly, inoperative. These causes are mainly the process of devitalisation which pathogenic bacteria undergo in natural, and more especially in surface waters, and the resistance offered by even a comparatively small thickness of soil or other porous material to the passage of micro-organisms. But although these causes are to be looked upon as tending to keep the evils which can result from contaminated drinking water within narrower limits than might have been anticipated, still the possibility of their failure must be constantly kept in view, and they must not be allowed to check the endeavour to substitute unimpeachable for suspicious sources of supply.

Every effort should be made to exclude avoidable sources of contamination, to select the best water which the source affords, and to submit it to the most effective purification available. The improvements which can thus be brought about in water supplies obtained from suspicious sources is conspicuously exemplified in the case of the London supply derived from the rivers Thames and Lea. Here, on the one hand, increasing vigilance has been exercised by the Thames and Lea Conservancy Boards in the exclusion of dangerous matters from the rivers and their tributaries, whilst on the other hand the authorities supplying water have removed their intakes to points on these streams above the most serious pollutions; by increasing their storage capacity they are enabled not only to

avoid drawing from the rivers in times of flood, but also to bring about a great amelioration in the quality of the water during its sojourn in the reservoirs, whilst by improving their filtering appliances they secure a more perfect purification of the water which they have abstracted. Thus the water supplied to London to-day is both chemically and hygienically very different from what it was 60 years ago, although still derived from the same streams, which in the ordinary course of events would be more polluted now than they were then.

Importance to be attributed to various ingredients of drinking water.—It is only possible here to give a brief account of the importance which is usually attributed to the several ingredients which are commonly determined in the analysis of drinking waters.

Dissolved gases.—The gases present in ordinary drinking waters are those of the atmosphere—oxygen, nitrogen, and carbon dioxide. Their quantitative determination is of little or no significance in connection with the quality of the water for drinking, excepting that through the absence of dissolved gases a water has the flat taste of that which has been recently boiled. It is sometimes supposed that the absence of a due proportion of dissolved oxygen in water is an indication of the presence of decomposing organic substances, but this can only be the case with surface waters, as the very purest subterranean waters are almost entirely destitute of it. In the following table the proportion of the several dissolved gases in different kinds of water is recorded:—

Gases dissolved in 100 cub. ins. of water	Rain-water	Cumberland mountain water	Loch Katrine water	Thames water	Deep chalk well water
	cub. ins.	cub. ins.	cub. ins.	cub. ins.	cub. ins.
Nitrogen	1·308	1·424	1·731	1·325	1·944
Oxygen	0·637	0·726	0·704	0·588	0·028
Carbon dioxide	0·128	0·281	0·113	4·021	5·520
	2·073	2·431	2·548	5·934	7·492

The large proportion of dissolved carbon dioxide in the Thames and deep chalk well water is mainly combined with calcium carbonate as bicarbonate.

Total solid residue.—It is only rarely that the amount of the residue left by a water on evaporation affords any evidence of its fitness for drinking. As a general rule, it may be stated that waters which contain very small residues are probably pure and unpolluted, but on the other hand many waters of organic purity contain large proportions of mineral matter in solution. It is impossible to assign limits to the proportion of mineral matter which may be present in water without interfering with its fitness for drinking, more especially as opinion is divided as to the influence of the several constituents on health (*v. also Hardness of water*). Nearly all the best drinking waters in the United Kingdom yield less than 50 parts of solid residue per 100,000, and most of them very considerably less. The use of waters yielding much larger residues is generally avoided by the inconvenience which attends

their employment for general domestic purposes, in consequence of their unfitness for boilers and washing.

Organic matter.—As will be pointed out (under *Water analysis*), the accurate determination of the organic matter in water is attended with great difficulties, and none of the methods of analysis in use claims to effect more than a partial determination. Thus in the 'combustion process' the organic carbon and nitrogen are determined with more or less accuracy; in the alkaline permanganate process that portion of the organic nitrogen is discovered which is readily convertible into ammonia, whilst in the 'permanganate' or 'oxygen' process the proportion of permanganate destroyed by the organic matter is taken into account. Although it may be stated generally that the smaller the proportion of organic matter the more desirable is the water for drinking, of still greater importance is the determination of the origin of the organic matter present, whether animal or vegetable. The presence of vegetable matter is of comparatively little consequence

more especially as even small amounts interfere with the palatability of the water, what is known as a 'peaty taste' being imparted by any amount yielding much in excess of 0.2 part per 100,000 of organic carbon. Sometimes much light may be thrown on the origin of the organic matter in water by the proportion which the carbon and nitrogen exhibit towards each other, especially when this is considered in connection with the proportions of ammonia, nitrates, nitrites, and chlorine. Inasmuch as animal matter in general contains a much higher proportion of nitrogen to carbon than does vegetable matter, it follows that the higher the ratio of nitrogen to carbon in the organic matter present in a sample of water, the more probability is there, *ceteris paribus*, of its being derived from animal sources and *vice versa*. The possibility of such diagnosis, however, is considerably limited by the fact that in the oxidation of peaty matter the organic carbon disappears much more rapidly than the nitrogen; whilst, on the other hand, in the oxidation of animal matter there is conversely a tendency for the organic carbon to become concentrated, thus leading to a simulation of animal matter in the case of vegetable, and a simulation of vegetable matter in the case of animal substances after oxidation.

It is thus essential that the evidence afforded by the proportion of organic carbon to nitrogen should be supplemented by an inspection of the source, and by a consideration of the mineral nitrogenous ingredients—ammonia, nitrates, and nitrites—all of which are principally derived from the decomposition of animal matters.

Albuminoid ammonia.—The ammonia yielded on distillation with alkaline permanganate is so frequently made the only measure of the organic matter present in water that a few words are necessary to indicate what is the importance to be attached to the results obtained in this simple process. According to its author, the late Mr. Wanklyn, 'deep spring water is often so pure as not to yield 0.01 part of albuminoid ammonia per million; and unless mixed

with surface water does not yield so much as 0.05 part.' 'The filtered water supplied by water companies—no matter whether derived from a lake, from clean mountain streams, or from defiled rivers—yields from 0.05 to 0.10 part of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to 0.05.' 'When the filters are over-taxed, as happens in the rainy season and in the winter, water companies supply imperfectly-filtered water, in which as much as from 0.10 to 0.20 part of albuminoid ammonia is found.' This statement must be accepted with great reserve, for in the winter months such surface waters almost invariably contain a much larger proportion of organic matter than during the dry season, thus accounting for the increase in albuminoid ammonia quite irrespective of any over-taxing of the filters. On the other hand, the albuminoid ammonia is the chemical ingredient in water which is most affected by filtration. It would appear, therefore, that suspended particles of vegetable and animal matter, which are removed by sand filtration, are particularly productive of ammonia on distillation with alkaline manganate. In fact, the chemical between a water before and after sand is often only attested by the diminution of albuminoid ammonia yielded by the filtered water.

Oxygen or permanganate process.—The analytical value of measuring the proportion of organic matter in water by the amount of permanganate it is capable of decolorising is discussed in the section of this article on *Water analysis*, and it will be sufficient here to give some idea of how the results are to be interpreted. As in the case of the organic elements determined by combustion, it has here again been attempted to establish a scale of classification, which, however, must also be used with the greatest caution and in conjunction with the other analytical data, as well as with regard to the water's source and history. Thus the following artificial standards have been suggested:—

	Oxygen absorbed in three hours at room temperature from potassium permanganate by 100,000 parts of water	
	For Upland Surface Water	For other Water
Class I. Water of great organic purity . . .	0-0.1 part	0-0.05 part
" II. " medium " . . .	0.1-0.3 "	0.05-0.15 "
" III. " doubtful " . . .	0.3-0.4 "	0.15-0.2 "
" IV. Impure water . . .	above 0.4 "	above 0.2 "

It will be readily understood that a great drawback to this permanganate process consists in its not distinguishing between nitrogenous and non-nitrogenous organic matter. Hence it is very desirable that, if the combustion process cannot be resorted to, it should be supplemented by a determination of the 'albuminoid ammonia,' or of the Kjeldahl nitrogen (see p. 403).

Mineral nitrogen (ammonia, nitrates, and nitrites).—The importance of these ingredients is an indirect one. In themselves they in no influence the wholesomeness of

water; but, on the other hand, they are of consequence as indicating what the previous history of the water has been. Thus, in the ordinary process of decomposition to which organic matters are subjected in nature, the nitrogen is principally liberated in the form of ammonia, and this, by subsequent fermentative oxidation, may become converted into nitrites and nitrates. Moreover, owing to the far average richness in nitrogen of animal vegetable matters, it is evident that these primary and secondary products of decomposition

furnish valuable evidence as to the previous contact of water with nitrogenous, and more especially animal, substances. As a general rule, the presence of ammonia indicates a more recent contact with such matters than does that of nitrates or nitrites, although in the case of some deep subterranean waters it appears that the nitrates originally present in the water have undergone reduction to ammonia, and hence the latter in such cases must be regarded as evidence of a more remote character even than the nitrates themselves. Again, in the ordinary course of nitrification in nature the ammonia is wholly converted into nitrate, the preliminary oxidation to nitrite being rapidly passed over; but if water containing nitrates is brought in contact with organic matter, these nitrates become more or less reduced to nitrites through the agency of certain micro-organisms (P. F. Frankland, Chem. Soc. Trans. 1888, 373; Warington, *ibid.* 742), and hence the presence of nitrites generally constitutes evidence of contamination with organic matter subsequent to the original nitrification, rather than to the latter having been imperfect. The fact must also not be lost sight of that nitrates can be reduced by certain microbes in the presence of organic matter with elimination of the nitric nitrogen in the free state, or as oxides of nitrogen, and that a contamination of the nitrified water may thus lead to the more or less complete removal of the mineral nitrogen. The absence of nitrates may thus, under some circumstances, actually indicate contact with animal matter instead of freedom from it (Munro, Chem. Soc. Trans. 1886, 632).

It must also be remembered that, in the case of surface waters, the mineral nitrogen may undergo removal through being taken up as food by plant-life, and thus the evidence of previous contact with animal matters be destroyed.

As the hygienic significance of contact with animal matters consists in the possibility of the ingress of pathogenic microbes (which may at any time be present in sewage and similar animal refuse), it is obvious that the evidence of such previous contact afforded by the presence of mineral nitrogen in any excessive proportion must be viewed as serious, if the history of the water furnishes no guarantee that any such organised poisons which may have gained access would have been subsequently removed, whilst the evidence is of far less consequence, or may indeed become entirely negligible, if in the subsequent history of the water it has undergone processes of purification which practically preclude the possibility of such poisons being still present. Until the application of bacteriology to questions of water supply, it was not possible to ascertain the efficiency of processes of water purification in this respect. But we now know that the exhaustive filtration through porous strata which spring and deep well water has undergone practically guarantees the removal of any micro-organisms which may have been originally present; in the case of river and shallow well waters, on the other hand, the chance of such removal is much less, and hence in such waters the evidence afforded by mineral nitrogen of previous contact with animal matters must be viewed with suspicion, whilst

in the spring and deep well waters it may often be disregarded altogether.

Chlorine.—This element is invariably in a state of combination—generally as sodium chloride, and hence quite innocuous. Its determination in potable water, however, is of importance as often affording information as to whether the water has been in contact with refuse animal matters or not. In this respect it is often more useful than the mineral nitrogen, as, once present in water, it cannot by any natural processes be removed. Its diagnostic value is due to the fact that human urine contains 500 parts of chlorine, or 824 parts of common salt in 100,000 parts. It is, of course, inapplicable in the vicinity of the sea and of natural salt deposits. In British waters free from animal pollution the average proportion of chlorine may be taken as 1 part per 100,000; but it is subject to very great variations.

There are, however, many other refuse liquids besides sewage which contain large quantities of chlorides, such as the effluents from dye and bleach-works, tanneries, paper-mills, alkali-works, and especially tin-plate and galvanising works, the proportion being often far in excess of anything ever found in sewage.

In America much attention has been bestowed on the proportion of chlorine present in unpolluted water at different distances from the sea-board. The points at which such waters exhibit the same amount of chlorine are joined by lines termed 'isochlors,' and these isochlors are found to be roughly parallel to the coast-line. Any water submitted for examination is then remanded for further inquiries if it exhibits more chlorine than is normal for the isochlor upon which the source of the particular water is situated. This is an attempt to make the chlorine a measure of the sewage contamination past and present, in much the same way as the proportion of total combined nitrogen has been employed by others. It has the advantage over the latter, inasmuch as the chlorine is practically permanent whilst the nitrogen is removable in various ways; but, on the other hand, the chlorine is subject to great variations within a small area, according to local circumstances, more especially geological. The chlorine, moreover, only testifies to contamination by liquid, and not by solid, excrements, and in this respect also is of less general applicability than the total combined nitrogen.

Hardness.—This term is applied to those ingredients in water which react with soap and produce an insoluble 'curd,' the principal substances in question being the various salts of calcium and magnesium, which, entering into double decomposition with sodium stearate (hard soap) or potassium stearate (soft soap), give rise to calcium and magnesium stearates, both of which are insoluble bodies, and soluble salts of sodium or potassium. On this account the salts of calcium and magnesium are manifestly detrimental to the fitness of the water for washing. As regards the influence of these salts upon the quality of drinking water, opinion is divided. Some consider the presence of a certain proportion of these salts desirable as furnishing the materials necessary for bone-formation; others contend that if present in more than a moderate proportion, they tend to

same calcareous concretions in the system, whilst, lastly, others regard their presence or absence as immaterial from a hygienic point of view. Further, by some authorities the sulphates and chlorides of calcium and magnesium (the so-called 'permanent hardness') are regarded as more objectionable than the bicarbonates or 'temporary hardness.' Again, there are many who view the presence of the salts of magnesium with more suspicion than those of calcium, and, indeed, magnesian waters are very generally credited with the power of causing phosphatic calculi, goitre, and cretinism. On this account it has sometimes happened that waters which were otherwise of most unimpeachable quality have been discarded in consequence of their containing a few parts per 100,000 of magnesia. All these views concerning the influence of calcium and magnesium salts are, however, based upon very unsatisfactory evidence. The Rivers Pollution Commissioners, in prosecuting their inquiry into this subject, found that 'where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is practically uninfluenced by the softness or hardness of the water supplied to the different towns, and the average rate of mortality in the different water divisions varies far less than the actual mortality in the different towns of the same division. They were of opinion that, whilst waters of excessive hardness may be productive of calculus and perhaps other diseases, soft and hard water, if equally free from deleterious organic substances, are equally wholesome.' The question of magnesia in drinking water has been discussed by the writer ('What is the Importance of Magnesia in Drinking Water,' P. F. Frankland, Transactions of the Internat. Congress of Hygiene and Demogr. London, 1891), from whose inquiry it appears that whilst the amount of magnesia in the water supplied to most large towns is very small—generally not more than 1-2 parts of MgO per 100,000—it is much larger than is generally supposed in the well-water consumed by such a large portion of the population. Thus in the case of fifty brewery waters from all parts of the kingdom, the average amount of magnesia (MgO) was 3.41 parts per 100,000. It must also be remembered that the geological formation richest in magnesia (the magnesian limestone) is only very slightly represented in this country, so that the proportions of magnesia met with in the dolomitic districts of the Continent must be much larger.

Until, therefore, a far more searching inquiry than hitherto has been made into the alleged effect of such waters upon health, it would appear undesirable that any importance should be attributed to such proportions of magnesia as the above in drinking waters which are otherwise of unimpeachable purity.

The effect of Clark's process on magnesian waters is noteworthy. As a general rule, the proportion of magnesia removed by the treatment with lime is small—much smaller than that of the lime removed; but it is particularly worthy of notice that in cases where caustic soda was used in conjunction with lime, as is frequently done in the softening of water for industrial purposes, the magnesia may be removed in a greater proportion than the lime,

and as a matter of fact magnesium hydroxide is less soluble even than calcium carbonate.

The hardness of water not unfrequently throws light upon its previous history, for the food of both man and animals is of necessity rich in lime, and nearly the whole of this is in adult life again found in the liquid and solid excreta; hence water obtained from soil which has been much polluted with animal matters always exhibits a large amount of permanent hardness.

PURIFICATION OF DRINKING WATER.

Inasmuch as the impurities are either suspended or dissolved, mineral or organic, and the organic either animate or inanimate, it follows that the subject of purification may be considered from different points of view, according to the particular class of impurities the removal of which is under discussion. Until recently all the more important processes of drinking water purification were filtration processes, those depending upon precipitation being more especially of importance in connection with water for industrial purposes (see p. 391). Now, however, methods of more or less sterilising water by means of hypochlorites, ozone, or ultra-violet light are sometimes being resorted to (see p. 417).

Purification of drinking water on large scale.—

All surface water is liable to turbidity, and in times of rain and flood the amount of suspended matter may become excessive. It is, therefore, desirable that all surface water, even that from upland sources, should be submitted to purification before distribution for domestic purposes. The purification of surface water is best initiated by permitting the water to remain at rest in storage reservoirs for some days or even weeks, the greater part of the suspended matter thus becoming precipitated, and some destruction even of the dissolved organic matter also taking place. During storage most important biological changes also take place (see later). The process of filtration resorted to on the large scale is almost invariably that through sand of different degrees of coarseness. This method was inaugurated by Simpson, the engineer to the Chelsea Company in 1829, and has since been adopted in an ever-increasing number of places all over the world. The filter beds, as usually constructed, are 10-16 ft. in depth, often upwards of an acre in area, made water-tight with masonry, concrete, or puddled-clay walls. On the bottom are collecting drains, upon which is placed a layer of broken stone about 6 ins. in thickness, following upon which are layers of coarse gravel, fine gravel, and uppermost a stratum of fine sand, 1-4 ft. in thickness. The water is kept at a depth of 1-4 ft. above the surface of the fine sand, the rate of filtration varying in different works. For construction and cost of filtration plant, see Donald Chisholm, *Modern Methods of Water Purification*, London, 1911, 125. The greater part of the suspended impurities is retained in the downward passage of the water by the first few inches of fine sand, and sooner or later, sometimes in the course of a few weeks, causes the clogging of the filter. When the rate of filtration is too much retarded for practical purposes, the

surface of the sand is removed, after which the filtration can be continued until the filter is again choked, when the surface is again scraped off, the process being repeated until the stratum of sand becomes too thin to be efficient, after which the original thickness of the sand-layer is restored by means of washed sand. The sand scraped off is generally thoroughly washed, allowed to dry, and then used again. The particulars for the several sections of the Metropolitan supply, shown below, will serve to illustrate the method of working.

Besides the filter beds just described, some of the works drawing from the Thames are now using an auxiliary process of filtration through the natural gravel beds which form the banks of the Thames at Hampton. These gravel beds are at all times full of water, which forms, as it were, an underground river, and underground pipes are laid in this gravel and connected with a pumping well in order to utilise this water, which is always clear and bright in consequence of the natural filtration which it has undergone. In order to increase the supply of this underground water the gravel bed is flooded with water directly from the Thames, for which purpose a second series of perforated pipes are laid parallel to the first and placed at a distance of about 30 yards from them. This second series of pipes is placed in direct communication with the Thames, but at the point of ingress is

placed a small vertical sand filter to arrest the coarser impurities.

Such sand filters, although very efficient in removing the suspended matter, have comparatively little action upon that which is dissolved. Thus the following figures exhibit the composition of the York water supply, before and after filtration through sand:—

(Results of Analysis expressed in parts per 100,000.)

	Before filtration	After filtration
Total solid matters	28.40	26.20
Organic carbon	0.123	0.119
Organic nitrogen	0.023	0.022
Ammonia	0	0
Nitrogen as nitrates and nitrites	0.077	0.089
Chlorine	1.6	1.6
Temporary hardness	11.5	10.9
Permanent hardness	7.1	7.1
Total hardness	18.6	18.0
Micro-organisms (colonies yielded by 1 c.c. of water on cultivation with gela- tin-peptone)	31,200	122

It was formerly supposed that such sand filtration could have little or no effect in removing the micro-organisms present in water, as the interstitial spaces between the grains of sand are so large in comparison with the minute dimensions of the microbes. It was first shown

METROPOLITAN WATER SUPPLY, JANUARY, 1911.

District works	Number of days' storage	Filtering area per million gallons of the average daily supply of 1910	Thickness of sand on filters		Average rate of filtration per square foot per hour
			Maximum	Minimum	
Eastern	52.5	acres 0.676	ft. ins. 2 6	ft. ins. 1 6	gallons 1.37
New River	10.7	0.590	2 3	1 7	1.84
Southern, Lambeth Works	35.7	0.986	3 0	2 6	2.13
„ Southwark „			3 0	2 3	1.05
Western, Chelsea Works			4 3	3 3	1.17
„ Grand Junction Works	11.5	1.007	3 0	2 3	1.43
„ West Middlesex Works			2 9	2 6	0.82 Hampton 0.70 Kew Bridge 1.17

Monthly Reports by Metropolitan Water Examiner to Local Government Board.

by Koch in Germany, and by the writer in this country, that nearly all the microbes in water may be removed by the sand-filters (Koch, Bericht der Deputat. f. die Verwaltung der Canalisationenwerke, Berlin, 1883; P. F. Frankland, Proc. Roy. Soc. 1885; Proc. Inst. Civ. Engineers, 1885-6; J. Soc. Chem. Ind. 1885, 1887), and this result has been since confirmed by many other investigators.

It was, in fact, supposed by Koch and his pupils that the sand filtration really removed all the microbes originally present in the water, and that those always found in the filtered water had gained access subsequent to filtration. The writer had, however, from the first shown that

London water supply there was an obvious relationship between the numbers of microbes in the unfiltered and filtered waters respectively necessitating the conclusion, therefore, that the sand filters can only be credited with removing a portion and not the whole of the micro-organisms present. This is sufficiently conspicuous from the tables on next page, which record some of the writer's results obtained with the London water supply during the year 1886, and reported to the Local Government Board (P. F. Frankland J. Soc. Chem. Ind. 1886). The unfiltered Thames water was in every case collected near the intakes of the several water companies at Hampton, and the filtered water from the mains of the Chelsea, West Middlesex, Southwark

TABLE I. 1886.

Total number of Colonies obtained by cultivation of one cubic centimetre of water.

— *	Description of water					
	Thames unfiltered	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	45,400	159	180	2270	4894	2587
February	15,800	305	80	284	208	265
March	11,415	299	175	1562	379	287
April	12,250	94	47	77	115	209
May	4,800	59	19	29	51	136
June	8,300	60	145	94	17	129
July	3,000	59	45	380	14	155
August	6,100	303	25	60	12	1415
September	8,400	87	27	49	17	59
October	8,600	34	22	61	77	45
November	56,000	65	47	321	80	108
December	63,000	222	2000	1100	1700	305
Average	20,255	146	234	524	630	475

TABLE II. 1886.

Percentage reduction in the number of developable micro-organisms present in the river waters before delivery by the companies.

—	Description of water				
	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	99.7	99.6	95.0	80.2	94.3
February	98.1	99.5	98.2	98.7	98.3
March	97.4	98.5	86.3	96.7	97.5
April	99.2	99.6	99.4	99.1	98.3
May	98.8	99.0	99.4	98.9	97.2
June	99.3	98.3	98.9	99.8	98.5
July	98.0	98.5	87.3	99.5	94.8
August	95.0	99.6	99.0	99.8	76.8
September	99.0	99.7	99.4	99.8	99.3
October	99.6	99.7	99.3	99.1	99.5
November	99.9	99.9	99.4	99.9	99.8
December	99.7	96.8	98.3	97.3	99.5
Average percentage reduction	98.6	99.1	96.7	98.2	96.2

Grand Junction, and Lambeth Companies respectively.

C. Fraenkel and Piefke (Zeitsch. Hygiene, 8, 1890, 1-40) subsequently demonstrated by direct experiment that particular species of bacteria purposely introduced into the unfiltered, were still present, although in greatly diminished numbers, in the filtered water.

The wonderful efficiency of these sand filters in removing microbes was at first very difficult to account for, but it is now recognised to depend upon the impervious nature of the slimy deposit which forms upon the surface of the sand, and until such a coating has been established the filter has but little effect in removing micro-organisms (Piefke, Aphorismen über Wasser-versorgung, Zeitsch. Hygiene, 7, 1889, 115-179). This slimy deposit consists not only of silt, mud, and colloidal matter, but also of a multitude of living forms—diatoms, green and blue algae, innumerable bacteria, fungi, and protozoa. Many of these forms actually feed on

bacteria. The rate at which filtration is carried on is also a most important factor, the more rapid the rate the less efficient being the purification (P. F. Frankland, Proc. Inst. Civ. Engineers, 1885-6). Although the removal of bacteria is not attributable to the sand particles as such, there is abundant evidence that the finer the sand and the greater its depth the more efficient is the filtration. This is doubtless due to a better support being given to the filtering skin, and to the finer and thicker layer of sand regulating the passage of water through the medium, whilst the water is also brought into more intimate and prolonged contact with the colloidal matter with which the sand of a matured filter is clothed. The statistics of the London water-works show that the cost of filtration as carried out by them averages about 0.6d. per 1000 gallons.

In countries liable to extreme cold—indeed, even in cold winters in this country—the process of sand filtration offers great difficulties, in consequence of the freezing of the filters; and this

has, in Berlin, been guarded against by the construction of a number of covered filter-beds. In the United States, where the same difficulty exists, the Hyatt system of filtration has been employed on a considerable scale. In this the water is first treated with a minute quantity of alum (about $\frac{1}{2}$ grain per gallon), after which it passes through a steel filtering chamber, consisting of a vertical cylinder the diameter of which is nearly twice its height. This cylinder is divided by a horizontal diaphragm, capable of withstanding the hydrostatic pressure necessary for rapid filtration. The lower half contains the filtering material, composed of 2 parts coke and 3 parts sand. The upper part of the cylinder is used for washing the filtering material, which at regular intervals is transferred into it in a state of violent agitation by hydraulic currents, the impurities flowing away through pipes situated near the top of the cylinder. In the process of filtration the water is admitted through pipes to the upper part of the lower section of the cylinder, and it is drawn off through perforated cups, which permit the water, but not the sand, to pass. It is claimed that the efficiency of the system depends more upon the successful precipitation and entanglement of germ life by the coagulant alumina than upon any special merits of the filter (Potable Water, Floyd Davis, Iowa, U.S. 1891). The cost of maintenance is said to be only one-fifth of that entailed by filter beds.

In recent years the use of mechanical filters has been gaining ground in Great Britain also, the Jewell, Bell, and Candy filters being those most commonly employed (see *Modern Methods of Water Purification*, Don and Chisholm, London, 1911; see also *Bacteriology of water*, below). The Puech-Chabal system consists in submitting the water to successive processes of filtration, sometimes as many as six stages, beginning with coarser grades of gravel and ending with fine sand, being employed. It is specially suitable for very turbid waters, as the life of the fine sand filter is greatly prolonged. It has been used at Magdeburg and other places (see Don and Chisholm, *l.c.*).

Of other methods of drinking-water purification on the large scale the only one that need be mentioned is Anderson's. The method consists in passing the water slowly through revolving iron cylinders about two-thirds filled with iron borings. A small quantity of the iron continuously passes into solution, so that the water becomes impregnated with ferrous iron, which subsequently, when the water flows into a settling tank, is converted into the ferric state with precipitation, a large proportion of the organic matter in solution being removed in the process, whilst a very considerable diminution in the number of vital germs is also effected. After undergoing oxidation in the settling tank, the water is finally filtered through sand before distribution. It takes $3\frac{1}{2}$ mins. for the water to pass through the rotating cylinder, the entire process occupying about 6 hours (Anderson *Proc. Inst. Civ. Engineers*; *Engineering*, 39, 525). This process has been used on a large scale at Antwerp and Paris.

Purification of drinking water on the small scale.—The filtration of water on the small scale was already known to the ancients. Thus Pliny mentions a method in which water was clarified

passage through wool. An immense number of different materials have been employed during recent years, but space will only permit of the brief consideration of a few of the more important ones.

Animal charcoal is employed in a number of common household filters, and from the invaluable services which it yields in sugar-refining it was anticipated that it would be highly efficient as a water filter. Unlike sand, it not only acts upon the suspended matters, but also removes a considerable proportion of the dissolved organic matter, and even some of the temporary hardness. Unfortunately, however, its action is very transient, and it generally soon becomes the seat of numerous organic growths, which are favoured by the calcium phosphate it contains, and the filtered water is then often rendered more impure than the unfiltered.

Vegetable charcoal has but little effect on the dissolved organic matters, although if in a sufficiently fine state of division it is an excellent strainer for suspended impurities (see table below).

Bischof's spongy iron, obtained either by reduction of hematite or of roasted pyrites, has a remarkable power of removing dissolved organic matters, as well as temporary hardness and nitrates, and this power is far more permanent than that of animal charcoal. It was for some time also employed on the large scale, in conjunction with sand, at the Antwerp Waterworks. The effect of filtration through animal charcoal and spongy iron respectively is exhibited in the table below.

Since the recent great advances in bacteriological science, it has become evident that the removal of micro-organisms from drinking water is a matter of much greater importance than the removal of organic matter, and hence it is in respect of this property that the value of filters is now generally estimated. The writer has shown (*The Removal of Micro-Organisms from Water*, P. F. Frankland, *Proc. Roy. Soc.* 1885) that several substances—such as coke, wood-charcoal, spongy iron, &c.—in a sufficiently fine state of division are capable of entirely removing all microbes in water passed through a stratum of a few inches of these materials. This power, which is quite independent of any chemical action (thus in the case of coke and wood-charcoal there is little or no removal of dissolved organic matter), is, however, not maintained unless the materials are frequently renewed; and in the case of animal charcoal which has been in use for a short time (one month) the number of microbes was found to be far greater in the filtered than in the unfiltered water. The most conspicuous instance of biological, as opposed to chemical, filtration is furnished by Chamberland's unglazed porcelain filter, which entirely removes microbes, but has no chemical action whatever (see table on next page).

A number of household filters in actual use have been examined with regard to their power of removing microbes by Plagge (*Public Health Section of Germ. Assoc. of Naturalists and Physicians*, 1886), who divides them into six classes, according to the materials used: (1) carbon filters, (2) stone and sand filters, (3) spongy-iron filters, (4) paper filters, of various kinds, (5) porous earthenware filters (Chamberland), (6) asbestos filters (Dr. H. H. H. H.).

and Schirmer). The carbon filters were found not only to admit of the free transmission of microbes, but in some cases the numbers in the filtrate greatly exceeded those in the unfiltered water. Thus in one case 68 colonies were obtained from 1 c.c. of the unfiltered, and 12,000 from 1 c.c. of the filtered water. The stone and sand filters were all found to be worthless. The spongy-iron filter yielded the following results: unfiltered water, 38,000 colonies from 1 c.c.; filtered, 18,000–24,000 colonies from 1 c.c. The paper filters all yielded very unsatisfactory results; the earthenware and asbestos filters, on the other hand, gave in nearly every instance a filtrate practically free from microbes. (For par-

ticulars concerning the sterilising power of the Chamberland filter, see also Miquel, *Analyses Bactériologiques des Eaux*, Paris, 1891.) The principal drawback to these porous earthenware filters is the rapid diminution in the rate of filtration which they exhibit. More satisfactory in this respect are the Berkefeld filters, similarly constructed of burnt infusorial earth (Nordt-meyer, *Zeitsch. Hygiene*, 1891, 10, 145; Bitter, *ibid.* 155). Neither the Chamberland nor Berkefeld filters permanently yield sterile water, some of the bacteria in the unfiltered water sooner or later growing through the pores. It is, however, doubtful whether any of the ordinary pathogenic bacteria would do this, as none of them are

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			No. of developable micro-organisms in 1 c.c. of water
								Temporary	Permanent	Total	
London water, unfiltered ¹	24.60	0.129	0.023	0	0.188	0.211	1.0	—	—	19.4	—
Ditto, after filtration through fresh animal charcoal ¹	19.40	0.029	0.007	0.013	0.194	0.212	1.0	—	—	15.2	—
London water, unfiltered ¹	25.94	0.164	0.030	0.002	0.062	0.094	1.9	—	—	19.7	—
Ditto, after filtration through animal charcoal in use 11 months ¹	25.10	0.010	0.002	0.002	0.125	0.129	1.0	—	—	19.1	—
London water, unfiltered ¹	25.28	0.120	0.013	0	0.166	0.179	1.7	14.5	6.7	21.2	—
Ditto, after filtration through fresh spongy iron ¹	13.70	0.025	0.004	0.002	0.031	0.037	1.7	7.4	4.6	12.0	—
London water, unfiltered ¹	24.10	0.188	0.034	0.001	0.120	0.155	1.95	11.8	7.3	19.1	—
Ditto, after filtration through spongy iron in use 8 months ¹	14.84	0.089	0.020	0.001	0	0.021	1.95	5.3	4.3	9.6	—
Water, before filtration ²	24.80	0.144	0.050	0	0.190	0.240	1.9	11.3	5.6	16.9	26,000
Ditto, after filtration through fine coke ²	25.00	0.107	0.038	0	0.202	0.240	1.9	11.3	5.6	16.9	0
Ditto, after filtration through fine wood charcoal ²	24.68	0.000	0.024	0	0.221	0.245	1.9	12.5	4.6	17.1	0
London water, before filtration ³	33.70	0.282	0.028	0	0.288	0.316	1.9	15.7	4.9	20.6	54
Ditto, after filtration through Chamberland filter ³	30.04	0.284	0.027	0	0.289	0.316	1.9	14.4	5.3	19.7	0

¹ Riv. Commis. 6th Rep.

² P. F. Frankland, *J. Soc. Chem. Ind.* 1885.

³ P. F. Frankland, *Proc. Roy. Soc.*, 1885, 390.

known actually to multiply extensively in ordinary drinking water (Kübler, *Zeitsch. Hygiene*, 1890, 10, 48).

W. E. Hall has described a simple apparatus for the extraction of micro-organisms from samples of water. The sample is collected in a small straining jar through which any quantity of water can be passed, and the organisms retained in a quantity of water convenient for carriage.

From this concentrated sample the organisms can be extracted by passing it through a filter paper about 1½ in. diameter placed over a small funnel attached to a vessel from which the air is extracted by means of an exhaustor consisting of a modified form of filter pump.

The organisms are finally washed off the filter paper by means of a wash bottle with about 2 c.c. of water in which the organisms can readily be examined in a stage trough or placed in small quantities on a compressor slide (*J. Soc. Chem. Ind.* 1924, 43, 280).

Purification of drinking water by distillation.—This is, of course, the most effectual mode of freeing water from all its impurities. It is

resorted to, on a considerable scale, at sea, both for steam and sailing vessels. (For description of forms of apparatus in actual use v. Fischer, *Technologie d. Wassers*, Brunswick, 1880, 201–208.) The insipid taste of the distilled water can be removed either by aëration, or by filtration through animal charcoal or other porous substances. Distilled water is also employed to some extent for the manufacture of aerated waters and for artificial ice.

Purification of drinking water by boiling.—The purification consists, of course, only in the destruction of living organisms present in the water, but this is from an hygienic point of view of the greatest importance. In its action it is far more reliable than any process of filtration, and should be invariably resorted to in the case of waters which bear any suspicion of sewage contamination. The rapid taste of the boiled water may be removed by passage through a filter, which, however, should be exclusively employed for this purpose and not for filtering unboiled water. A convenient form of apparatus for sterilising large quantities of water—e.g. for hospitals, barracks, &c.—is described by

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Miquel (*Mannuel d'Analyse bactériologique des Eaux*, Paris, 1891, 1893). The more extensive use of boiled instead of filtered water is one of the chief sanitary desiderata of the day. Although absolute sterility cannot be *guaranteed* by a few minutes' ebullition, yet the reduction in the number of microbes by this simple process is so great that it may be safely regarded as ample for practical purposes. Thus Miquel and Wada (*ibid.* 185) found in the case of the Ourcq-canal water of Paris:—

Temperature.	Bacteria in 1 c.c.
14°C.	460,800
50° for 10 minutes	600
60°	(60)
70°	88.8
80°	62.4
90°	26.4
100°	0.5
100° for 20 minutes	0.0

WATER FOR INDUSTRIAL PURPOSES.

Of the numerous industrial uses to which water is put, the most general and important is the raising of steam. The composition of the water supplied to steam-boilers is a matter of great consequence, as the use of unsuitable water may cause the corrosion of boiler-plates and the formation of deposits, which not only occasion a serious loss of heat but may also lead to most disastrous explosions (*v.* **BOILER INCORUSTATIONS AND DEPOSITS**).

Water for other industrial purposes.—(1) For *brewing*, see art. **BREWING**. For use in bakeries, the water should be in all respects of the same degree of purity as is demanded for drinking purposes.

(2) For the *textile industries* the character of the water employed is often of great consequence. Thus in bleaching and dyeing the presence of iron and manganese, even in very small quantities, is highly deleterious, giving rise to iron and manganese stains on the bleached goods, and causing spots and modifications in the shades of dyed materials. Hard water, again, involves the use of larger quantities of alkali and soap in the several operations of boiling, scouring, and milling, and the insoluble lime-soap is left adhering to the fibre, often preventing the subsequent application of mordant or dye. In those operations, again, in which dyed fabrics are soaped, the lime-soap often injures the brilliancy of the colour, whilst in other cases the earthy soaps precipitated on the fibre act as mordants, and attract the colouring matters on those parts of the goods where it is not wished to fix them. In general, hard water has the effect of dulling many colours, and if due to bicarbonates retards, or even prevents, the dyeing of such colours as require an acid bath (e.g. cochineal scarlet). In some cases hard water containing bicarbonates wastes the mordants by precipitation in the bath instead of on the fibre, whilst it is sometimes actually beneficial for the washing of goods which have been mordanted with basic mordants. Such water is unsuitable for the solution of many coal-tar colours—e.g. methyl violet—a portion of the latter being lost as a tarry precipitate, whilst the goods are often spotted. For dyeing with some colours—e.g. alizarin and logwood—the

presence of a certain amount of lime is almost indispensable; a pure water to which a known quantity of lime-salt has been added is, however, preferable to a naturally hard water, especially if the latter is of variable composition. Water containing alkaline carbonates is sometimes advantageous, e.g. in wool-scouring, and in those dyeing operations in which the addition of sodium carbonate is prescribed; but in mordanting, in the dyeing with many colours, and in the washing of dyed goods, it is often very prejudicial; in these cases it should be neutralised with sulphuric or acetic acid. Acid waters are generally highly injurious, and should be neutralised with sodium carbonate. Sulphuretted hydrogen in water is also very objectionable in many operations of dyeing, more especially in mordanting with metallic salts (*Hummel, Dyeing of Textile Fabrics*). For the manufacture of *paper*, water containing iron is highly objectionable, giving rise to stains, whilst the presence of hardness is objectionable in causing the decomposition of the rosin-soap.

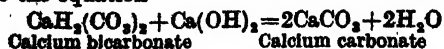
(3) For *tanning*, pure water is also a desideratum. Water much contaminated with organic matter causes injury to the surface of the leather, and sometimes a corrosion from the flesh-side of the skin. Water containing carbonic acid, or the bicarbonates, or calcium and magnesium sulphates, causes the hides to swell, whilst the chlorides prevent the swelling, and hence sea-water cannot be employed for the purpose. Hard water occasions a less perfect utilisation of the tanning materials, and an excess of chlorides retards the tanning process and causes the leather to attract moisture; the presence of iron is not so objectionable as is commonly supposed (*Fischer, Das Wasser*, 49–51).

(4) In *sugar-refining* the sulphates and alkaline carbonates are more productive of molasses than the chlorides, whilst nitrates are specially objectionable, as they prevent the crystallisation of six times their weight of sugar (*Fischer, Technologie d. Wassers*, p. 286).

Purification of water for industrial purposes.

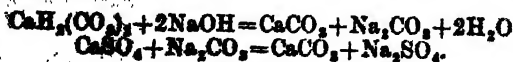
As already pointed out, some substances, although unobjectionable in drinking water, operate prejudicially when the water is employed for many industrial purposes, and numerous methods have been devised for removing these impurities or for counteracting their effects. But few methods of purification have found favour in actual practice, and to these alone will any attention be given here. The processes which have for their object the removal of matters in suspension and organic substances have been already described under *Purification of drinking water* (*v.* p. 386), whilst the processes intended for the improvement of industrial water supplies are chiefly directed to the removal of lime and magnesia salts in solution, which, as has been shown above, interferes with the success of so many industrial operations. This removal of lime and magnesia salts is frequently spoken of as 'water-softening,' in consequence of the water after such treatment requiring less soap when used for purposes.

Purification with lime (Clark's process).—This method of purification was first proposed by Clark, of Aberdeen, in 1841, and consists in the decomposition of calcium bicarbonate or 'temporary hardness' of water by the addition of a suitable quantity of slaked lime, according to the equation



Thus both the lime in solution as bicarbonate as well as that added in the form of hydroxide are precipitated as normal carbonate, which is almost insoluble in water. The calcium hydroxide is sometimes added in the form of milk of lime, sometimes in that of clear lime-water, but the latter is far preferable, as the quantity added can be more easily controlled and an excess avoided. The necessary quantity of calcium hydroxide is most easily ascertained by adding such an amount that, after thorough mixing, a small quantity of the water taken out yields a yellow or brown colour with a solution of silver nitrate, more water is then added, until, on similarly testing, no coloration with the silver nitrate is obtained. This test should invariably be resorted to even in the case of such waters as are of very constant composition, and which, therefore, admit of the lime being proportioned by experience, as otherwise an excess or deficiency of lime is nearly sure to result. In its original form the Clark process is carried out in large tanks in which the water can remain at perfect rest for about 16 hours, although by the use of a floating exit-pipe the clear surface water can often be drawn off after 2 or 3 hours, and before the whole of the precipitate has reached the bottom. This method has been most successfully employed on a large scale at the Colne Valley Waterworks, near Bushey, at Canterbury, Caterham, and many other places on a small scale. The 'temporary hardness' only is, of course, removed, and even this not completely, as under the most favourable circumstances a small proportion of calcium carbonate remains in solution, whilst in the case of waters containing magnesium bicarbonate the removal of the latter is generally far less complete. In addition to these bicarbonates, the salts of iron and much organic matter are also removed.

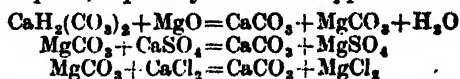
In order to obviate the large amount of storage capacity required for Clark's process, several modifications have been introduced, in which the precipitate formed by the treatment with lime is either removed by filtration or made to subside rapidly by artificial means. The most notable of these improved processes are the so-called 'Porter-Clark,' in which the precipitate is removed with a filter-press, and Gaillet and Huet's process, in which subsidence is promoted by causing the water to take a circuitous zig-zag and upward path after the addition of the lime. In this latter process both lime and caustic soda are frequently employed in conjunction as the softening agents; in this manner both 'temporary' and 'permanent' hardness can be, to a great extent, removed, thus:—



does not permit the description of a number of other water-softening apparatuses

which are now on the market, and which only differ from each other in the special mechanical devices for supplying the chemicals (milk of lime, lime water, sodium carbonate, or caustic soda, as the case may be) and for removing the deposit. The Arobbutt-Deeley process, however, possesses certain features of interest. In this the clarification of the treated water is accelerated by stirring it up with the sludge of calcium carbonate obtained in previous precipitations, this being effected by blowing in compressed air through perforated pipes. The subsequent sedimentation takes place very rapidly, and the clear water is drawn off from the surface by means of a floating arm. Further, the danger of subsequent deposition of calcium carbonate in the service pipes, which often occurs when an insufficient time is allowed for sedimentation, is avoided by injecting carbon dioxide (obtained from a coke-stove, the gas being scrubbed with limestone to remove sulphur compounds) into the clarified water as it is drawn from settling tank.

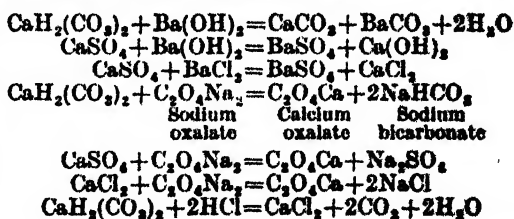
Magnesia has also been employed to a limited extent for softening instead of lime. Under these circumstances the following reactions may take place, especially if heat is applied:—



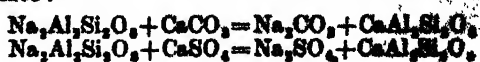
(Fischer, Chem. Technol. d. Wassers, Brunswick, 1880, 264).

The formation of magnesium chloride is obviously disadvantageous for boiler purposes.

A number of other processes of chemical purification have from time to time been suggested, but none of them have met with any great success. Thus attempts have been made to utilise the following reactions:



In the *Permutite* process, devised by Dr. Gans of Berlin, the water is softened by filtration through artificial zeolite (a hydrated silicate of alumina and soda) to which the name of *Permutite* has been given. The latter is made by fusing together silica or quartz, alumina or china-clay, and sodium carbonate. The fused mass is extracted with water, a crystalline body ($\text{SiO}_2 = 46$, $\text{Al}_2\text{O}_3 = 22$, $\text{Na}_2\text{O} = 13.6$, $\text{H}_2\text{O} = 18.4$ p.c.) being obtained. When waters containing calcium or magnesium salts are filtered through this material, the following reactions take place:—



It is claimed for this process that the whole of the hardness is removed and that the calcium or magnesium zeolite formed can be reconverted into the original permutite or sodium zeolite treatment with a strong

Gans uses a mang

WATER.

alkaline, and a higher oxide of manganese) for the removal of iron and manganese in water. This material can be regenerated by treatment with a solution of potassium or calcium permanganate. The manganese-permutite can also be employed for the sterilisation of water; the water is treated with permanganate in sufficient concentration to destroy bacteria, and, on subsequent filtration through manganese-permutite, the whole of the manganese is said to be retained by the filter. Calcium-permutite has been used for removing potash from molasses, lime passing into solution; the lime may be replaced by soda by passing through sodium-permutite. The plant and materials for the Permutite process can be obtained from 'Water Softeners, Ltd.,' Kingsway, London, W.C.

For the effect of softening processes on the bacteria in water, *v. p.* 417.

The action of water on lead, zinc, copper, and aluminium.—The action of water on these metals, and especially on lead, is of great importance in connection with the distribution and storage of water. The Romans employed leaden pipes, and Vitruvius and Galen were aware that some waters were thereby rendered deleterious. On the other hand, certain waters have so little action on lead that pipes of this material have been in use for upwards of 200 years without showing any trace of corrosion (Fischer, *Technologie d. Wassers*, 317). As a general rule, hard waters, and more especially those containing bicarbonates, do not act on lead; the greater number of active waters are soft, and generally entirely destitute of bicarbonates. The activity has been ascribed by different authorities to the presence or absence of a great variety of ingredients in the water—*e.g.* the presence of dissolved air (Yorke), ammonium nitrite (Medlock), ammonium carbonate (Böttcher). Some have contended that organic matters diminish the activity (Horsford), others that they increase it (Hofmann, Graham, Miller, and Noad). The latter authorities were of opinion also that the presence of dissolved oxygen and the absence of more than 3 vols. of carbon dioxide in 100 vols. of water are amongst the conditions necessary for the attack upon lead. It has also been contended that a minute proportion of calcium phosphate prevents a soft water from attacking lead (*Riv. Pollut. Commis.* 6th Rep. 224), whilst according to others, again, the protecting ingredient is silica (Crookes, Odling, and Tidy, *Report on the Action of Water on Lead*, London, 1886). In many cases the activity of the water is due to the presence of organic acids (Allen), this being doubtless a fruitful cause of moorland waters acting on lead. The activity of many waters is confined to new untarnished lead, whilst others continue to act, sometimes with increased vigour, on the old and tarnished metal (P. F. Frankland, *The Action of Water on Lead*, J. Soc. Chem. Ind. 1889, 241).

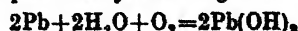
Numerous expedients have been resorted to in order to destroy this activity of some soft waters. When acidity is the presumable cause the most obvious remedy is the filtration of the water through finely-divided limestone; in practice, however, this is found to be only of temporary service, as the surfaces of the limestone become coated with a film which prevents their

being further acted on by the water. It has been found more effective to mix the water continuously with a milk of finely-divided calcium carbonate, and allowing this to subside before the water is distributed.

It is now generally admitted that the action of water on lead is of two different kinds. Of these the most obvious is that due to the acidity¹ of some waters; such acidity may be due to organic or even mineral acids, and can be determined by titration with appropriate indicators. Such acid waters have, in general, a continuous action on lead. The acidity can, of course, be neutralised by the addition of lime, finely-divided calcium carbonate, or most effectively by sodium carbonate. It was, however, shown many years ago by the writer that such neutralisation does not necessarily entirely stop the action of the water on lead, and that this is often only secured by adding a considerable excess of sodium carbonate. Similarly there are many natural waters, which, although slightly alkaline with small proportions of calcium bicarbonate, nevertheless act on lead. Such action of neutral or even slightly alkaline waters is now usually termed '*erosive*' as distinguished from the '*plumbosolvent*' action of acid waters. These remarkable phenomena have only received a satisfactory explanation since the recent advances in physical chemistry have illuminated the subject of chemical equilibrium.

This matter is very ably dealt with in an important paper by Paul, Ohlmüller, Heise, and Auerbach (*Arbeiten a. d. kais. Gesundheitsamte*, 1906, 23: *Untersuchung über die Beschaffenheit des zur Versorgung der Haupt- und Residenzstadt Dessau benutzten Wassers, insbesondere über dessen Bleilösungsfähigkeit*). The conclusions arrived at by these authors are:—

1. *Dissolved oxygen* is necessary for the solution of metallic lead in pure water. Experiments made with distilled water, which had been saturated with air freed from carbon dioxide, showed that nearly the whole of the oxygen (amounting to about 9 mgms. per 1 litre) was taken up presumably according to the equation:



The water, which was at 18°, took up about 115 mgms. of lead per 1 litre. By increasing the proportion of oxygen in the air used for saturating the water the amount of lead taken up was at first also increased (up to about 140 mgms. Pb per 1 litre), but this was followed by a sudden drop to an amount which remained practically constant (about 108 mgms. per 1 litre for about 14.5 mgms. O₂ dissolved in 1 litre water). This sudden drop is referred to the appearance of a precipitate (*solid phase*) preventing further supersaturation of the water with lead hydroxide. (The authors did not determine the exact composition of the solid phase, which may have been Pb(OH)₂, or more probably one of its anhydrides.)

2. *Free carbonic acid* diminishes the plumbosolvent effect of the simultaneously present dissolved oxygen. Thus, in an experiment with distilled water made to contain about 8 mgms. O₂ and 40 mgms. CO₂ in 1 litre, the amount of lead

¹ See a paper on 'The Acidity and Alkalinity of Natural Waters,' by James Walker and S. A. Kay (*J. Soc. Chem. Ind.* 1912, 31, 1073).

taken up was about 11 mgms. per 1 litre, or about $\frac{1}{10}$ of that dissolved when the same proportion of dissolved oxygen was present in the absence of carbonic acid. This diminished plumbosolvency is, of course, attributable to the formation of a more insoluble solid phase, viz. either PbCO_3 , or more probably some basic carbonate such as $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$.

3. *Sodium bicarbonate* in the absence of any appreciable quantity of free carbonic acid greatly reduces the plumbosolvency of water; thus in similar experiments, in which the same proportion (about 9 mgms. O_2 per 1 litre) of dissolved oxygen was retained, but along with 35 mgms. of NaHCO_3 per litre, the amount of lead taken up was only 0.6 mgm. per litre of water. This, again, is attributable to the diminished solubility of the solid phase in the solution of the sodium bicarbonate. The amount of lead taken up by the water is limited by the *solubility product*; thus a saturated solution of lead carbonate will contain a small concentration of PbCO_3 molecules, together with $\text{Pb}^{++} + \text{CO}_3^{--}$ ions, of which only the PbCO_3 -molecules are in direct equilibrium with the solid phase (precipitated lead carbonate). The concentration of the PbCO_3 molecules will always remain constant as long as there is any of the solid phase present, but this concentration is very small. The concentration of the ions, on the other hand, is determined by the dissociation equilibrium. Thus, representing the molecular concentrations of the respective bodies by the formulæ enclosed in brackets, we have—

$$[\text{Pb}^{++}] \times [\text{CO}_3^{--}] = k \times [\text{PbCO}_3]$$

in which k is a constant. But in saturated solutions, as already seen above, $[\text{PbCO}_3]$ is constant, therefore $k \times [\text{PbCO}_3]$ is also constant, and can be represented by S , which is termed the *solubility product*, thus—

$$[\text{Pb}^{++}] \times [\text{CO}_3^{--}] = S$$

$$\therefore [\text{Pb}^{++}] = \frac{S}{[\text{CO}_3^{--}]}$$

which obviously signifies that the concentration of the Pb^{++} -ions will be the smaller the greater the concentration of the CO_3^{--} -ions. (If the solid phase is a basic carbonate, then it can be shown that the concentration of the Pb^{++} -ions must be inversely proportional to the concentrations of the CO_3^{--} - and the OH^- -ions.)

In solutions of free carbonic acid the concentration of CO_3^{--} -ions is very small (because carbonic acid being a very weak acid is only very slightly dissociated into ions), whilst in solutions of NaHCO_3 the concentration of CO_3^{--} -ions is much greater, and, therefore, the concentration of the Pb^{++} -ions will be correspondingly diminished, or, in other words, a much smaller proportion of lead will pass into solution. (It should be mentioned that the phenomena may be complicated by the circumstance that the nature of the solid phase may be different according as the metallic lead is placed in contact with a solution of free carbonic acid or bicarbonate respectively.)

4. The simultaneous presence of free carbonic acid and sodium bicarbonate leads to the following considerations:—



further $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, whilst to a much less extent $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$. These dissociations are expressed by the equations

$$(1) [\text{H}^+] \times [\text{HCO}_3^-] = k_1 \times [\text{H}_2\text{CO}_3]$$

$$(2) [\text{H}^+] \times [\text{CO}_3^{--}] = k_2 \times [\text{HCO}_3^-]$$

in which the values

$$k_1 = 3.04 \times 10^{-7}$$

$$k_2 = 1.3 \times 10^{-11}$$

are known (J. Walker and W. Cormack, Chem. Soc. Trans. 1900, 77, 5; Bodländer, Zeitsch. physikal. Chem. 1900, 35, 23).

From equation (2)

$$[\text{CO}_3^{--}] = k_2 \times \frac{[\text{HCO}_3^-]}{[\text{H}^+]}$$

and combining this with equation (1) we have

$$[\text{CO}_3^{--}] = \frac{k_2}{k_1} \times \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3]}$$

but with PbCO_3 as solid phase we had

$$[\text{Pb}^{++}] = \frac{S}{[\text{CO}_3^{--}]}$$

which can, therefore, be written

$$\text{Pb}^{++} = \frac{S \times k_1}{k_2} \times \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]^2}$$

But, inasmuch as free carbonic acid is very little, and sodium bicarbonate very much dissociated, the value of $[\text{H}_2\text{CO}_3]$ may be taken as proportional to the molecular concentration of the free carbonic acid, and $[\text{HCO}_3^-]$ to that of the sodium bicarbonate, and thus the concentration of the Pb^{++} -ions will be directly proportional to that of the free carbonic acid, and inversely proportional to the square of that of the sodium bicarbonate.

This important theoretical deduction was experimentally verified by placing lead in contact with water containing 8.3 mgms. O_2 , 35.3 mgms. NaHCO_3 , and about 33 mgms. CO_2 per 1 litre, with the result that the amount of lead in solution was found to be about 1 mgm. per 1 litre, and thus slightly but distinctly greater than in the previous experiment in which there was no free carbonic acid present, and in which 0.6 mgm. Pb per 1 litre was taken up by the water.

In ordinary natural waters the phenomena are complicated by the simultaneous presence of other salts, especially chlorides and sulphates. Both PbCl_2 and PbSO_4 are considerably more soluble than the carbonate. On adding 71 mgms. Na_2SO_4 per 1 litre to the last artificial water mentioned above, it was found that the proportion of lead taken up was about tripled, being about 3 mgms. per litre. This increase must, of course, depend on the presence of PbSO_4 molecules in solution, and not on an increase in the concentration of the Pb^{++} -ions, which it was shown was already fixed by the concentrations of the carbonic acid and bicarbonate. Now by removing some of the free carbonic acid (e.g. by adding Na_2CO_3) the concentration of the Pb^{++} -ions will be diminished, and this will have the effect of also diminishing the amount of lead in solution due to the solubility of the PbSO_4 , for the amount of undissociated PbCO_3 is dependent on the concentration of the Pb^{++} -ions, and if the latter be, through any cause,

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diminished, the amount of undissociated PbSO_4 must be diminished also, with the result that the total amount of lead passing into solution will be less. This was experimentally verified by using the same artificial water as in the last-mentioned experiment, excepting that by the addition of Na_2CO_3 the free carbonic acid was reduced to about 9.5 mgms. CO_2 per litre, and the NaHCO_3 consequently raised to about 128 mgms. per litre, with the result that the lead taken up amounted to only 1.3 mgm. per litre of water.

Experience has also shown that some waters act powerfully on lead when the pipes are charged intermittently, whilst the action becomes very much diminished if they are kept under constant pressure. The effect of pressure on the activity ought, therefore, always to be specially determined (P. F. Frankland, *J. Soc. Chem. Ind.*

In investigating the action of water on lead, the water should either be put in contact with strips of the metal or placed in leaden pipes for a definite period of time, after which it should be removed and tested for lead both in solution and suspension, fresh portions of the water under examination are then placed in contact with the metal and again tested after a definite interval of time, this procedure being repeated a number of times. Thus it is often found that a water has a considerable initial action on the metal, but as the latter becomes coated with deposit, the action moderates and may practically cease altogether. Some waters, on the other hand, act continuously on the metal.

Some polluted waters have a very strong and continuous action on lead (Riv. Pollut. Commiss. 6th Rep. 226), and in such cases the obvious remedy is the abandonment of the source.

It is worthy of note that hot water generally acts much more violently on lead than cold, and further that the lead dissolved in water is entirely removed by passage through any of the numerous forms of animal charcoal filters.

As regards the quantity of lead in water from which danger to health is to be apprehended, it is now generally admitted that water containing anything above one-twentieth grain of lead per gallon, or 0.07 part per 100,000, may, by continued use, produce mischief.

Of the action of water on zinc but little is known beyond the fact that many waters do act on it, and that it is therefore not to be recommended for the construction of cisterns, &c., in which drinking water is to be stored. The solution of the zinc takes place with special facility if metallic iron is also in contact with it (Heaton, *Chem. News*, 49, 85; P. F. Frankland, *ibid.* 115; Stevenson, *ibid.* 107).

Copper appears to be continuously acted on by water, especially if simultaneously in contact with air, and hence should not be used in connection with drinking water.

The action of water and other liquids on aluminium is now a matter of some importance owing to its use for domestic and industrial purposes (see *An Investigation of Aluminium, with Special Reference to its Suitability for the Construction of Brewery Plant*, A. C. Chapman, *J. Inst. Brewing*, 1911). Although acted on by moist air the layer of oxide exerts a marked protection to further attack; alkalis and alkali

chlorides increase the tendency to corrosion. Chapman considers that it may be safely used for the construction of brewing plant, especially fermenting tuns and vessels intended for the treatment of chilled and filtered beers.

THE CHEMICAL ANALYSIS OF WATER.

As the qualitative analysis of the ingredients of water is of no practical importance, and involves no special methods, the quantitative examination will alone be considered here. In order that the analysis may be of any value, especially for sanitary purposes, it is of the greatest importance that the samples should have been collected with care.

Suspended matter.—The suspended matter, if considerable in amount, should be separately determined, but if only present in minute quantity it is advisable to regard it as part of the dissolved matter, in which case it is necessary that the sample should be well shaken before taking out each portion for analysis, so that the suspended particles may be uniformly distributed. If it is decided to determine the suspended matter separately, the sample should be well shaken, and 250 or 500 c.c. measured out and passed through a filter previously dried at 100° and weighed. The matter on the filter is washed with distilled water, and dried at 100° until of constant weight. Some analysts prefer to dry at 105° , 110° , or even 120° , but in all cases the temperature should be specified. The filter and its contents are then incinerated in a coil of platinum wire and dropped into a weighed platinum crucible, gently ignited until free from organic matter, and then treated with a few drops of a solution of ammonium carbonate, and dried at 150° . The loss in weight represents organic matter and water of hydration. It is sometimes of importance to determine the proportion of carbon to nitrogen in the organic part of the suspended matter. For this purpose some of the suspended matter is collected on an ignited plug of asbestos or glass wool, transferred to a small flask, and boiled with 20 c.c. of sulphurous acid and some distilled water free from ammonia and organic matter, and then further treated, as in the determination of organic carbon and nitrogen, by the combustion process (p. 402). If the suspended matter has been thus separately determined, the remainder of the analysis should be performed on the water, after filtration through Swedish paper, rejecting the first 250 c.c. which pass through; or if the suspended matter completely settles on standing the clear water may be siphoned off. The suspended matter may, of course, in exceptional cases also have to be submitted to a complete mineral analysis, or examined for some special ingredient.

An ingenious method of determining minute traces of suspended matter has been devised by Dibdin (*Analyst*, 1896, 21, 2). In this method the volume of the moist suspended matter is measured in a capillary tube.

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Total solids.—250 or 500 c.c. of the water are evaporated to dryness in a watch-dish on a water- or steam-bath,

supported on a glass or porcelain, but not on a metallic ring. The dish and residue are then dried until constant at 100°, 105°, 110°, 120°, or even at 180°. The residue may be further utilised for the determination of nitrates and nitrites by the mercury method (*v. infra*).

Ammonia.—A measured volume of the water (varying from 100–1000 c.c., according to the proportion of ammonia present) is distilled in a capacious flask or retort connected with a Liebig's condenser, about 1 grm. of recently ignited sodium carbonate having been previously added. It is essential that the whole apparatus should have been carefully freed from ammonia immediately before use, which can be done by distilling some water in the apparatus until the distillate gives no reaction with Nessler solution. The remainder of the water in the flask or retort is then thrown away, and the measured quantity of the sample under examination introduced along with the sodium carbonate. The distillation should be carried on briskly, and the distillate collected in colourless glass cylinders of 50 c.c. capacity. If less than 500 c.c. has been used, this volume should be made up with distilled water free from ammonia before distillation. If the quantity of water has been well chosen, the whole of the ammonia will be found in the first three cylinders of the distillate, and in most cases it will all be contained in the first. The quantity of ammonia in each cylinder is estimated by adding 1 c.c. of Nessler solution, and comparing the coloration obtained with that similarly produced by known quantities of a standard solution of ammonium chloride, added to 50 c.c. of distilled water free from ammonia. The Nessler reaction is so delicate that by its means 1 part of NH_3 in 100,000,000 parts of water can be easily detected. The colour produced by more than 10–15 c.c. of a solution of NH_4Cl (containing 0.00001 grm. NH_3 per litre) is too deep for accurate comparison, and should one of the cylinders require more than this the determination must be repeated on a smaller volume of water. This may be generally avoided, however, by adding the Nessler solution to the second and third cylinders of distillate before the first, and if it is found that the second cylinder gives a colour requiring more than 5 c.c. of the above solution of ammonium chloride for its imitation the first cylinder should be diluted, and an aliquot part taken for testing with the Nessler reagent.

The Nessler solution is prepared by dissolving 62.5 grms. of potassium iodide in 250 c.c. of distilled water; set aside 10 c.c. of this, and run into the remainder a cold saturated solution of mercuric chloride until a permanent precipitate is formed, then add the above 10 c.c. of potassium iodide, which will cause its solution, after which very carefully add more of the mercuric chloride until a slight precipitate remains on stirring. Now add 150 grms. of potassium hydroxide dissolved in distilled water, and dilute the whole to 1000 c.c. After settling, decant the clear liquid into a bottle for use.

As the 'albuminoid ammonia' is commonly determined in one operation with the 'free' ammonia, the method of estimating the former will now be described, instead of considering it under the methods for determining organic matter, where it more properly belongs.

'Albuminoid ammonia' process.—Whilst the determination of the free ammonia is being proceeded with as above, the solution of alkaline permanganate must be prepared for this process, as it is required immediately the free ammonia has passed over. The volume of the alkaline permanganate (for preparation *v. below*) taken must be at least one-tenth of the volume of the sample being distilled for ammonia, and it should not exceed that volume unless the water contains a very large amount of organic matter. The alkaline permanganate taken is then diluted with four times its volume of distilled water, and boiled in a flask during the whole of the time that the distillation for free ammonia is going on as above, and when the latter is finished it is added to the water remaining in the distilling flask or retort (the whole volume in this must now be not less than 500 c.c.), and distillation is then continued until the distillate is free from ammonia. The distillate is collected and Nesslerised, as in the determination of free ammonia above. The ammonia thus evolved by distillation with alkaline permanganate is generally recorded as 'albuminoid ammonia' (*v. 403*). The alkaline permanganate solution is prepared by dissolving 200 grms. of potassium hydroxide and 8 grms. of pure potassium permanganate in 1100 c.c. of distilled water, then boiling the solution rapidly until concentrated to about 1000 c.c.

Chlorine.—(a) *Mohr's method.* 50 or 100 c.c. of water are treated with a few drops of a solution of potassium chromate, and a standard solution of silver nitrate is then run in from a burette until the precipitate becomes of a faint but distinctly red colour. The water must be well agitated after each addition of the nitrate, the reaction depending upon the decomposition of the red silver chromate by dissolved chlorides with formation of silver chloride and soluble chromate. As soon as the last trace of chloride is precipitated as silver chloride, the red colour of the silver chromate makes its appearance. By using a solution of silver nitrate containing 2.3944 grms. per litre, the number of c.c. employed gives at once (if 50 c.c. of water have been taken) the parts of Cl per 100,000, whilst if 100 c.c. of water are taken the silver nitrate solution should be of double this strength.

Mohr's method cannot be employed if the water is acid, and if this is the case a given volume of the water should be boiled with an excess of pure calcium carbonate (free from chlorides), filtered, the filtrate made up to known volume, and the chlorine determined in a part of this. In the presence of reducing substances, much organic matter, sulphuretted hydrogen, and sulphites, the method is also inapplicable, and in such cases it is desirable to determine the chlorine gravimetrically, which should also be done if the proportion of chlorine is large.

(b) *Volhard's method.* 50 or 100 c.c. of the water are treated with an excess of decinormal silver nitrate, the mixture being well agitated so as to cause the silver chloride to settle in flakes; the latter is filtered off and washed, and then to the filtrate about ten drops of a cold saturated solution of iron-alum are added, and subsequently enough strong nitric acid (free from nitrous acid) to remove the colour of the ferric

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salt. Decinormal ammonium thiocyanate is then added from a burette, stirring well all the time, until the liquid acquires a light yellow-brown colour, which remains permanent on leaving the liquid at rest for about 10 mins. By deducting the number of c.c.'s of thiocyanate from that of the silver nitrate added, the remaining silver nitrate indicates the proportion of chlorine present in the water. The advantage of this method consists in its being applicable to acid liquids. The method depends upon there being no formation of red ferric thiocyanate until the whole of the silver in solution has been precipitated as thiocyanate (*Annalen*, 180, 24).

Nitrogen as nitrates and nitrites.—A number of different methods have been devised for the determination of oxidised nitrogen; there are, however, only a few which have been largely adopted in practice, and such alone will be described here.

(a) *Crum's method.* This depends on the decomposition which nitrates and nitrites undergo when dissolved in strong sulphuric acid on being shaken up with mercury, and which leads to the evolution of the whole of the nitrogen as nitric oxide, the volume of which is then determined. The residue obtained in the estimation of the total solids (see p. 395) may be conveniently used for this determination also. This residue in the platinum or glass dish is repeatedly treated with a very small quantity of hot distilled water, which is brought into thorough contact with the residue by detaching the latter with a small glass rod covered with a piece of india-rubber. The aqueous extracts, which should in all not exceed about 10 c.c., are passed through a small filter and collected in a little beaker. This aqueous extract, containing all the soluble salts in the water residue, is evaporated nearly to dryness on a water-bath, after which it is dissolved again in a minimum quantity (1 or 2 c.c.) of water, and introduced into a Lunge nitrometer (*Ber.* 11, 434); the beaker is repeatedly rinsed with a few drops of hot water, and these rinsings added to the nitrometer. The beaker is then further rinsed with pure strong sulphuric acid (free from oxides of nitrogen), and this also is transferred to the nitrometer. About $1\frac{1}{2}$ volumes of sulphuric acid must in all be used to 1 volume of aqueous extract. If the water contains soluble carbonates there will be an evolution of carbon dioxide when the sulphuric acid mixes with the aqueous extract; the gas should be allowed to collect without shaking the tube, and should then be expelled. The contents of the nitrometer tube are now violently agitated with the mercury, and then in the course of a minute or so the evolution of nitric oxide will commence, and the agitation should be continued as long as any gas continues to come off. If the water contains a considerable quantity of chlorides some hydrogen chloride may have been given off with the nitric oxide, but this may be removed by admitting a little water into the nitrometer. When the gas has cooled to the temperature of the air, its volume is measured at atmospheric pressure. The determination is rendered more accurate, especially if the quantity of nitrates and nitrites is only small, by measuring the nitric oxide in Frankland's gas apparatus, in

which case the decomposition with mercury and sulphuric acid is effected in a small tube standing in a mercury trough, the evolved nitric oxide being then transferred to the gas apparatus (see Sutton's *Volumetric Analysis*). This method, which is by far the most convenient for ordinary water analysis, becomes inapplicable in the presence of very large quantities either of organic matter or of chlorides.

(b) *Methods of Schulze-Tiemann, and of Schlösing-Reichardt,* depend upon the decomposition of nitrates and nitrites by ferrous chloride and hydrochloric acid, and the measurement of the evolved nitric oxide. Of these methods, which closely resemble each other, the former, as the more convenient, need alone be considered here.

100–500 c.c. of the water are concentrated by evaporation to about 50 c.c., which are then introduced into a flask of about 150 c.c. capacity, provided with an india-rubber stopper, perforated by two narrow pieces of glass tubing, of which one (A) extends about an inch into the flask, and is constricted below, whilst the other (B) only just penetrates the stopper; the tube (B) is externally connected by means of a short piece of india-rubber tubing provided with a pinch-cock, with a delivery tube dipping into a trough containing 10 p.c. caustic soda solution previously boiled to expel air. The tube (A) is also connected with india-rubber and pinch-cock to another piece of glass tubing, which is allowed to hang vertically downwards. The water in the flask is vigorously boiled with the pinch-cocks open until the air is completely expelled by the steam, then the pinch-cock on (B) is closed whilst that on (A) is left open until the volume of water in the flask is reduced to about 10 c.c.; this pinch-cock is then also closed, and the flame removed from beneath the flask. The glass tube attached to (A) is carefully filled with water up to the pinch-cock; 15–20 c.c. of a saturated solution of ferrous chloride are introduced into the flask, in which there is now a partial vacuum, by siphoning from a small beaker through (A), the pinch-cock being temporarily opened, and about an equal quantity of strong hydrochloric acid is made to follow in the same manner into the flask. The flask is now carefully heated, and when the internal pressure rises the pinch-cock on (B) is opened, and the evolved gas allowed to pass through the delivery tube into a measuring tube filled with the 10 p.c. caustic soda solution standing in the trough. The heating of the flask is continued until the volume of gas in the measuring tube ceases to increase. The measuring tube is transferred to a tall glass cylinder full of water, and after the gas has acquired the temperature of the room the volume is measured at the atmospheric pressure, a correction being of course made for the tension of aqueous vapour.

This method is specially applicable to the case of water containing excessive quantities of organic matter and chlorides (*Ber.* 1873, 1041; Tiemann and Gärtner's *Untersuchung d. Wassers*, 170).

For Schlösing-Reichardt's method, see *Zeitsch. anal. Chem.* 1870, 24, or Tiemann and Gärtner's *Untersuch. d. Wassers*, 175.

(c) *The aluminium and zinc copper couple methods* depend upon the conversion by nascent

hydrogen of the oxidised nitrogen in the water into ammonia, and estimation of the latter by Nessler solution.

Aluminium method.—100 c.c. of the water are introduced into a flask together with 10 c.c. of caustic soda solution free from nitrates and nitrites, the mixture being boiled until it is reduced to about one-fourth of its volume. It is then diluted to about its original bulk with distilled water free from ammonia, and a piece of aluminium foil, about 2 ins. square and wrapped round a piece of glass rod, is dropped into the flask, which is then fitted with a stopper and small U-tube containing glass beads moistened with hydrochloric acid free from ammonia. After the evolution of hydrogen has continued for about 6 hours, the glass beads and washings of the U-tube are transferred to the liquid in the flask, the latter is then attached to a Liebig's condenser, and the ammonia determined by distillation and Nesslerising in the ordinary way (see p. 396). According to Tiemann and Gartner (*Untersuchung des Wassers*, 208), only the equivalent of 72–90 p.c. of the nitric acid is thus recovered as ammonia.

Zinc-copper couple method.—The residue obtained in the determination of 'total solids' is extracted with about 25 c.c. of hot distilled water, and this is boiled down with a fragment of recently-ignited pure lime about the size of a hemp-seed to one-fourth of its bulk. This liquid, together with the washings of the dish containing the residue, is transferred through a stoppered funnel into an eight-ounce Wurtz flask, attached to a Liebig's condenser, and containing the requisite amount of the zinc-copper couple. The distillation is carried on until the greater part of the water has passed over, after which hot distilled water is repeatedly run into the flask and the distillation continued until about 100 c.c. of distillate have been collected; the latter is then 'Nesslerised' in the ordinary way (Thorpe, *Chem. Soc. Trans.* 1873, 541). According to Tiemann and Gartner, from 88 to 95 p.c. of the nitric acid is thus obtained.

In the writer's laboratory the process is carried out as follows: A stoppered bottle (about 200 c.c. capacity) is loosely filled with strips of zinc, which, after cleaning with dilute sulphuric acid, are covered with copper sulphate solution (1 p.c.). The copper-coated strips are repeatedly washed with distilled water, and finally with the water under examination, care being taken not to detach the copper film. The bottle is then completely filled with the sample of water and a crystal of oxalic acid is added, and the bottle, loosely stoppered, is allowed to stand over night. A definite volume is withdrawn by means of a pipette, and this is distilled with a suitable volume of ammonia-free water in the ammonia apparatus as usual, a small quantity of ignited sodium carbonate being added. Before withdrawing the water from the bottle for distillation, a small quantity should be tested for nitrite to ensure that the reduction to ammonia is complete. Waters containing free or saline ammonia must have this distilled off before being placed in contact with the zinc-copper couple.

A rapid method of estimating nitrates in water is due to Harrow (*Chem. Soc. Trans.* 1891, 899), depending on the reduction to nitrite

by zinc-dust and estimation of the nitrous acid by sulphanilic acid and α -naphthylamine (Griess' test). This reagent is prepared by dissolving 1 grm. of α -naphthylamine, 1 grm. sulphanilic acid, and 25 c.c. strong hydrochloric acid in about 200 c.c. distilled water; boiling with a small quantity of animal charcoal, filter, and making up to 500 c.c. The process is conducted thus: 50 c.c. of the water are placed in a beaker of 100 c.c. capacity, and in three similar beakers 50 c.c. of three standard solutions of potassium nitrate, containing (1) 1.0 part N, (2) 0.1 part N, (3) 0.01 part N per 100,000; to each beaker 10 c.c. of the above test-solution are added, and afterwards a very small quantity (7–8 mg.) of zinc-dust. If nitrate is present in the water a pink colour appears, which must be compared with that yielded by the three standard solutions after 15 mins. This gives an approximate idea of the amount of nitrate present, whilst in order to obtain an accurate result the water must be diluted until the colour produced is almost identical with that given by one of the standards. The results appear to be accurate, but it is especially necessary to avoid the addition of large quantities of zinc-dust, which would decolorise the solution.

(d) *The indigo method* differs from those previously described in being a simple volumetric method depending upon the decolorising action of nitric acid on indigo solution. The results are only accurate when the greatest uniformity is preserved in the conditions under which the experiments are made—the process is, in fact, entirely empirical. It may be carried out as follows: 25 c.c. of the water are mixed with 50 c.c. of pure strong sulphuric acid; a dilute solution of indigo is then immediately added from a burette, shaking the whole time, until the solution acquires a bluish-green colour. In a second experiment nearly the whole volume of indigo which was found necessary in the first experiment is added at once, and the blue colour is then obtained by further small additions, and in this manner, by shortening the time taken in the titration, a more accurate result, generally higher than in the preliminary experiment, is obtained. The solution of indigo must be standardised under precisely similar conditions by means of a solution of potassium nitrate of known strength. The indigo solution should be chosen of such strength that 6–8 c.c. correspond to 0.001 grm. N_2O_5 ; and if 25 c.c. of the water contains more than 0.003–0.004 grm. N_2O_5 , it should be diluted before a final titration is made. The method is only suitable for use by an operator in continual practice (Warington, *Chem. Soc. Trans.* 1879, 578; *Water Analysis*, E. Frankland, 31). The results are too low if there is a large amount of organic matter in the water.

The methods described above do not distinguish between nitrous and nitric acids. Indeed, the indigo method is altogether unreliable in the presence of any notable proportion of nitrous acid, as is also Cram's method, should it be necessary to allow any carbon dioxide to escape before shaking with mercury (see p. 397). As nitrous acid is, however, generally only present in natural waters in minute traces, these difficulties do not frequently arise, and the

nitrous acid may be most conveniently estimated by colorimetric methods, of which there are several in vogue. Of these may be mentioned:

Table of hardness in parts per 100,000, 50 c.c. of water being used.

(a) *Preuss-Tiemann's method*, depending upon the production of Bismarck brown when an acid solution of a nitrite acts upon *m*-phenylenediamine. 100 c.c. of the water are placed in a colourless glass cylinder, 1 c.c. of dilute sulphuric acid (1 : 3) is added, and then 1 c.c. of solution of *m*-phenylenediamine (5 grms in 1000 c.c. distilled water, decolorised if necessary with animal charcoal); if the colour appears in less than 1 or 2 mins. the experiment must be repeated with a smaller quantity of water, in each case diluted, however, to 100 c.c. The coloration is then imitated under precisely similar conditions with a standard solution (the standardisation can be effected either by the potassium permanganate, or, better, by the urea method) of potassium or sodium nitrite. The final tint is not arrived at until the mixture in the glass cylinder has stood for 20-25 mins., which is the great drawback of the process (*see* also Warington, *The Detection of Nitric and Nitrous Acids*, Chem. News, 1885, 51, 39).

A preferable method (Zambelli, Chem. Soc. Abstr. 1887, 533) consists in adding to the water a few drops of a saturated solution of sulphanilic acid in dilute sulphuric acid, then a few drops of a saturated aqueous solution of phenol, after which the mixture is rendered alkaline with ammonia. The presence of nitrous acid is indicated by the appearance of a coloration, varying from faint yellow to intense reddish yellow, according to the quantity of nitrous acid present. The author claims that this method is capable of revealing the presence of 1 part of nitrous nitrogen in 40,000,000 parts of water. It has the great advantage that the reagents employed are permanent in solution.

For larger quantities of nitrous acid, as also for the standardisation of solutions of sodium and potassium nitrite, the urea method devised by the writer is to be recommended (Chem. Soc. Trans. 1888, 364).

Hardness.—The determination of the hardness of a water consists in empirically ascertaining the amount of soap which has to be destroyed by a given volume of the water before a lather can be obtained, and expressing this in terms of the amount of calcium carbonate which must be dissolved in the same volume of water to destroy the same amount of soap. Accurate results can only be obtained by preserving uniformity in the conditions of experiment.

50 c.c. of the water are measured into an 8-oz. stoppered bottle, which is then violently agitated and the air sucked out by means of a glass tube to remove any carbon dioxide which may be given off by the water. A standard solution of soap (*v. infra*) is then added in diminishing quantities not exceeding 0.5-0.10 c.c. at a time, even at first, violently shaking after each addition, until the froth produced remains unbroken over the surface for a period of 5 mins. when the bottle is placed at rest on its side. The quantity of calcium carbonate corresponding to the volume of soap solution employed can then be ascertained by reference to the empirical table

C.c. of soap solution	CaCO ₃ per 100,000	CaCO ₃ per 100,000	C.c. of soap solution	CaCO ₃ per 100,000
·7	0·00	5·9	7·29	11·0
·8	·16	6·0	·43	·1
·9	·32	·1	·57	·2
1·0	·48	·2	·71	·3
·1	·63	·3	·86	·4
·2	·79	·4	8·00	·5
·3	·95	·5	·14	·6
·4	1·11	·6	·29	·7
·5	·27	·7	·43	·8
·6	·43	·8	·57	·9
·7	·56	·9	·71	12·0
·8	·69	7·0	·86	·1
·9	·82	·1	9·00	·2
2·0	·95	·2	·14	·3
·1	2·08	·3	·29	·4
·2	·21	·4	·43	·5
·3	·34	·5	·57	·6
·4	·47	·6	·71	·7
·5	·60	·7	·86	·8
·6	·73	·8	10·00	·9
·7	·86	·9	·15	13·0
·8	·99	8·0	·30	·1
·9	3·12	·1	·45	·2
3·0	·25	·2	·60	·3
·1	·38	·3	·75	·4
·2	·51	·4	·90	·5
·3	·64	·5	11·05	·6
·4	·77	·6	·20	·7
·5	·90	·7	·35	·8
·6	4·03	·8	·50	·9
·7	·16	·9	·65	14·0
·8	·29	9·0	·80	·1
·9	·43	·1	·95	·2
4·0	·57	·2	12·11	·3
·1	·71	·3	·26	·4
·2	·86	·4	·41	·5
·3	5·00	·5	·56	·6
·4	·14	·6	·71	·7
·5	·29	·7	·86	·8
·6	·43	·8	13·01	·9
·7	·57	·9	·16	15·0
·8	·71	10·0	·31	·1
·9	·86	·1	·46	·2
5·0	6·00	·2	·61	·3
·1	·14	·3	·76	·4
·2	·29	·4	·91	·5
·3	·43	·5	14·06	·6
·4	·57	·6	·21	·7
·5	·71	·7	·37	·8
·6	·86	·8	·52	·9
·7	7·00	·9	·68	16·0
·8	·14			

In performing the titration as above, the experienced operator is guided by the ear as well as by the eye, for the sound produced on shaking serves to indicate how the reaction between the hardening constituents of the water and the soap is progressing, for as this approaches completion the sound becomes softer, and when an excess of soap has been added the agitation is all but noiseless.

giving more than

16 c.c. of soap solution for the 50 c.c. of water, it is necessary to take a smaller volume of the water and dilute to 50 c.c. with boiled distilled water. The presence of magnesia salts is indicated in the soap test by the formation of a characteristic light curd, and also by the premature formation of a lather, which again disappears on the further addition of soap solution and shaking. If these signs are exhibited, only such a volume of water should be taken as, when diluted to 50 c.c., requires not more than 7 c.c. of the soap solution; indeed, it is a very good practice invariably to dilute waters so that not more than 7 or 8 c.c. of soap solution are required. In the presence of magnesia salts the results are always less accurate, and, unless great care is exercised, may become wide of the truth.

Permanent hardness.—The permanent hardness is most conveniently determined by taking a small flask with a *very short neck* (the Erlenmeyer shape is very suitable), and adding the water to it until a definite weight (e.g. 250 grms.) has been made up. The water is then maintained in gentle ebullition for exactly half-an-hour, and, after cooling, the weight is again made up to the original by the addition of boiled distilled water, the soap titration being then performed on a measured portion of this, as described above.

Some analysts prefer to take a given volume of water and restore the volume after boiling, then removing the precipitated carbonates of lime and magnesia by passing through a dry filter.

The *standard solution of soap* is prepared as follows. A cake of Castile soap is scraped with a knife, and about 7 grms. of the shavings are dissolved in 500 c.c. of a mixture of 2 vols. of methylated spirit with 1 vol. of distilled water. Filter off the insoluble matter, and dilute the soap solution with half its volume of water. A portion of this solution is then further carefully diluted with a mixture of 2 vols. methylated spirit and 1 vol. water until 7.8 c.c. are required to form a permanent lather with a mixture of 25 c.c. of the standard calcium chloride solution (prepared by dissolving 0.2 gm. of Iceland spar in dilute hydrochloric acid, and, after driving off excess of acid on the water-bath, making up to 1000 c.c. with distilled water) and 25 c.c. of distilled water.

Poisonous metals.—Of these the only ones which are of practical importance in water analysis are lead, zinc, copper, arsenic, and barium. As they are generally present in only very minute proportions, it is necessary to evaporate large volumes (5 litres and upwards) of water in order to obtain gravimetric determinations in the ordinary way; but the following special methods may be generally employed.

For *lead*, take 100 c.c. of the water, acidify with a few drops of acetic acid, and then add about 5 c.c. of a saturated solution of sulphuretted hydrogen. The colour produced is imitated by adding a known quantity of a standard solution of a lead salt to 100 c.c. of distilled water. Even such small proportions as 0.03 part Pb per 100,000 should invariably be recorded. (For the standard solution of lead, dissolve 0.1831 gm. crystallised normal lead acetate in 1000 c.c. distilled water; 1 c.c. = 0.0001 Pb.)

For *copper*, the same colorimetric method may be employed as for lead, using for comparison a solution of copper sulphate containing 0.0001 gm. Cu in 1 c.c. (0.3929 gm. crystallised copper sulphate per litre). In the absence of iron a very delicate colorimetric method may be employed, based upon the reaction between copper salts and potassium ferrocyanide, the water being acidified with hydrochloric acid, whilst in the presence of iron the blue coloration produced by ammonia may be used.

The presence of *zinc* is generally indicated by the gradual formation of a film of carbonate on the surface of the water when the latter is exposed to the air. Some of this film ignited on platinum foil should leave a residue, which is yellow when hot and white on cooling. The quantity of the zinc may be approximately determined, in the absence of other heavy metals, by acidifying 100 c.c. of the water with dilute hydrochloric acid, and then adding a solution of potassium ferrocyanide. The white turbidity produced is then compared with that obtained from a known quantity of a standard solution of a zinc salt (Snijders, Ber. 1878, 939).

Arsenic is best detected and estimated by Marsh's test; 500 c.c. of the water are rendered slightly alkaline with caustic soda or potash free from arsenic, and evaporated to dryness. The residue is extracted with strong hydrochloric acid, and the liquid introduced into a Marsh's apparatus. The gas is passed through a small U-tube containing pumice soaked in solution of lead acetate, and then through a piece of combustion tube constricted in the middle, where it is heated to redness. The passage of gas through the heated tube is continued for an hour, although nearly all the arsenic is liberated in 5 or 10 mins. The metallic ring formed is compared with a number of standard rings similarly obtained with known quantities of arsenic. A blank experiment must invariably be performed previously, to control the purity of the chemicals employed.

Barium may be detected and determined by concentrating a considerable volume of the water, acidifying with hydrochloric acid, and after filtering, if necessary, adding a solution of calcium sulphate. The barium sulphate precipitated is then collected and weighed in the ordinary manner.

Iron can generally be estimated colorimetrically by means of ferrocyanide or thiocyanate. Its determination is frequently of importance in waters used for industrial purposes.

In the ferrocyanide method, the water residue is dissolved in hydrochloric acid and diluted to 100 c.c. Of this 10 c.c. are transferred to a 100 c.c. cylinder; add 1 c.c. of strong nitric acid, dilute to 100 c.c., stir, and then add 1 c.c. of potassium ferrocyanide solution and mix well. The colour produced is compared with that obtained from a standard iron solution, but the same quantity of nitric acid must be present in each case (Sutton, Volum. Analys. 6th ed. 194; v. also Carter Bell, J. Soc. Chem. Ind. 8, 175).

In the thiocyanate method, two 100 c.c. cylinders are taken, and into each 5 c.c. of dilute hydrochloric acid (1 : 5) and 5 c.c. of dilute nitric acid (1 : 5), together with 15 c.c. of thiocyanate solution, are poured; then introduce a

measured volume of the liquid to be tested into the one cylinder, and after filling up both cylinders to the mark with distilled water, imitate the red colour obtained with the liquid under examination by running in a standard solution of iron from a burette into the other cylinder. In this way one part of iron is said to be recognisable in fifty millions of water (Thompson, Chem. Soc. Trans. 1885, 493).

Determination of organic matter.—A number of processes have been devised for the determination either of the whole or part of the organic substances present in water. Of those which lay claim to discovering the whole of these organic materials, none is entitled to any confidence, whilst even those which attempt to determine a part, or to indirectly obtain a comparative measure of the organic matter, are also open to objections on the score of accuracy. Only those methods more commonly in use by water analysts will be described here.

(1) *Methods depending on the reduction of potassium permanganate.*

(a) *Kubel's process.*—In this the reduction is effected in acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity and treated with 5 c.c. dilute sulphuric acid (1 : 3), and then with such a quantity of standard dilute permanganate (equivalent to centinormal oxalic acid) that the liquid is of a strong red colour. The mixture is then boiled for 10 mins., and the excess of permanganate added must be such that the colour is not discharged in the operation. 10 c.c. of centinormal oxalic acid are now added, and into the resulting colourless liquid standard permanganate is then run until a faint red colour is obtained. The amount of oxygen consumed by the organic matter in the water can then be calculated.

(b) *Schulze's process.*—In this the reduction is commenced in an alkaline and completed in an acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity, 0.5 c.c. caustic soda solution (1 : 2) are added, as well as 10–15 c.c. of standard dilute permanganate (equivalent to centinormal oxalic acid). The liquid is boiled for 10 mins., allowed to cool to 50° or 60°C. and then 5 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of centinormal oxalic acid are added, the liquid being shaken and gently warmed until the colour has quite disappeared. Then the standard dilute permanganate is run in until a faint red colour, remaining permanent for at least 5 mins., is obtained. The oxygen consumed by the organic matter of the water is then calculated.

(c) *Forchhammer process.*—This resembles Kubel's method, inasmuch as the reduction of the permanganate is effected in an acid solution, but the temperature employed, instead of being defined, is that of the air of the laboratory.

Two flasks are carefully cleaned and into one 250 c.c. of the water, into the other 250 c.c. of distilled water, are introduced. To each 10 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of standard permanganate (containing 0.395 gm. per litre or 0.001 gm. available oxygen in 10 c.c.) are added, and the mixture is allowed to stand for three hours. At the end of this time the excess of permanganate remaining is deter-

mined by adding two drops of potassium iodide (1 : 10) to each flask, and then running in a standard solution of sodium thiosulphate (1 gm. per litre) until the whole of the free iodine is removed, a drop of clear starch solution being added at the close of the operation. The amount of permanganate destroyed in the blank experiment must of course be deducted from that destroyed in the case of the water, and from the difference the oxygen consumed by the organic matter of the water can be calculated (Tidy, Chem. Soc. Trans. 1879, 66).

In this country it is now almost the invariable custom of water analysts to allow the acid permanganate to act for 4 hours at 80°F. (26.7°C.); Thorpe (Metropolitan Water Reports, 1904) has also used 1 hour at 122°F. (50°C.), under which conditions a larger amount of oxygen is consumed.

It must be pointed out that in these several methods depending on the reduction of permanganate, the results are only comparative for the same kind of organic matter, a given weight of organic carbon in different kinds of water consuming different quantities of oxygen from permanganate under the same conditions. Thus it has been found that for surface waters, such as those of the rivers Thames and Lea, by multiplying the oxygen consumed in the Forchhammer process by the factor 2.38, the proportion of organic carbon (as determined by combustion) is approximately obtained, whilst in the case of deep well water the factor which must be employed is 5.8 (Woodland Toms).

Again, all these methods are affected by the presence of nitrites, ferrous salts, and larger quantities of ammonia compounds, all of which exercise a reducing action on permanganate. By determining the nitrous acid, a correction can be made for this, whilst the ferrous can generally be converted into ferric iron by shaking up the water several times in a half-filled bottle previously to the oxidation with permanganate; and the error due to ammonium salts is so small that it can generally be neglected (even one part NH₃ per 100,000 has no appreciable reducing effect) (Preusse and Tiemann, Ber. 12, 1906).

(2) *Determination of organic carbon by oxidation of organic matter with potassium dichromate and sulphuric acid* (Wolff, Degener, and Herzfeld).—500–1000 c.c. of the water are introduced into a capacious retort, the neck of which is drawn out and bent downwards and is connected with a Liebig's condenser. This arrangement enables the retort to be turned upwards and the condenser downwards, thus preventing any loss by spurting during distillation, which is carried on until 250–700 c.c. (according to the volume of water employed) have passed over. The distillate is submitted to Kubel's method (*v. supra*) to ascertain whether any volatile organic matters are present. Alkaline waters should be saturated with carbon dioxide, and acid waters carefully neutralised with sodium carbonate before the above distillation. The water remaining in the retort is evaporated down to 15 c.c. in a glass dish on a water-bath, the access of dust being carefully avoided. This concentrated liquid is introduced into a flask of 250–300 c.c. capacity, and the dish and retort are rinsed with 10 c.c. of dilute sulphuric acid (1 : 3),

these rinsings also being added to the water in the flask. The decomposition of carbonates caused by the addition of this acid is completed by heating to 50°C. and shaking, and the evolved carbon dioxide completely displaced by air. After cooling the flask and its contents, 10 grms. of finely-powdered potassium dichromate are added, and the flask is then attached to the remainder of the apparatus. An india-rubber stopper with three holes is placed in the flask; through one hole passes a thermometer dipping into the liquid, through a second passes nearly to the bottom of the flask the tube of a bulb-funnel (A) provided with a stopcock, whilst through the third passes the bent tube of an inverted Liebig's condenser (B). The upper extremity of the condenser (B) is connected with two U-tubes (C and D) filled with fused calcium chloride, whilst between these is a third U-tube (E) containing coarsely-powdered antimony. Of these, C and D are intended to absorb the moisture passing the condenser, and the intermediate one, E, to retain any chlorine. Following on these tubes is a set of weighed potash-bulbs (F) for the absorption of carbon dioxide, and these bulbs are, of course, protected from ingress of moisture on the other side by means of a calcium chloride tube, which can be attached to an aspirator at the close of the experiment. The apparatus having been thus put together, 50-60 c.c. of diluted sulphuric acid (3:2) are gradually added through the stoppered funnel (A). During the first half-hour the temperature is kept at 50-55°C., whilst during the second half-hour it is gradually raised to boiling, which is maintained from 5-10 mins. The aspirator is then attached, the air which enters by the funnel (A) having been previously freed from carbon dioxide by bubbling through caustic potash. The increase in weight of the potash bulbs (F) gives the weight of carbon dioxide evolved, from which the carbon itself can be calculated (Ber. 1886, 2618; Tiemann-Gärtner, *Untersuch. d. Wassers*, 247).

For a somewhat similar method of determining organic carbon in which permanganate is used instead of dichromate, see Blair, *Organic Analysis of potable Waters*, Churchill, 1891, 83. The method appears worthy of more extended trial.

(3) *Determination of organic carbon and nitrogen by combustion.*—(a) *Frankland and Armstrong's process* (Chem. Soc. Trans. 6, 77). This method, which is unquestionably the most rational and exact, has been adopted to a comparatively limited extent by water analysts in consequence of the special apparatus and manipulative skill which it entails. The method will be described only in outline here, and for full particulars the reader is referred to Sutton's *Volumetric Analysis*, whilst for a critical survey of the methods employed in the organic analysis of water he should not fail to consult Mallet, *Report of the United States National Board of Health*, 1882.

The process is divisible into three parts: (1) the evaporation of the water, (2) the preparation and combustion of the residue thus obtained, and (3) the measurement of the gases evolved in the combustion.

For the *evaporation*, from 100 c.c. (in the case of sewage and highly polluted waters) to

1000 c.c. (in the case of very pure waters) are measured into a clean flask, 20 c.c. of a saturated solution of sulphurous acid being added together with a drop of a solution of ferric chloride; the liquid is then boiled rapidly for a few seconds. This treatment secures the decomposition of carbonates, nitrates, and nitrites, whilst any ammonia is fixed by the sulphurous acid, and this ammoniacal nitrogen, which has previously been determined, must be deducted from the total amount of nitrogen obtained in the combustion. The water is now rapidly cooled, and the evaporation commenced in an apparatus specially designed for the purpose. This consists of a nearly hemispherical glass dish about 4 ins. in diameter and without a lip. It is floated in a shallow copper basin heated below by a water-bath provided with constant feed, and on the flange of this copper basin there rests a truncated conical ring, constructed of lead or copper, and about 3 ins. in height, whilst upon a flange at the top of this again rests a tall glass shade about 12-18 ins. in height. The water for evaporation is placed in a flask which is provided with a delivery tube of special construction ground on to its neck, and which serves, when the flask is turned upside down, to maintain the water at a constant level in the glass dish in which the evaporation is proceeding, for this delivery tube is made to pass through a notch in the truncated conical metal ring, just beneath the glass shade which the latter supports, and delivers into the centre of the glass dish within. In the writer's laboratory, the evaporation of 500 c.c. of water is found to take from 10-12 hours. The evaporation should be continued until the residue is quite dry, and if the water contains only a small amount of total solids it is advisable to add a little ignited calcium phosphate to the dish before commencing the evaporation. In the analysis of sewage, or waters containing much ammonia and no nitrates or nitrites, it is advantageous to use 10 c.c. of a solution of metaphosphoric acid (1:10) instead of the sulphurous acid, as ammonium phosphate loses much less ammonia during evaporation than ammonium sulphite. A little ignited calcium phosphate should also be added to dry the residue in this case. But if there are no nitrates and nitrites and much ammonia, the more satisfactory, although more laborious, plan is to use a little ignited borax instead of the sulphurous or metaphosphoric acid. In this way the ammonia is completely dissipated on evaporation, and as no correction has, therefore, to be applied to the organic nitrogen found, the result is more correct. But as boric acid does not entirely decompose carbonates the accuracy of the organic carbon found by this method may be seriously affected, and it is advisable to make a separate determination of the carbon in a second experiment in which the sulphurous acid method is employed. Unless this method be adopted the results for organic nitrogen in the presence of much ammonia are nearly sure to be highly inaccurate.

If the water contains more than 0.5 part per 100,000 of nitrogen as nitrates and nitrites, the 20 c.c. of sulphurous acid employed above may not improbably prove insufficient for their complete destruction, and in the case of such waters the residue in the dish should be further treated

with 10 c.c. of sulphurous acid, this evaporated off, and if the amount of nitric or nitrous nitrogen exceed 1 part per 100,000 this treatment of the residue with further quantities of sulphurous acid may be repeated twice or three times to secure complete destruction of the nitrates and nitrites.

The *preparation and combustion of the residue* thus obtained is effected by thoroughly mixing with the latter in the dish a small quantity of finely divided and carefully ignited copper oxide. This is then completely transferred to a narrow piece of combustion tubing about 18 ins. long and sealed at one extremity. The dish is again rinsed with a little fine oxide, and this also transferred to the tube. Coarse and carefully ignited oxide of copper (preferably from wire) is then introduced to a depth of about 10 ins., whilst the fine oxide previously introduced will occupy about 2 ins. Upon the stratum of coarse oxide follows a copper gauze cylinder 3 ins. in length, and then another layer of coarse oxide about 1 in. long. The open extremity of the tube is now drawn out over the blowpipe, so that it can be connected with a Sprengel mercury pump. The tube is completely exhausted, and the combustion performed *in vacuo* in the ordinary way, the evolved gases being then drawn over by the pump and collected in a test tube filled with mercury and placed over the lower open extremity of the fall tube in the trough below.

The *volumetric measurement of the gases* (consisting of carbon dioxide, nitrogen, and possibly also nitric oxide and sulphur dioxide) collected as above is carried out in the Frankland gas apparatus, which admits of the measurement of very minute quantities of gas. Three measurements are only necessary. In the first place the gas is treated with a few drops of a saturated solution of potassium dichromate to absorb any sulphur dioxide that may be present. The volume of the gas is then accurately measured, after which it is treated with a few drops of strong caustic potash, which rapidly removes the carbon dioxide, after which the volume of the remaining gas is again carefully ascertained. The residual gas now consists of nitrogen, with possibly a little nitric oxide. It is mixed with a bubble of pure oxygen in order to convert any nitric oxide into nitrous and nitric acids, which are immediately absorbed by the caustic potash present, and then, on adding a drop or two of solution of pyrogallous acid, the excess of oxygen is absorbed and the remaining gas, which consists of nitrogen, is carefully measured. The diminution in volume effected by the caustic potash in the first instance obviously represents the carbon dioxide, whilst the final volume of residual gas, together with one-half of the contraction resulting from the addition of oxygen and pyrogallous acid, represent the total volume of nitrogen. From these volumes the weights of carbon and nitrogen respectively can be calculated. As already pointed out, if sulphurous or metaphosphoric acid has been used in the evaporation, and ammonia is present in the water, the ammoniacal nitrogen (subject to an empirical correction for loss of ammonia during evaporation) has to be subtracted from the total nitrogen found by combustion. A small correction (ascer-

tained by blank experiments made from time to time with the reagents employed in the evaporation and combustion) has also to be applied to the carbon and nitrogen thus determined.

For *Dupré and Hake's method*, see Chem. Soc. Trans. 1879, 159.

In *Dittmar and Robinson's method* of determining organic carbon, the gases proceeding from the combustion tube are first passed through a U-tube containing a solution of chromic acid in 60 p.c. sulphuric acid to absorb moisture and sulphurous acid (the water is evaporated with sulphurous acid for the preparation of the residue), the carbon dioxide being absorbed in a weighed soda-lime tube (Chem. News, 1877, 36, 26). A method of determining organic nitrogen has also been devised by Dittmar and Robinson, and is described below.

(4) *Methods for determination of organic nitrogen only*.—Of these the most common one in use is the well-known

(a) '*Albuminoid ammonia*' process of Wanklyn, Chapman, and Smith (Chem. Soc. Trans. 1867, 591), which does not yield the whole, but only very variable proportions, of the organic nitrogen in different nitrogenous organic substances, although in the case of some—such as leucine, aspartic acid, tyrosine, &c.—which frequently appear as decomposition products of albuminous matters, nearly the whole of the nitrogen is obtained as ammonia (Preusse and Tiemann, Ber. 12, 1906; Mallet, U.S. National Board of Health Report, 1882).

The method has already been described on p. 396.

(b) *Dittmar and Robinson's process*.—In this process the residue, obtained in the same way as for the combustion process, is heated with fused caustic soda, or soda and baryta, in a copper or silver boat placed in a combustion tube in a current of hydrogen, the evolved ammonia being absorbed by very dilute hydrochloric acid, which is subsequently 'Nesslerised' (Chem. News, 1877, 36, 26). The results are accurate, and coincide with those obtained by the combustion process of Frankland and Armstrong.

(c) *Kjeldahl's process*.—This well-known and now much-employed method for determining organic nitrogen was adapted for use in water analysis by Drown and Martin (Chem. News, 59, 272). It appears to give accurate results uninfluenced by the presence of nitrates and nitrites in such quantities as are found in ordinary waters, 500 c.c. of the water are placed in a round-bottomed flask of about 900 c.c. capacity; the volume is then reduced to about 200 c.c. by boiling, and to this, after cooling, 10 c.c. of pure concentrated sulphuric acid are added. The mixture is then cautiously boiled, with the flask in an inclined position, until all the water has been driven off and the acid remains of a white or very pale-yellow colour. After removing the source of heat, add a little powdered permanganate until, on shaking, the liquid becomes green, showing that excess has been added. If a purple instead of a green colour appears, it shows that the whole of the water has not been driven off. When cool, 200 c.c. of water free from ammonia are added, care being taken to rinse round the neck of the flask, and thus wash in any acid which may be adhering there.

WATER.

100 c.c. of sodium hydroxide solution are then added, and the mixture distilled with a Liebig's condenser. (The sodium hydroxide solution is prepared by dissolving 200 grms. of good caustic soda in 1250 c.c. of distilled water, adding 2 grms. potassium permanganate, and boiling down until the volume is rather less than 1000 c.c. making up to 1000 c.c. when cold.) The distillate is collected in a flask containing 50 c.c. of water free from ammonia, and 1 c.c. of dilute pure hydrochloric acid, and during the distillation of the first 50 c.c. the delivery tube of the condenser is made to dip into this acid liquid, whilst during the remainder of the distillation the flask is lowered so that the delivery tube is just above the liquid. The distillation is carried on until the whole of the ammonia has passed over, and the contents of the receiver are then 'Nesslerised' in the ordinary way. The most scrupulous care must be exercised to prevent access of ammonia from the air and reagents; a blank experiment should also be made for control.

Determination of dissolved oxygen.—Much importance is, with very little reason, attributed by some analysts to this determination; it can, moreover, be rarely applied, as the samples must be collected with special precautions if the results are to have any value at all. The various processes in use have been examined by Kisch (Chem. Soc. Abstr. 1892, 98). *Reichardt's* method (Zeitsch. anal. Chem. 1872, 11, 271), as modified by Preusse and Tiemann (Ber. 1879, 12, 1768; Tiemann-Gärtner's Untersuch. d. Wassers, 278), consists in boiling a measured volume of water, and collecting the gases over a hot solution of caustic potash, the oxygen being then estimated either by explosion with hydrogen, or by absorption with potassium pyrogallate. In *Mohr's* method (*Mohr's* Titrimethoden) the sample is mixed with an acid solution of ferrous sulphate of known strength, then with caustic soda to throw down ferrous hydroxide, and after remaining for a few hours (air, of course, fully excluded), the precipitate is re-

in sulphuric acid, and the remaining ferrous sulphate titrated with permanganate. In the *Schützenberger-Risler* process (Bull. Soc. chim. 1873, [ii.] 19, 152; 20, 145; Tiemann-Gärtner's Untersuch. d. Wassers, 277, 288; Catherine Williams and Ramsay, Chem. Soc. Trans. 1886, 760; Bernthsen, Ber. 13, 2277; Roscoe and Lunt, Chem. Soc. Trans. 1889, 552; Dupré, Analyst, 1885, 10, 156) the water is allowed to act on a solution of sodium hydrindigotin disulphonate, which oxygen converts into the blue compound; a standard solution of sodium hydrosulphite is then run in until the liquid again becomes colourless. In *Winkler's* process (Ber. 21, 2843) the water is mixed with a solution of manganous chloride, and then with potassium iodide and caustic potash; the precipitated manganous hydroxide absorbs the oxygen, passing into a higher state of oxidation. On adding hydrochloric acid the higher oxide of manganese gives rise to the liberation of an equivalent quantity of iodine, the amount of which is determined by titration with sodium thiosulphate. According to Kisch (*l.c.*), the results by the *Reichardt-Preusse-Tiemann* method are decidedly lower than those obtained by the *Winkler* process, which is in harmony

with the experience of the writer. The results by *Mohr's* and *Schützenberger's* methods accord very well with those of *Winkler*; but *Winkler's* appears, on the whole, to be the most trustworthy, and the easiest to carry out. A modification of *Winkler's* method has been made by *Rideal* and *Stewart* (Analyst, 1901, 26, 141), and a more recent one reducing it to a colorimetric process by *Rideal* and *Burgess* (*ibid.* 1909, 34, 193).

A full description and discussion of the several methods will be found in *Sutton's Volumetric Analysis*.

The determination of dissolved oxygen has, in recent years, been much practised in connection with the rate at which dissolved oxygen is absorbed by sewage and effluents from sewage works. This matter is of importance as affording a measure of the readiness with which such liquids will remove the dissolved oxygen from a stream into which they are discharged. For *Scudder's* method, see *Fowler's Sewage Works Analyses*, or *Sutton's Volumetric Analysis*.

Determination of carbon dioxide.—(1) The total carbonic acid is determined by completely precipitating as calcium carbonate with an excess of calcium hydroxide (a sufficient quantity of calcium chloride being added to decompose alkaline carbonates), then filtering off the precipitate, and determining the carbon dioxide in it in the usual way (Fresenius, Quant. An.; Tiemann-Gärtner, Die Untersuch. d. Wassers, 213). If the water is saturated with carbon dioxide under pressure, the above method must be preceded by *Rochleder's* process for estimating the gas which escapes on reducing the pressure to that of the atmosphere.

(2) The free and semi-combined carbon dioxide is determined by *Pettenkofer's* method, in which the water is treated with an excess of standard calcium hydroxide solution, and, after the precipitate has separated in a crystalline form, the clear liquid is decanted off, and the excess of lime ascertained in an aliquot part by titration with standard dilute oxalic acid, using phenolphthalein as indicator. If the water contains alkaline carbonates, sufficient neutral calcium chloride solution must be added to decompose them, whilst if there is a considerable proportion of magnesia salts, some ammonium chloride must also be added.

If the carbonic acid thus determined is subtracted from the total obtained according to (1), then the difference represents the combined carbonic acid. To this combined carbonic acid here corresponds, of course, an equal quantity of semi-combined, so that only an excess over and above this can be regarded as free carbonic acid. It must, however, be pointed out that the determination of total carbonic acid generally yields results which are below the truth by 1-1.5 units in 100,000 parts, in consequence of the solubility of normal calcium carbonate itself (v. Walker and Kay, J. Soc. Chem. Ind. 1912, 31, 1013).

Determination of sulphuretted hydrogen.—Colorimetrically with a solution of sodium nitroprusside, using for comparison a standard solution of sulphuretted hydrogen. The latter is standardised by taking a measured volume and adding an excess of decinormal sodium arsenite; shake well, and then acidify with hydrochloric acid. After the arsenious sulphide has com-

pletely subsided, dilute to 300 c.c., and filter through dry paper. Take 100 c.c. of the filtrate, remove acidity by means of solid sodium carbonate, add a drop of starch solution, and then run in decinormal iodine until a blue colour is obtained. This method may, of course, also be employed for the determination of the sulphuretted hydrogen in the water itself if present in sufficient quantity.

In using the colorimetric method, 300 c.c. of the water are treated with 5 c.c. sodium carbonate and 3 c.c. sodium hydroxide; allow the precipitate to subside for 1-2 hours, then decant or filter. To 250 c.c. of the filtrate in a colourless cylinder add 1 c.c. of sodium nitroprusside solution (4 grms. per litre), and for comparison take 245 c.c. distilled water, to which add 2 c.c. sodium hydroxide and as much of the standard solution of sulphuretted hydrogen as is required to produce precisely the same tint as is obtained with the water above. In this manner 0.1 part H_2S per 100,000 can be determined (Tiemann-Gärtner, *Untersuch. d. Wassers*, 232).

Sulphuretted hydrogen may also be accurately determined by means of centinormal iodine solution. 10 c.c. or other suitable volume of the latter are placed in a 500 c.c. flask, and the water added until the colour completely disappears; 5 c.c. of starch solution are then added, and centinormal iodine is run in until a blue colour is obtained, pure distilled water being added up to the 500 c.c. mark from a burette. On subtracting the sum of the volumes of iodine, starch solution, and distilled water added from 500 c.c., the volume of water which reacted with the iodine solution employed is ascertained. A correction should be made for the volume of iodine solution required to produce a blue colour.

BAACTERIOLOGY OF WATER.

The great progress during the past half century made in our knowledge of infectious diseases and of the processes dependent on bacterial life, has necessitated that the subject of water supply should be considered from a bacteriological, as well as a chemical, point of view.

It had even previously been recognised that in making determinations of organic matter, ammonia, nitrates, &c., with a view to ascertaining the fitness or otherwise of water for drinking purposes, the concomitants of the living poisons of zymotic disease and not the morbid matters themselves, which were still more or less hypothetical entities, were being tested for, and that the living poisons themselves must be explored by biological, and not by purely chemical, methods.

Liquid and solid media.

The classical investigations on bacteria by Pasteur, Tyndall, Lister, Nägeli, Cohn, Fitz, Schloessing, Muntz, and others prior to 1880 were practically all made with liquid culture media only. Such culture media labour under several serious disadvantages:—

(1) Facility with which they become contaminated with bacteria and other organisms from the air and other surroundings;

(2) The competition which arises between

the different microbes present may lead to the entire suppression of some through the overwhelming multiplication of others;

(3) The great difficulty of obtaining pure cultivations of specific micro-organisms.

The introduction of solid culture media by Koch at the beginning of the 'eighties, in the last century, led to great developments in bacteriology. An immense variety of investigations were now rendered possible which had long been awaiting attack. These new methods of bacteriological study were at once applied to the identification of the specific micro-organisms of numerous diseases, and to the investigation of the bacteria present, in *air, water, soil*, and all our other surroundings.

By means of *gelatin-plate-culture* it became possible to ascertain the number and the nature of most bacteria present in any material. Thus in the case of water the number and nature of the bacteria present in any sample could be determined, and by this means it was possible to ascertain the effect of any treatment or process of purification on the bacteria present in water. Thus it was applied by the writer in 1885 to the study of the removal of bacteria from water by artificial and natural *filtration*, by *subsidence*, and by *precipitation*.

The results obtained in investigations of this kind led to a great modification of the opinions which had previously been entertained with regard to the value of these processes in removing the zymotic dangers of water. Thus it was found that bacteria could be almost wholly removed from water by the process of sand filtration which had a comparatively insignificant effect on the organic matter and other ingredients discoverable by chemical analysis.

Similarly these methods of bacteriological investigation enabled such processes of water purification to be readily controlled. Thus if the safety of a water-supply depends on the efficiency with which the removal of bacteria by filtration is carried out, it is obvious that this efficiency should be continually controlled by bacteriological examination, so that any defect in the working of the filters may at once be detected and rectified. The systematic control of water-works by bacteriological examination is now being very widely carried on with great benefit to the communities concerned.

With the discovery of the specific bacteria of cholera, of typhoid fever, and of many other diseases, attempts were naturally made to find these specific pathogenic bacteria in contaminated water-supplies. The chance of such discovery by the ordinary method of plate-cultivation is, of course, hopelessly remote, because a single pathogenic organism must almost inevitably be accompanied in water by a host of non-pathogenic individuals, and amongst these multitudes of harmless forms the few harmful ones will under ordinary circumstances be overlooked, whilst, in the small quantities of water operated on, the pathogenic forms may be absent, although present in a larger bulk.

To surmount these difficulties, the natural device was to provide conditions which would be favourable to the particular pathogenic form being sought for and less favourable or even antagonistic to the multitude of non-pathogenic forms with which it would be accompanied.

We may call the provision of such conditions the method of *enrichment or preferential culture*.

Such a method of enrichment was very satisfactorily applied by Koch to the discovery of the *cholera-bacillus* in the water of the Elbe at Hamburg during the epidemic of 1892. If 90 c.c. of the water under examination be incubated for 18 hours at 37° with 10 c.c. of a solution containing peptone 10 p.c., and sodium chloride 10 p.c., cholera bacilli will be found in the thin surface pellicle, and from this cultures are made.

Typhoid fever is, of water-borne diseases, the most important in Western Europe. An enormous amount of labour and ingenuity have been devoted in recent years to the discovery of the bacillus of this disease in water. That the problem is a very difficult one may be gathered from the fact that until recently its detection even in the discharges of typhoid patients was very frequently abortive.

The special difficulty attending the discovery of the typhoid bacillus depends on the circumstance that even in the intestine of the typhoid patient it is enormously outnumbered by other bacteria, and especially by the *Bacillus coli communis*, which, discovered by Escherich in 1886, has in recent years achieved the very greatest celebrity in the bacterial world.

Practically all conditions which are favourable to the typhoid bacillus are equally or even still more favourable to the *B. coli*, and for a long time all methods of favouring the typhoid bacillus at the expense of the *B. coli* proved futile. Much interest was, therefore, excited when in 1903 Roth announced that the *B. coli* was more disadvantageously affected than the typhoid bacillus by solutions of caffeine.

Experiments made by Kloumann¹ in 1904, however, showed that the differential effect on the two bacilli was only very slightly in favour of the typhoid bacillus.

A method of testing for typhoid bacilli in water and other liquids was elaborated by Hoffmann and Ficker in 1904; it was also based on the inhibitory action of caffeine and of crystal-violet on the *B. coli*. The method will be best understood by the following description of the manner in which it was successfully employed by Jaksch and Rau (1904) to detect typhoid bacilli in the drinking water supplied to Prague:—

900 c.c. water from a service tap were added to the Hoffmann and Ficker culture-medium, consisting of 10 grms. nutrose, 5 grms. caffeine, and 0.01 gm. crystal-violet, in 100 c.c. water.

The mixture was then incubated at 37° for 13 hours, when it was to be presumed that any typhoid bacilli originally present would have extensively multiplied. Loopfuls of this large cultivation were then withdrawn and spread on the surface of Drigalski and Conradi Plates (agar, meat extract, peptone, nutrose, lactose, sodium chloride, crystal violet and litmus), which were then incubated at 37° for 24 hours. On these plates the *B. coli* colonies are red (acid litmus) and non-transparent, whilst those of the typhoid bacillus are blue with a violet-tinge, transparent, resembling dewdrops, and smaller than the *B. coli* colonies. In the Prague experiments these plates gave only a few red

blue and transparent.

The latter were sub-cultured, and, according to Jaksch and Rau, gave results in the most varied tests (including agglutination, toxicity, and immunisation) which were identical with those obtained with the true typhoid bacillus.

Other solid media which have proved of great value in distinguishing between coli-like and typhoid-like colonies are Loeffler's malachite-green agar, and McConkey's bile-salt-neutral-red agar, both of which will be referred to later.

By far the most extensive, interesting, and systematic search which has ever been made for the typhoid bacillus in natural waters is that carried out by Houston on the waters of the three rivers—Thames, Lea, and New River—from which the greater part of the London water supply is obtained. As this investigation illustrates the most approved methods which are now available to the bacteriologist, it will be considered here in some detail.

Two hundred and ninety-four experiments in 8 series were made with 156 samples of raw river water (52 Thames, 52 Lea, and 52 New River) during the 12 months ended July 31, 1908. The total volume of water dealt with was $294 \times 100 = 29,400$ c.c. The total number of bacteria in this volume of water (as ascertained by gelatin-plate cultivation for 3 days at 20°–22°) was 135,687,500. The total number of colourless (or nearly colourless) colonies sub-cultured from the Drigalski or similar plates was 7329. These 7329 selected colonies form but a small fraction of the millions of bacteria which were excluded owing to the temperature of incubation, the composition of the media employed, and the fact of their appearing on the plate-cultures as coloured colonies.

The following tabular summary indicates the method adopted in this exhaustive investigation:—

Direct Plating on Solid Media.

Series I. 100 c.c. of the sample of water were centrifuged and the resulting deposit spread over a number of plates consisting of malachite-green (1 in 5000), saccharose, dulcitol, salicin, neutral-red, bile-salt, peptone, lactose, agar. The plates were incubated at 40°–42° for 24 hours, and the colourless colonies sub-cultured into special media, as described in the next table.

Series II. Same as Series I, but the proportion of malachite-green was 1 in 10,000.

Series III. Same as Series I, but the medium used in the plates contained no malachite-green.

Series IV. Same as Series I, but the proportion of malachite-green was 1 in 20,000, 1 in 40,000, and 1 in 80,000.

Primary Liquid Cultures followed by Plating on Solid Media.

Series A. 100 c.c. of the sample of water were added to bile-salt-glucose-peptone medium containing malachite-green in proportion of 1 in 1000, 1 in 2000, 1 in 4000. This liquid was incubated at 40°–42° for 24 hours, and then plated on the same medium as was employed in Series I, 10 colourless colonies were in each case sub-cultured and tested as described.

Series B. Same as Series A, but malachite-green in the liquid medium was in proportion

¹ Kloumann, *Centralbl. f. Bakteriologie*, 1904, 36, 312.

of 1 in 8000, 1 in 16,000, 1 in 32,000. Subsequently plated on same medium as that used in Series II.

Series C. Same as Series A, but the liquid culture medium consisted of meat-broth only without malachite-green or any other additions. Subsequently plated on same medium as that used in Series I.

Series D. Same as Series C, but instead of cultivating 100 c.c. of water in one

portion, 10 cultures of 10 c.c. each were made.

The following table shows the behaviour of 32 strains of the typhoid bacillus, on the one hand, and of the 7329 suspicious colonies isolated from the raw waters, on the other. *It will be seen that not one out of all these 7329 different microbes, although suspicious in certain features, gave reactions agreeing in their entirety with those of the typhoid bacillus.*

VERIFICATION TESTS FOR TYPHOID BACILLUS.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Description of microbe.	Proskauer's and Capaldi's No. 2 medium ¹ (with inner tube).	Lactose-saccharose dulcitate-salicin-medium (with inner tube).	Proskauer's and Capaldi's No. 1 medium ² modified (with inner tube).	Glucose-neutral red broth cultures (with inner tube).	Peptone-water medium.	Gelatin sugar media:—galactose, glucose, levulose, maltose, and mannite respectively.
RESULTS CHARACTERISTIC OF TYPHOID BACILLUS.						
32 strains of typhoid bacillus from a number of different laboratories.	Acid, no gas	No visible change (No acid, no gas.)	No visible change. (No acid, no gas.)	Purplish tint. (No gas, no fluorescence.)	No indole	Acid, but no gas with all five sugars. No liquefaction.
RESULTS WHICH EXCLUDE, AS NOT TYPHOID BACILLUS, THE SUSPECTED MICROBES.						
7329 colourless (or nearly colourless) colonies, sub-cultured.	No acid, or acid and gas	Acid or gas-formation.	Acid or gas-formation, or decided growth.	Gas or fluorescence. (Absence of purplish tint.)	Indole	Gas formation in one or all of the sugar media. (Liquefaction.)

¹ Solution of peptone and mannite.

² Solution of asparagine, mannite, glucose, galactose, levulose, maltose, magnesium sulphate, sodium chloride, calcium chloride, potassium hydrogen phosphate, and litmus.

From the very nature of this investigation—the search for a specific microbe in a natural water which at some period in its history is practically certain to have received this microbe in comparatively small numbers—it is impossible to make it really exhaustive. Houston has, however, amplified his previous investigation in a very suggestive manner. Realising that the objection might be raised that the method adopted may not be capable of detecting a very small number of typhoid bacilli in the presence of a very large number of other microbes, he devised a mode of procedure which enabled him to affirm that in each particular sample of water examined there were *not more* than a certain definite number of typhoid bacilli in a given volume. The method adopted was this:—

Each sample of raw river water was divided into two equal portions of 500 c.c. (A and B). The A sample was inoculated with a very small number of typhoid bacilli. The B sample was not so infected, and was, therefore, normal raw river water. The subsequent procedure was exactly the same in each case, both samples A and B being treated exactly alike. The 500 c.c. of water were centrifuged and the resulting deposit spread over 16 plates prepared with solid medium of the following composition:

Agar, 2 grms.; peptone, 2 grms.; bile-salt, 0.5 grm.; lactose, saccharose, adenite, raffinose,

and salicin, each 0.2 grm., made up with water to 100 c.c. and tinted with 0.4 c.c. of a 1 p.c. solution of neutral red. In some of the experiments malachite-green was added to the above, in the proportion of either 1 to 10,000, or 1 to 5000 of the medium.

Of the 24 experiments, 14 were carried out with raw Lea, and 10 with raw Thames, water. These waters contained on an average 62,688 bacteria per 1 c.c. (gelatin at 20°–22°, 3 days' incubation). The worst sample contained 760,000 and the best sample 1200 bacteria per 1 c.c. Thus in the 12 litres (500 c.c. × 24) of raw water (B samples) examined for typhoid bacilli there were 752,256,000 bacteria present.

The total number of colonies selected for study was 5451 from the infected A samples, and the same number (5451) from the non-infected B samples. The average number of typhoid bacilli artificially added to the A samples was 2.242 per 1 c.c. or 1121 per 500 c.c. The average number of typhoid bacilli isolated from the A samples was 14.54 per 500 c.c. of sample. It may be argued fairly, therefore, that if only $\frac{1}{14.54}$ of the above number of typhoid bacilli had been present in the infected sample this microbe would still have been detected by the method of investigation adopted; but $\frac{1}{14.54} \times$

2-242=0.154 typhoid bacillus per 1 c.c., or 1 typhoid bacillus in 6.5 c.c. would have been detected.

From the uninfected B samples, out of the 5451 colonies selected for special study, one, and only one, consisted of bacteria which resembled the typhoid bacillus very closely.

It will be instructive to record the observations which were made on submitting this typhoid-like microbe (Lea W. 694 ? *B. typhosus*, Houston) to the several tests used in the diagnosis of typhoid bacilli.

*Characterisation of typhoid-like bacillus from raw river water (Lea W. 694 ? *B. typhosus*, Houston).*

Morphology.—A motile multiflagellate bacillus. The rods seemed shorter than in most strains of *B. typhosus*.

Gelatin and agar slope-cultures.—Possibly the growth was slightly less filmy in character than that of the true *B. typhosus*.

Glucose-bile-salt agar-slope (neutral red).—The streak somewhat brighter and cleaner red than in most strains of *B. typhosus*.

Lactose-bile-salt agar-slope (neutral red).—Colourless streak.

Potato.—No visible growth (5 days at 37°).

Nitrate-broth.—Reduces nitrates to nitrites.

Peptone-water at 55°F.—No visible growth after 5 days; on transferring tube to incubator at 37°C. growth occurred within 24 hours.

Indole test.—No indole formation (5 days at 37°).

Liquid peptone (1 p.c.) media containing separately 1 p.c. of the substances stated and tinted with litmus. Sorbite and inosite are only used in 0.2 p.c. solution. Acid but no gas in sorbite, mannite, glucose, levulose, galactose, and maltose respectively (2 days at 37°). No change in inulin, inosite, saccharose, salicin, adonite, lactose, dulcete, and raffinose respectively (5 days at 37°).

Gelatin glucose medium tinted with litmus.—Acid but no gas formation.

Voges and Proskauer's reaction.—Negative result, 5 days.

Gelatin.—No liquefaction after one month at 20°.

Litmus milk.—Slight acid but no coagulation (5 days at 37°).

Glucose-neutral-red-broth cultures.—No gas, no fluorescence characteristic purplish tint.

Lactose-saccharose-dulcete-salicin-peptone medium tinted with litmus.—No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 1 (modified).—No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 2.—Acid but no gas.

Agglutination experiments and tests for pathogenicity.

Anti-typhoid serum.—Microscopically, 1 : 200 almost instantaneous clumping, 1 : 800 very fair clumping, 1 : 2000 little or none. *B. typhosus* tested with the same serum gave very similar results but appeared to be clumped slightly more rapidly and in slightly higher dilutions. The difference, however, if any, was not well marked.

* *Serum of an animal immunised with the suspected microbe (Lea W. 694 ? *B. typhosus*, Houston).*—Microscopically, 1 : 200 very rapid and satisfactory clumping; 1 : 2000 good, but not quite complete clumping within half an hour.

B. typhosus tested with the same serum gave very similar results, but was perhaps clumped a little more slowly and in slightly lower dilutions. The difference, however, if any, was not well marked. Microscopically, the titre limit was about 1 : 8000 (18 hours) and was practically the same for both microbes.

Pathogenicity.—2 c.c. of a broth-culture injected subcutaneously into a guinea-pig produced a swelling and illness with recovery. A guinea-pig intraperitoneally inoculated with 5 c.c. of a broth-culture died in less than 24 hours.

On the results of this laborious investigation, which had extended over more than two years and which had been conducted with the most meticulous care and regardless of time or money, Dr. Houston very cautiously remarks: 'If this microbe had been isolated from a case of typhoid fever (or from a suspected case) I do not think any serious hesitation would have been felt in describing it as *B. typhosus*.'

It would be impossible to produce more eloquent testimony than the above as to the enormous and almost prohibitive trouble which a systematic and conscientious search for the typhoid bacillus in natural water entails.

Comparative unimportance of searching for the typhoid bacillus in water.—The almost hopeless nature of the search for the typhoid bacillus in natural waters is of the less importance as the anxiety to detect this microbe in water is, for the most part, based upon an entire misconception of the objects of water examination. The object of a water examination is, in general, not to determine whether the particular sample of water contains typhoid bacilli and is, therefore, capable of carrying typhoid to the consumer, but to discover whether the water is likely at any time to contain such infective material.

Now any water which receives sewage matters must be regarded as a possible carrier of typhoid infection, for at any time these sewage matters may be derived from persons suffering from typhoid. Thus any sewage-contaminated water is a potential carrier of typhoid unless it has been subjected to conditions which would ensure the removal of the possibly present typhoid bacillus. Thus the all-important thing is to ascertain whether a given water has been contaminated with sewage, in what proportion such contamination has taken place, and whether the water since such contamination has been submitted to conditions which would remove or destroy typhoid bacilli should they have gained access with the sewage matters.

Firstly, as regards the detection of sewage contamination. Excremental contamination, if sufficient in amount, can be revealed with more or less certainty by chemical analysis, which can indeed even distinguish between whether such pollution is recent or remote in point of time, but in order to ascertain the fate of bacteria gaining access to water recourse must be had to biological methods. If there were bacteria absolutely characteristic of sewage, the determination of their presence would be sufficient to

prove the danger of a water. Unfortunately we do not know of any bacteria which satisfy the condition of being *absolutely* characteristic of sewage, so we must be satisfied with a second best qualification for diagnostic purposes by those which are *very* characteristic of sewage.

The microbe which is most characteristic of the intestinal discharges of man and the higher animals is, as its name implies, the *B. coli communis*, and a great amount of time and ingenuity has been devoted to its accurate and expeditious discovery in water and other materials.

In identifying a particular organism, whether plant or animal, we depend on recognising in the individual a certain group of specific characters which are more or less arbitrary. The botanist at first tried to classify and distinguish bacteria by external appearances alone; he measured the length and breadth of these minute organisms; he counted the number of flagella with which some of them are provided; he was very careful to observe whether they were square or round at the ends, and so forth.

These morphological characters have, however, long been recognised as inadequate for purposes of identification, since organisms exhibiting the closest morphological similarity have been found to differ enormously in other respects.

After the introduction of Koch's methods much attention was directed to the macroscopic appearances to which the organisms give rise when grown on a variety of solid media, by which means microscopically similar bacteria can often be differentiated.

Some 35 years ago the writer commenced distinguishing bacteria, which were similar in form and in cultural appearances, by differences in the chemical changes which they could bring about in certain media. Thus he found that the capacity to reduce nitrates to nitrites was in some cases a valuable means of distinguishing between otherwise similar bacteria. This reduction of nitrates has been extensively used for diagnostic purposes, more especially by American bacteriologists. Somewhat later he devoted much attention to the fermentation of carbohydrates, polyhydric alcohols, and hydroxy-acids, by means of pure cultivations of micro-organisms, and showed how capricious is the power possessed by different bacteria in this respect. Thus perhaps one microbe will ferment glucose, mannite, and glycerol, but not dulcitol or glyceric acid, another will ferment glucose, mannite, and dulcitol, &c.

There are, however, many bacteria which more or less simulate the characters of the typhoid bacillus on the one hand, and of the *B. coli* on the other; such forms exhibit almost every degree of approximation to one or other of these two types, from which they can only be distinguished by applying a number of tests. Such forms are designated as *atypical*, and what their relationship to the typical typhoid and coli bacteria may be is a matter of uncertainty. Possibly in some cases they may have been typical forms originally, but under the particular conditions to which they have been submitted they have lost some of their characters. Thus it is often found that the *B. coli*, on prolonged

artificial culture, may lose either or both its indole-producing and milk-curdling properties.

This mode of differentiating between otherwise very similar forms of bacteria has been greatly extended within recent years. In the following table the classification of the Typhoid-coli group of bacteria into seven sub-groups has been attempted:—

TYPHOID-COLI GROUP.

Sub-groups	Glucose	Acid gas	Lactose	Acid gas	Dulcitol	Acid gas	Saccharose	Acid gas
I.								
<i>B. Typhosus</i> :	+	-	-	-	-	-	-	-
<i>B. dysenteriae</i> :	+	-	-	-	-	-	-	-
<i>B. faecalis-aeruginosa</i> :	-	-	-	-	-	-	-	-
II.								
<i>B. enteritidis</i> (Gaertner) :	+	+	-	-	+	+	-	-
<i>B. paratyph</i> :	+	+	-	-	+	+	-	-
<i>B. paracoli</i> :	+	+	-	-	+	+	-	-
III.								
Bacillus from urine :	+	+	-	-	-	-	+	+
IV.								
<i>B. acid lactici</i> (Huppe) :	+	+	+	+	-	-	-	-
V.								
<i>B. coli</i> (Escherich) :	+	+	+	+	+	+	-	-
VI.								
<i>B. pneumoniae</i> (Friedländer) :	+	+	+	+	+	+	+	+
VII.								
<i>B. capsulatus</i> (Pfeiffer) :	+	+	+	+	-	-	+	+
<i>B. lactis aerogenes</i> (Escherich) :	+	+	+	+	-	-	+	+
<i>B. cloacae</i> (Jordan) :	+	+	+	+	-	-	+	+

It is obvious that by increasing the number of biochemical tests many further variations of a given type of organism may be discovered, and, for the purpose of more precisely defining a particular microbe, bacteriologists have introduced biochemical tests involving the use of a variety of organic compounds—more especially carbohydrates, polyhydric alcohols, and glucosides. These tests generally consist in ascertaining whether an organism under investigation gives rise to acid or gas, or both, or neither, in a suitable nutritive medium containing one of these substances. The following list of substances employed in this manner will give some idea of the degree to which these biochemical tests have been complicated in recent years: adonite, asparagine, dextrin, dulcitol, erythrite, galactose, glucose, glycerol, glycol, isodulcitol, lactose, laevulose, maltose, mannite, mannose, nutrose, raffinose, sucrose, salicin, sorbite, and starch. The above list by no means exhausts the number of organic substances which are acted on by bacteria, and by means of which, therefore, differences can be established.

Although such tests are extremely useful for the more precise definition of particular micro-organisms, they must be employed with discrimination, for as the writer long ago pointed out, these fermentations, as well as other characters of bacteria, are liable to be lost through conditions of environment, and he has also shown how in some cases they may

restored by resorting to particular methods of culture and training.

It is obvious that it would be impracticable to resort to such numerous tests in the ordinary bacteriological examination of water in which we are concerned with the detection of sewage or excremental contamination, unless some very great advantage should result from such multiplication of tests, and this is not the case at present.

Quantitative determination of B. coli in water.

—If we regard the *B. coli* provisionally as the best indicator of contamination with the living bacteria of animal refuse, we shall obviously view its presence with the more suspicion the larger the numbers in which it is discovered in a given volume of water.

The numerous methods which have from time to time been devised for detecting *B. coli* will be passed over, and only the one which in this country at any rate has superseded all others will be described.

An important departure in practical bacteriology was the introduction by McConkey and Hill ('Bile-salt broth. A simple test for faecal contamination.' Thompson-Yates Laboratories Report, 1901, 4, [i.] 151) of a medium for the preferential culture of the *B. coli* and allied microbes from mixtures of micro-organisms. The essential ingredients of this medium are sodium taurocholate (bile-salt) 5 grms., glucose 5 grms., peptone 20 grms., water (tinted with litmus) 1000 c.c. Incubated in this liquid at 37°-42° bacteria of the *B. coli* group give acid and gas in 48 hours. Some bacteriologists use lactose instead of glucose, thus restricting the gas production to *B. coli* and its still closer allies. With this liquid medium in Durham fermentation-tubes cultivations of the water are made in the following quantities: 100, 10, 1, 0.1, 0.01, 0.001, 0.0001, 0.00001 c.c. The concentration of the medium should in all cases be approximately the same as that given above. In order, therefore, that the volumes of liquid incubated may not be inconveniently large, the 10 and 100 c.c. of water are introduced into correspondingly stronger McConkey media.

A positive reaction, i.e. the production of acid and gas, in any of these culture-tubes signifies that at least one coli-like microbe must have been introduced with the portion of water added. Thus, if acid and gas had been obtained, in a particular case, with all the tubes from 100 to 0.1 c.c., this would mean the 'presumptive' presence of at least one *B. coli* in 0.1 c.c., and its absence in 0.01 c.c. and smaller volumes of water.¹

¹ There is one element of uncertainty connected with such tests made in liquid media which appears to be tacitly ignored by all bacteriologists who make use of them, and that is that the particular microbe sought for may in the process of cultivation in the liquid medium become hopelessly outnumbered or even suppressed by the much more abundant proliferation of some other microbe or microbes present in the mixture.

Thus the McConkey medium may be taken as especially favourable for the proliferation of bacteria of the *B. coli* type, but the water-bacteriologist is in general restricting his search to those bacteria which are sufficiently like typical *B. coli* as to produce acid and gas in the medium. Is it not possible that the bacteria capable of producing both acid and gas may be so greatly outnumbered by microbes not giving this reaction that the more typical *B. coli* forms may be so much kept in abeyance that no acid and gas reaction is obtained? Under these circumstances he would

• In order to ascertain whether the 'presumptive' *B. coli* is typical or not, the tube containing the smallest portion of water which has given rise to acid and gas in the McConkey medium is plated on a solid medium of the following composition: Agar 20 grms., peptone 20 grms., sodium taurocholate (bile-salt) 5 grms., lactose 10 grms., neutral red (1 p.c. solution) 4 c.c., made up to 1000 c.c. with water. After 12 hours' incubation at 37°, the colonies will be distinctly visible, and those which are most likely to be *B. coli* will have a strong red colour owing to the acid produced by this microbe in the medium. Five of the most typical red colonies are separately inoculated into 5 glucose-litmus broth tubes, which are then incubated at 37°. Any of these 5 tubes which develop acid and gas are then each further inoculated into tubes of the following media which are then incubated at 37°:—

(a) Neutral red broth to be examined for fluorescence.

(b) Litmus lactose-broth to be examined for acid and gas.

(c) Ordinary broth to be examined for indole.

(d) Litmus-milk to be examined for acid and coagulation.

(e) Gelatin to be examined for non-liquefaction.

The above glucose-tubes from which these inoculations have been made are also microscopically examined to see whether the microbe possesses the characteristic form and motility of the *B. coli*.

A microbe fulfilling these conditions has been designated by Houston as 'Flaginac' *B. coli*, from Fl—fluorescence in neutral-red broth, ag=acid and gas in lactose, in=indole in peptone broth, ac=acid and coagulation in litmus-milk.

The typical *B. coli* from human faeces gives these reactions, but, of course, it is possible to further differentiate between coli-bacteria by additional tests, such as fermentation of sucrose, dulcitol, mannitol, &c., but at present there would not appear to be any advantage in such multiplication of tests in the ordinary examination of water.

The following table summarises an interesting investigation made by Houston on the proportion of 'Flaginac' *B. coli* found amongst the coli-like microbes obtained from different sources:—

FLAGINAC *B. COLI*.

Source	Number of specimens of <i>B. coli</i> or coli-like microbes on which flaginac percentage is based	P.c. of microbes which flaginac <i>B. coli</i> .
Milk	343	61
Human faeces	101	85
Sewage	several hundreds	65-85
Oysters	464	43
Estuarial waters	183	66
Water-cress	81	40
Washings of cress	52	52
Water in which was grown	42	76
London filtered water	232	31

obviously draw the conclusion, and quite erroneously, that acid and gas producing microbes (and, therefore, *B. coli* amongst them) were absent. This is a matter which requires much further investigation before the conclusions as to absence of *B. coli* generally drawn can be justified.

In the following table are recorded the results of some very suggestive pioneering experiments made by McConkey (1905), undertaken with the object of ascertaining whether there is any marked difference in the types of *B. coli* found in the excreta of man and some of the common domestic animals respectively. Should it be possible to establish such a difference, an important means of distinguishing between human and animal excrementitious contamination of water would be obtained.

Such an investigation would have to be enormously extended before results capable of being used for diagnostic purposes could be obtained.

An attack on the same important problem was also made by Dr. Wm. G. Savage (1904-5) in an extremely laborious investigation, which he has summarised in the foregoing table.

The absence of streptococci in the faeces of the pig is extremely remarkable.

It is convenient to classify waters tentatively

B. COLI FROM HUMAN AND ANIMAL EXCRETA (McCONKEY).

Group	Fermentation of		Number of lactose-fermenting Coll-form microbes isolated and experimented with			Results in percentages		
	Saccharose	Dulcitol	Human	Animal ¹	Total	Human	Animal	Average
I.	—	—	83	37	120	34	15	25
II.	—	+	93	85	178	38	36	37
III.	+	+	36	74	110	15	31	23
IV.	+	—	29	43	72	12	18	15
			241	239	480	100	100	100

¹ Twenty-five samples of animal excreta, of which 5 were from horses, 6 from cows, 3 from rabbits, 1 from a monkey, and 14 from a cat.

Source	Approximate number per 1 gram of excreta		
	<i>B. coli</i>	<i>Streptococci</i>	<i>B. enteritidis sporogenes</i> spores
Horse No. 1	Over 1 million	$\frac{1}{10}$ to 1 million	10 to 100
Horse No. 2	$\frac{1}{10}$ to 1 million	Over 1 million	100 to 1000
Horse No. 3	1000 to 10,000	Over 1 million	100 to 1000
Cow No. 1	$\frac{1}{10}$ to 1 million	10,000 to 100,000	100 to 1000
Cow No. 2	10,000 to 100,000	$\frac{1}{10}$ to 1 million	10 to 1000
Cow No. 3	1 to 10 millions	Over 10 millions	10 to 100
Cow No. 4	1 to 10 millions	$\frac{1}{10}$ to 1 million	100 to 1000
Pig No. 1	Over 100 millions	Absent	$\frac{1}{10}$ to million
Pig No. 2	10 to 100 millions	Absent	10,000 to 100,000
Pig No. 3	70 millions	Absent	1000 to 10,000
Sheep No. 1	10 to 100 millions	1 to 10 millions	10 to 100
Sheep No. 2	10 to 100 millions	10 to 100 millions	10 to 100

according to the results of the examination for *B. coli*, thus :—

CLASSIFICATION OF WATER BY B. COLI TEST. (1 c.c. of sewage is assumed to contain 100,000 *B. coli*.)

Class	Volume of water examined	<i>B. coli</i> per 1 c.c.	Pollution in sewage
	c.c.		per cent.
I	— in 100	0	—
II	+ in 100	0.01	0.00001
III	+ in 10	0.1	0.0001
IV	+ in 1	1	0.001
V	+ in 0.1	10	0.01
VI	+ in 0.01	100	0.1
VII	+ in 0.001	1,000	1
VIII	+ in 0.0001	10,000	10
IX	+ in 0.00001	100,000	100 (pure sewage)

This classification must not, however, be interpreted too rigidly, as it is based on the assumption that *B. coli* is always derived from faeces and that this microbe is incapable of multiplication under any circumstances after incorporation in what is known as 'sewage.'

In the two following tables are recorded the results of the ordinary bacteriological examination of a number of typical waters. The tables sufficiently explain themselves.

Storage of water.—In 1886 (Water Purification, its Biological and Chemical Basis, Trans. Inst. Civil Engineers, 1886) the writer pointed out the great importance from a theoretical point of view of storage for the purification of surface waters. In 1892, again, he investigated the influence of storage on the bacteriological purity of the river waters abstracted for the supply of London, and showed that there is a most striking reduction in the number of

WATER.

BIRMINGHAM WATER SUPPLY. (P. F. Frankland.)
Averages for 1910.

	Number of bacteria				<i>Bacillus coli</i> (typical)						
	Gelatin at 20°C.		Carbollic gelatin at 20°C.	Taurocholate agar at 37°C.	100 c.c.	100 c.c.	10 c.c.	1'0 c.c.	0'1 c.c.	0'01 c.c.	0'001 c.c.
	2 days	7 days	7 days	4 days	—	+	+	+	+	+	+
Whitacre ¹ —					p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Unfiltered .	3300	—	167	1232	—	—	—	8'3	16'7	58'3	16'7
Filtered .	12	87	0	5	75'0	25'0	—	—	—	—	—
Frankley ¹ —											
Inlet .	37	237	0'7	13	18'2	45'5	36'4	—	—	—	—
Reservoir .	54	258	1'6	40	41'7	33'3	25'0	—	—	—	—
Filtered .	5	38	0	3	91'7	8'3	—	—	—	—	—
City mains .	19	59	0'03	5'5	78'4	16'2	5'4	—	—	—	—

LONDON WATER SUPPLY. (Houston.)
Averages for 1908-9 and 1909-10.

	<i>Bacillus coli</i> (typical)										
	No of bacteria gelatin at 20°C 3 days	100 c.c.	100 c.c.	10 c.c.	10 c.c.	0'1 c.c.	0'01 c.c.	0'001 c.c.	0'0001 c.c.	0'00001 c.c.	0'000001 c.c.
Raw River Waters—											
Thames at Hampton, 1908-9 .	2558	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Thames at Hampton, 1909-10 .	5268	0'5	0'5	6'3	26'9	52'9	12'8	—	—	—	—
Lea at Ponder's End, 1908-9 .	8794	—	0'8	5'2	34'9	38'8	15'5	3'0	0'8	—	—
Lea at Ponder's End, 1909-10 .	37,071	—	0'5	6'3	31'4	39'7	13'2	7'3	0'5	0'5	0'5
New River at Hornsey, 1908-9 .	1118	2'1	9'1	40'0	38'8	8'2	0'8	—	—	—	—
New River at Hornsey, 1909-10 .	2801	0'9	8'3	41'7	36'8	9'8	2'4	—	—	—	—
Filtered Waters—											
Thames, 1908-9 .	89	83'4	11'8	3'9	0'7	0'06	—	—	—	—	—
" 1909-10 .	55	81'8	14'6	2'7	0'7	0'09	0'02	—	—	—	—
Lea, 1908-9 .	163	85'1	10'1	4'1	0'7	—	—	—	—	—	—
" 1909-10 .	237	88'1	8'9	2'3	0'6	—	—	—	—	—	—
New River, 1908-9 .	7	88'3	9'4	2'0	0'07	0'07	—	—	—	—	—
" " 1909-10 .	16	82'6	14'1	2'0	0'3	—	—	—	—	—	—
Deep Wells—											
Kent, 1908-9 .	6	92'3	4'7	1'2	1'7	—	—	—	—	—	—
" 1909-10 .	8	96'2	3'3	0'4	—	—	—	—	—	—	—
Lea Valley, 1908-9 .	19	79'1	13'6	2'7	4'5	—	—	—	—	—	—
" " 1909-10 .	16	89'0	8'8	2'1	—	—	—	—	—	—	—

suspended micro-organisms during storage in large reservoirs.¹

¹ Appendixes to Minutes of Evidence, Roy. Commission on Metropolitan Water Supply, 1893, 469-475. See also "Micro-organisms in Water," P. Frankland and G. O. Frankland, London, 1894, pp. 99, 126, 181-142, 184.

The great importance of storage from the hygienic point of view was further manifest from the experiments made on the fate of pathogenic bacteria introduced into natural waters, and which showed that the duration of life of these bacteria under such conditions is generally very short.

In 1891-4 the writer had the opportunity of greatly extending his observations on this subject, as he was requested by a Committee of the Royal Society to make, in conjunction with the late Professor Marshall Ward, F.R.S., a special inquiry into the vitality of pathogenic bacteria in potable waters (see Proc. Roy. Soc.). The experiments were restricted to the study of the behaviour of the anthrax bacillus (and its spores), the typhoid bacillus, and the *B. coli communis*, and the potable waters employed were those of the Thames, Loch Katrine, and deep-well water from the chalk, these being fairly typical of the different kinds of water used for drinking purposes in this country. Experiments were made with these waters in their natural, and also in a sterilised, condition.

The results obtained may be summarised as follows:—

(1) Unsterilised water infected with anthrax bacilli containing spores was still virulent after being kept for 7 months.

(2) Anthrax bacilli taken directly from an animal dead of anthrax, and, therefore, free from spores, died rapidly (mostly in 5 days) when introduced into unsterilised water kept at low temperatures (5° and 13° in these experiments), but when introduced into the same waters and kept at 19°, the bacilli formed spores, and the latter were still present in enormous numbers even 42 days later, and doubtless for a much longer period still. This remarkable difference in behaviour is accounted for by the fact, previously discovered by Koch, that anthrax bacilli do not form spores below 16°.

The following results were obtained by introducing typhoid bacilli from one and the same cultivation and in the same numbers into each of the waters at one and the same time:—

Unsterilised water	Life of typhoid bacilli
Thames water (Oct. 19, 1893) 9°-12°	Between 0 and 13 days
Loch Katrine water (Oct. 19, 1893) 9°-12°	
Deep well water (Oct. 10, 1893) 9°-12°	
In two other separate experi- ments with unsterilised Thames water (May 11, 1893)	" 25 " 34 "
and (Jan. 16, 1894) : :	" 20 " 27 "

In all these experiments only 1 c.c. of water was examined for typhoid bacilli, and the method of search, the best known at the time, was that due to Parietti, in which the water is cultivated in a phenol-broth medium at 37°, which on becoming turbid is submitted to plate-cultivation, the colonies obtained being then examined in detail for identification.

It is particularly interesting to compare with the above results those obtained by Houston in a perfectly similar inquiry and making use of all the most modern developments of bacteriological technique. Dr. Houston made 18 experiments on raw Thames, Lea, and New River waters, infecting them with typhoid bacilli (the number added being in all but three experiments very large, see table below). The presence of the bacillus was tested for at weekly intervals in 1 c.c. by means of a medium con-

taining *Agar-bile-salt-dulcitol-lactose-saccharose-salicin-peptone-neutral-red-malachite-green*, and which is specially designed to favour the growth of this microbe whilst repressing that of most others. The results may be summarised in the following statement:—

In 3 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 1 week.

In 10 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 3 weeks.

In 16 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 4 weeks.

In 18 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 5 weeks.

Thus, notwithstanding the great advances made in the technique of testing for the typhoid bacillus, the results obtained by Houston are essentially similar to those obtained by the writer 15 years previously. Houston has, however, extended the investigation in an interesting manner by ascertaining the length of time required before even 100 c.c. of the infected water gave a negative result on being tested by the most modern methods for the presence of the typhoid bacillus. The whole of Houston's investigations (both for 1 c.c. and for 100 c.c. of water tested) is instructively summarised in the table on p. 414.

This table shows, on the one hand, that whilst in each case nearly all the typhoid bacilli are destroyed by a single week's residence in these raw river waters, a few individuals persist for a much longer period of time. This illustrates in a very interesting and instructive manner a principle emphasised by the writer some 16 years before, 'that one of the factors determining the longevity of pathogenic bacteria placed in water, or for the matter of that placed in any unfavourable surroundings, is the absolute number in which they are present. In other words, amongst, for instance, 1000 bacteria taken from a given source there may be *some individuals* which will resist a particular reverse influence, whilst amongst 10 bacteria taken from the same source there may be *none* capable of resisting the adverse influence in question' (P. F. Frankland, Proc. Roy. Soc. 1894, 66, 486).

Before leaving the subject of the behaviour of the typhoid bacillus in water, mention must be made of some extremely interesting and ingenious experiments by the American bacteriologists, Jordan, Russel, and Zeit, in 1903. These investigators endeavoured to imitate natural conditions more closely than has been done in any other experiments by placing the typhoid-infected waters in permeable sacs made of celloidin and parchment, and then by submerging these in river, canal, or lake water, their contents were exposed to the influence of the dialysable substances present in the water under natural conditions.

Zeit experimented with Lake Michigan water and Chicago river water, the natural bacterial content of which varies between 68 and 2000 microbes per 1 c.c. in the case of the Lake, and between 80,000 and 1,500,000 microbes per 1 c.c. in that of the river water. Parallel experiments were made with infected water placed in ordinary bottles and in permeable sacs respectively. The typhoid bacilli introduced varied between 500 and 2,000,000 per 1 c.c. The destruction of the typhoid bacillus

was taken as complete when negative results were obtained on cultivating 5 c.c. of the water, the death of the typhoid bacillus being generally confirmed by the subsequent cultivation, a few days later, of much larger volumes, sometimes as much as 800 c.c. of the water. Nine experiments were made with the Michigan Lake water, the typhoid bacillus being never found after the eighth day. Five experiments were made with the Chicago River water, the typhoid bacillus being never found after the third day.

Jordan experimented with the water of the Chicago Drainage Canal, which usually contains from 100,000 to 400,000 bacteria per 1 c.c. This water was infected with from 180 to 857,000 typhoid bacilli per 1 c.c. In these experiments, however, the maximum volume

submitted to cultivation appears to have been only 1 c.c., and from negative results with even smaller volumes the death of the typhoid bacillus seems to have been concluded. Twenty-eight experiments were made in permeable sacs submerged in the canal, the typhoid bacillus being never detected after the second day, excepting in one experiment in which it was still found on the tenth day.

Russel's experiments were made with the Illinois River water, which contains from 1800 to 4000 bacteria per 1 c.c. This water was infected with 540 to 20,000 typhoid bacilli per 1 c.c. However, in these experiments, again, 1 c.c. appears to have been the maximum volume of water cultivated for the detection of the typhoid bacillus. Fourteen experiments

Description of water	Initial No. of typhoid bacilli in 1 c.c. of infected water	Number of typhoid bacilli in 1 c.c. of infected water after					Number of weeks required for destruction of typhoid bacillus in 100 c.c. of infected water
		1 week	2 weeks	3 weeks	4 weeks	5 weeks	
Thames (I)	40	(p.c. reduction) 100					5
Lea (I)	40	100					5
New River (I)	40	100					6
Thames (II)	170,000	9	99.9	2	0		6
Lea (II)	170,000	53	99.9	2	0		5
New River (II)	170,000	40	99.9	0	0		6
Thames (III)	470,000	480	99.9	31	5	0	8
Lea (III)	470,000	850	99.8	11	7	0	7
New River (III)	470,000	1430	99.7	14	7		7
Thames (IV)	8,000,000	3000	99.9	30	4	0	8
Lea (IV)	8,000,000	2000	99.9	20	5	0	8
New River (IV)	8,000,000	400	99.9	22	2	0	9
Thames (V)	525,000	12	99.9	1	0		8
Lea (V)	525,000	32	99.9	2	0		7
New River (V)	525,000	29	99.9	3	0		5
Thames (VI)	475,000	210	99.9	12		1	9
Lea (VI)	475,000	80	99.9	11	2	0	8
New River (VI)	475,000	30	99.9	3	0		7

were made in permeable sacs submerged in the Illinois River, the typhoid bacillus being never found after the third day, excepting in one case in which it was detected on the ninth day.

More recently, again, Houston has taken typhoid bacilli not from cultivations but from the human subject and introduced them into raw Thames water. He found that such bacilli perished very rapidly—much more quickly in fact than had been his experience with cultivated strains of the microbe.

The uncultivated typhoid bacteria were obtained from the urine of a 'typhoid carrier,' and on Aug. 9, 1910, the centrifuged deposit (3.5 c.c.) from 389 c.c. of urine was added to 8000 c.c. of raw Thames water; the number of typhoid bacilli was determined as follows:—

At time of mixture, 770,000 typhoid bacilli per 1 c.c. of river water.

After 1 week, 4 typhoid bacilli per 1 c.c. of river water.

After 2 weeks, 0 typhoid bacilli in 100 c.c.

On the 24th day from the commencement of the experiment half-a-pint (about 284 c.c.) of the infected water was drunk, this quantity of water having originally contained 218,680,000 typhoid bacilli. Similar amounts were drunk with impunity on the 25th, 26th, 27th, and 28th days after the beginning of the experiment.

On Aug. 19, 1910, the experiment was repeated with a fresh sample of urine, the number of typhoid bacilli per 1 c.c. of river-water being 1650. A week later no typhoid bacilli could be found, and on the 23rd, 24th, 25th, 26th, and 27th day from the beginning half-a-pint of the infected water was drunk each day without any ill-effect (Sixth Research Report, Metrop. Water Board, Nov. 1910, p. 7).

If this drinking part of the experiment is to prove anything it would be necessary for Dr. Houston to follow it up by drinking a similar number of fresh typhoid bacilli from the same

patient and contracting the disease, for without this last act we have no certainty that Dr. Houston is susceptible to this malady, and, therefore, a fit *corpus vile* on which to make this crucial test.

Vitality of the Spirillum of Asiatic cholera in potable water.—Experiments were made by Houston with the cholera spirillum on exactly the same lines as those which he had previously adopted in the case of the typhoid bacillus in raw Thames, Lea, and New River water. The principal conclusions arrived at may be summarised as follows (4th Report on Research Work, Metrop. Water Board, June, 1909):—

(1) Cholera vibrios die very rapidly in raw Thames, Lea, and New River water as the result of storage in the laboratory. At least 99.9 p.c. perished within one week, and in none of the experiments could any cholera vibrios (recognisable as such) be found even in 100 c.c. of water 3 weeks after its infection. In more than half the experiments the results were negative by the second week.

(2) The isolation of cholera vibrios from artificially infected raw river water presents no insuperable difficulties even when the number artificially added is very small, both actually and relatively to the bacteria nominally present in the river water.

(3) On the other hand, microbes liable (after careful study) to be mistaken for true cholera vibrios were not found in comparable, but non-infected, river water samples examined under precisely similar conditions.

Thus the cholera vibrios are much more perishable in these raw river waters than are the typhoid bacilli under similar conditions.

The comparatively short duration of life of pathogenic bacteria when introduced into natural waters and more especially into surface waters, which these numerous and independent investigations establish, clearly show that the process of storage in large reservoirs must form a very important safeguard against the water-carriage of zymotic diseases. This safeguard, which is supplementary to and quite independent of that of filtration, has the great advantage of being under perfect control and much less liable to accidental disturbances than are most other methods of water-purification. It is, however, unfortunate that many reservoirs attached to water works have not been designed so as to secure the maximum advantages of storage, and their rearrangement with this object in view is generally a matter of great expense and sometimes impracticable. It is to be hoped that in future engineers will be more careful to arrange for such a circulation of the water that each particle of water entering shall remain as long as possible in the reservoir before passing out.

The influence of storage on the bacteriology of surface waters has recently been made the subject of very extended and interesting investigations by Houston in connection with the London water supply. There can be no doubt that adequate storage brings about the following beneficial changes:—

(1) Reduces the number of bacteria of all sorts.

(2) Reduces the number of bacteria capable of growing on agar at blood heat.

(3) Reduces the number of bacteria capable of growing in a bile-salt medium at blood heat.

(4) Reduces the number of coli-like microbes.

(5) Reduces the number of typical *B. coli*.

(6) Alters certain bacteriological ratios for river-waters, e.g. it reduces the number of typical *B. coli* to a proportionately greater extent than it reduces the number of bacteria of all sorts.

(7) If sufficiently prolonged, it devitalises the microbes of water-borne disease (e.g. the typhoid bacillus and the cholera vibrio).

(8) Reduces the amount of suspended matter.

(9) Reduces the amount of colour.

(10) Reduces the amount of ammoniacal nitrogen.

(11) Reduces the amount of oxygen absorbed from permanganate.

(12) Usually reduces the hardness and may reduce (or alter the quality of) the albuminoid nitrogen.

(13) Alters certain chemical ratios for river-waters; e.g. the colour results improve more than the results yielded by the permanganate test.

(14) Has a marked 'levelling' effect on the totality of water delivered to the filter-beds.

(15) Tends generally to lengthen the life of the filters (only under exceptional conditions is the contrary true).

(16) An adequately stored water is to be regarded as a 'safe' water, and the 'safety change' which has occurred in a stored water can be recognised by appropriate tests.

(17) The use of adequately stored waters renders any accidental breakdown in the filtering arrangements much less serious than might otherwise be the case.

The experimental basis for many of the above statements with regard to the benefits of storage will be found in the table on p. 416 (Houston, Annual Report, March 31, 1910, p. 52):—

Fæcal streptococci in water.—Attempts have been made to supplement the indications of fæcal contamination yielded by the presence of *B. coli*. The most recent and noteworthy of these is the examination of water for the presence of certain streptococci which are usually very abundant, sometimes even more abundant, in human fæces than is the *B. coli*. This matter has been engaging the attention of Dr. Houston since 1898, and he has (June, 1910) given a special account of the results which he has obtained.

At the outset it should be pointed out that these streptococci are not peculiar to human excreta, but are also abundantly present in those of the higher animals, many of Houston's experiments having been made with streptococci obtained from cow-dung. The study of these micro-organisms does not, therefore, at present put us in possession of that all important desideratum—a means of distinguishing between contamination due to the excrement of man and that which is due to the lower animals.

According to Houston, human fæces contain, roughly, 100,000 streptococci per 1 gm. On the other hand, in some stools streptococci are either absent or present in such small numbers relatively to those of other bacteria that search

for them is useless. Their presence in water has hitherto been ascertained by spreading 1 c.c. of the water on a Drigalski-Conradi plate, on which medium, after incubation at 37°, the streptococci give rise to very minute colonies, which can then be sub-cultivated for determination of their biochemical characters.

Of 100 different cultures of streptococci

obtained by Houston from sewage works faeces: (a) 100 produced acid in lactose and in raffinose media, and all of them clotted milk. (b) None reduced nitrates to nitrites. (c) Only four produced acid in a mannite medium. (d) 97 produced acid in a salicin medium. (e) 49 produced acid in a saccharose medium.

The grouping of these properties is best

LONDON WATER SUPPLY.

Influence of storage shown by samples collected during 12 months ending March 31, 1910 (Houston).

No of bacteria per 1 c c				<i>B. coli</i> (typical)												
Gelatin	Agar	Tauro	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
20°	37°	Agar	100	100	100	100	100	100	100	100	100	100	100	100	100	100
22°C.	37°C.	37°C.	—	+	+	+	+	+	+	+	+	+	+	+	+	+
3 days	2 days	2 days														
				p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Raw Thames water before storage	5,268	495	63	0.5	0.5	0.3	26	0.5	2	9	12	8				
Thames water after storage at Staines Reservoirs	240	88	3	21	4	17	1	25	7	4	3	14				
Thames water after storage at Chelsea Reservoirs	442	63	8	11	3	28	0	21	3	9	3					
Thames water after storage at Lambeth Reservoirs	354	54	8	20	8	43	0	31	0	4	2					
Raw Lea water before storage	37,071	837	50	0.0	0.5	6.3	31	1	30	7	13	2	7.8	0.5	0.5	0.5
Lea water after storage at Walthamstow Reservoirs	121	21	4	60	0	10	6	8	0	1	3					

indicated by means of a convention similar to that employed in the case of *B. coli*, in which syllables are made to represent definite biochemical reactions, thus:—

la = acid in a lactose medium.
 ma = " mannite
 mi = clot milk
 ra = acid raffinose
 sac = " saccharose
 sal = " salicin

The 100 streptococci examined may then be thus classified:—

la-mi-ra-sal . . . 49	la-ma-mi-ra-sac-sal 4
la-mi-ra-sac-sal . . 44	la-mi-ra-sac . . . 1
	la-mi-ra 2

Thus 97 p.c. clotted milk, and produced acid in lactose, raffinose, and salicin media, and of these 48 produced acid and 49 no appreciable acidity in a saccharose medium.

During the year 1909 Houston examined the raw (unfiltered and unstored) Thames, Lea, and New River waters for streptococci, employing 1 c.c. of each sample on Drigalski plates as above, with the following results:—

	No. of times streptococci were found in 1 c.c.
52 weekly samples of Thames water	13
52 weekly samples of Lea water	13
52 weekly samples of New River water	2

As regards the types of streptococci found in the above 28 samples of the 71 sub-cultures of

streptococci examined the following combinations were found:—

	Thames	Lea	New River
La-ma-mi-ra-sac-sal . . .	1	2	0
La-ma-mi-sac-sal . . .	1	3	0
La-mi-ra-sac-sal . . .	9	17	0
La-ma-sac-sal . . .	0	1	0
La-ma-mi-sac . . .	0	3	0
La-mi-sac-sal . . .	4	9	0
La-mi-ra-sac . . .	2	10	0
La-sac-sal . . .	0	1	2
La-mi-sal . . .	0	1	0
La-mi-sac . . .	2	0	0
La-ra-sac . . .	0	3	0
Total	19	50	2

The above results are especially interesting as showing that the two impurer waters (Thames and Lea) contained streptococci much more frequently than the far purer water (New River), and further, that the streptococci actually discovered in the latter were of a type more remote from that of those which are usually discovered in faeces.

Bearing in mind that, on an average, upwards of 90 p.c. of the raw Thames and Lea samples, and about 50 p.c. of the raw New River samples contain typical *B. coli* in 1 c.c. or under, whilst in only 25 p.c. of the raw Thames and Lea samples, and in only 3.8 p.c. of the raw New River samples were streptococci found, it follows that the streptococci are a far less delicate index of contamination than is the *B. coli*. The absence of streptococci in 1 c.c. of a water

cannot, therefore, be regarded as any criterion of its purity. The relative scarcity of streptococci in waters which have undoubtedly received a considerable amount of sewage matters is accounted for by the fact, established by Houston, that streptococci very rapidly die off when placed in water. This circumstance points, of course, to the presence of streptococci serving as an indication of very recent contamination.

Recent bacteriological methods applied to other processes of water purification.—From the evidence already brought forward it appears that confidence in the purification which can be effected by storage and sand-filtration, under favourable conditions, has been distinctly strengthened by the application of the more recent developments of bacteriological water examination—search for *B. coli* and other microbes more or less connected with sewage contamination.

Certain other processes of water-purification which are employed on the large scale may now be briefly considered.

Mechanical filters.—The use of mechanical filters originated in America, and their employment in our own country is becoming more and more common. Such filters are in use at Bolton, Burnley, Heywood, Edinburgh, Crewe, Gloucester, Shrewsbury, and other places in Great Britain, whilst they have also been installed in India, Japan, and some of the colonies. Space does not permit the discussion of the relative merits of the two different processes of filtration. They each possess their advantages and disadvantages; they can each be made to yield good and bad results according to the manner in which they are employed. The following results may serve as an illustration of the very high degree of purification which can be secured

PURIFICATION OF RIVER WATER BY MECHANICAL FILTERS.

	Number of bacteria in 1 c.c.				<i>B. coli</i> (typical) in			
	Gelatin at 20° C.		Carbollic gelatin at 20° C. 7 days	Bile-salt agar at 37° C. 4 days	100 c.c.	10 c.c.	1'0 c.c.	0'1 c.c.
	2 days	7 days						
Raw river water	3700	—	35	19	+	+	+	+
Ditto after passing sand filters	130	405	2	2	+	+	0	0
Ditto after further passing mechanical filters	8	33	0	0	0	0	0	0

by means of mechanical filters, which, in this instance, were employed to further purify a river water, which was being very imperfectly purified by some defective sand-filters.

Clark's process of softening.—Already in 1885 the writer showed that in softening water with lime, a very large proportion of the bacteria are carried down with the precipitated chalk, but that if the latter is allowed to stand in contact with the softened water bacteria again pass from the precipitate into the water. In the softening process this removal of bacteria may, under favourable conditions, amount to upwards of 90 p.c.

Recently the writer had occasion to deal with a chalk well water, which was causing anxiety in consequence of its frequently containing *B. coli* in rather small volumes. The most obvious and unobjectionable method of purification which suggested itself was softening with lime, inasmuch as the water contained plenty of calcium bicarbonate in solution. The following table shows the results obtained in a number of small-scale experiments in which this water was treated with lime, and sometimes with aluminoferric, and in which the softened water was sometimes decanted, sometimes filtered through paper without disturbing the precipitate ('clear filtration' in the table), and sometimes filtered after deliberately disturbing the precipitate ('turbid filtration' in the table).

A great many experiments were made in addition to those recorded below, but always with the same disappointing result, that not-

withstanding a large percentage reduction in the total number of bacteria taking place, it was only in rare cases that the *B. coli* was banished from 100 c.c. of the water by the precipitation process. It must be remembered that the demands now commonly made on a purification process with regard to the removal of *B. coli* are much more stringent than with regard to the removal of bacteria in general. Thus, should an untreated water contain 1000 bacteria per 1 c.c., if by treatment the number were reduced to 50 per 1 c.c., this would represent a purification of 95 p.c., and the water would be regarded as quite satisfactory from the point of view of the total number of bacteria present. But, if an untreated water contained the *B. coli* in 0'1 c.c., and after treatment this microbe were not present in less than 10 c.c., this would signify a removal of 99 p.c. of the *B. coli* present in the original water. But so high is the standard of purity at present often demanded in respect to freedom from *B. coli*, that the water which had thus been purified to the extent of 99 p.c. might still be regarded as of a questionable degree of purity.

Ozone treatment.—The bactericidal properties of ozone have long been demonstrated,¹ but it is only in quite recent years that it has been used on a large scale for the sterilisation of town water-supplies. In France the drinking waters

Arbatten a. d. Kaiserl. Gesundheits-Anstalt.

BRUNNEN, 1890, 110; CHLORINE AND OZONE FOR THE PURIFICATION OF WATER, 1891, 117; PROSKAUER and SCHÜLER, Zeitsch. Hygiene und Infektionskrankheiten, 41, 227, 243; 42, 269; OZONISATION DE L'Eau, Pasteur, 1890, 13, 244.

PURIFICATION OF WATER BY LIME AND ALUMINO-FERRIC.

	Gelatin		B. coli in				
	No. of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1° c.c.	0°1 c.c.
Raw well water	10	2	+	+	+	0	0
	259	7					
Ditto after filtration through sterile paper	7	2	+	+	+	0	0
	236	7					
Ditto+lime water, filtered through sterile paper after 1 hour's subsidence	0	2	+	+	0	0	0
	90	7					
Ditto+lime water and aluminoferric, filtered after 1 hour	0	2	+	0	0	0	0
	39	7					
Ditto+lime water; clear filtration after 3 hours	1	2	+	0	0	0	0
	74	7					
Ditto+lime water and aluminoferric; "clear filtration after 3 hours	1	2	+	+	0	0	0
	44	7					
Ditto+lime water; turbid filtration after 3 hours	0	2	+	+	0	0	0
	41	7					
Ditto+lime water and aluminoferric; turbid filtration after 3 hours	0	2	0	0	0	0	0
	41	7					
Ditto+lime water; clear filtration after 25 hours	3	2	+	+	+	0	0
	96	6					
Ditto+lime water and aluminoferric; clear filtration after 25 hours	0	2					
	14	6	+	0	0	0	0

of the towns of Nice, Chartres, and Cosne are being subjected to ozone treatment, whilst a plant for the treatment of 10 million gallons of water was projected in connection with the Paris waterworks. In Germany there are installations at Paderborn, Schierstein, and Hermannstadt.

The writer has made experiments with ozone in connection with the practicability of purifying the chalk well-water to which reference has just been made above. The extraordinary efficacy of this agent will be apparent from the foregoing results obtained in experiments in which the impurities of the chalk

OZONE TREATMENT OF WATER.

	Gelatin		<i>B. coli</i> in						
	No of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1° c.c.	0°1 c.c.	0°01 c.c.	0°001 c.c.
Chalk well-water	7,000	2	+	+	+	+	+	+	+
+4 p.c. polluted canal-water	10,000	7							
Ditto after treatment with 5 times its volume of ozonised air during 2 hours; cultivations made 2 hours later . .	0	2	0	0	0	0	0	0	0
	0	7							
Chalk well-water	4,000	2	+	+	+	+	+	+	+
+4 p.c. polluted canal-water	7,000	7							
Ditto after treatment with its own volume of ozonised air during 24 minutes; cultivations made 1 hour later. (The ozonised air contained 0·23 p.c. ozone)	0	2	0	0	0	0	0	0	0
	3	7							

well-water were enormously exaggerated by the addition of 4 p.c. of polluted canal-water.

Bleaching-powder treatment.—The bactericidal action of hypochlorites, again, has been long known, and bleaching powder is one of the

oldest and commonest of disinfectants. The use of hypochlorites for the sterilisation of water-supplies was first brought into prominence in this country by Houston, who used 'Chlorox' which is an electrolysed solution of common

PURIFICATION OF WATER BY TREATMENT WITH BLEACHING POWDER.

Untreated chalk well-water						Chalk well-water after treatment with bleaching-powder						Millions of parts of water treated per 1 part of available chlorine used	
No. of bacteria gelatin at 20°C.		B. coli in					No. of bacteria gelatin at 20°C.		B. coli in				
		+	+	+	+	+			+	+	+		
2 days	7 days	100 c.c.	50 c.c.	10 c.c.	10 c.c.	0.1 c.c.	2 days	7 days	100 c.c.	50 c.c.	10 c.c.		10 c.c.
First series of experiments													1 part chlorine per 1 million 1 part chlorine per 1 million 1 part chlorine per 2 million 1 part chlorine per 2 million 1 part chlorine per 2 million 1 part chlorine per 2 million 1 part chlorine per 2 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million
98	640	+	+	+	0	0	17	83	+	+	0	0	
13	260	+	0	0	0	0	0	5	0 ¹	0	0	0	
20	356	+	+	+	0	0	0	33	0 ¹	0	0	0	
22	202	+	+	+	0	0	0	1	0	0	0	0	
13	539	+	+	+	0	0	0	9	0	0	0	0	
18	528	+	+	+	0	0	0	1	0	0	0	0	
9	315	+	+	+	+	0	0	4	0	0	0	0	
16	794	+	+	0	0	0	0	5	0	0	0	0	
9	152	+	+	0	0	0	0	2	0	0	0	0	
12	80	+	+	0	0	0	0	9	0	0	0	0	
14	115	+	+	0	0	0	0	10	0	0	0	0	
54	350	+	+	+	0	0	9	63	0	0	0	0	
17	116	+	+	+	0	0	12	37	0	0	0	0	
17	507	+	+	+	0	0	10	22	0	0	0	0	
—	—	—	—	—	—	—	8	38	0	0	0	0	
Av. 24	358						Av. 4	21					
Second series of experiments													1 part chlorine per 1 million 1 part chlorine per 2 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 4 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million 1 part chlorine per 8 million
6	79	+	+	0	0	0	1	4	+	+	0	0	
1	105	+	0	0	0	0	0	3	0 ¹	0	0	0	
6	353	+	0	0	0	0	0	0	0	0	0	0	
3	305	+	0	0	0	0	0	1	0	0	0	0	
1	129	+	+	0	0	0	0	3	0	0	0	0	
4	181	0	0	0	0	0	1	1	0	0	0	0	
5	244	+	+	0	0	0	0	0	0 ¹	0	0	0	
0	111	+	+	0	0	0	0	9	0	0	0	0	
5	102	+	+	+	0	0	0	3	0	0	0	0	
1	181	+	+	0	0	0	0	15	0	0	0	0	
2	157	+	+	0	0	0	—	—	—	—	—	—	
9	289	+	+	0	0	0	0	1	0	0	0	0	
0	316	+	+	0	0	0	0	0	0	0	0	0	
1	120	+	0	0	0	0	0	0	0	0	0	0	
2	80	+	0	0	0	0	0	0	0	0	0	0	
Av. 3	183						Av. 0	3					

¹ *B. coli* found absent even in 500 c.c.

salt, for the treatment of the Lincoln water-supply during the memorable epidemic of typhoid which occurred in that city in 1904-5.¹

The writer had occasion some years ago to investigate the efficiency of the bleaching-powder treatment on a chalk well-water, the experiment being made with a large experimental plant.

From the results given above it will be seen what a high degree of purification is obtained by this simple and inexpensive method of treatment, even when extremely small quantities of bleaching-powder are added to the water.

¹ In that epidemic there were as many deaths (119) from typhoid in six months as had occurred from the same cause during the previous eighteen years.

Thus the only occasions on which *B. coli* found even in 100 c.c. of the treated water was on the first day of each of the two series of experiments and thus when the apparatus had presumably not yet been completely washed out with treated water. On several occasions even 500 c.c. of treated water was examined for *B. coli*, and this microbe was on each such occasion found to be absent even in that large volume.

Similar results have been obtained by Sims, Woodhead, Thresh, Hehner, Rideal, and others.

For the more recent experience in the chlorination of drinking water, and for a summary of many other important points, the reader

should consult Houston, *Progress in Water Purification*, Trans. Inst. of Water Engineers, 27, 1922, p. 117.

Treatment with ultra-violet light.—The known bactericidal action of the ultra-violet rays has been applied by Victor Henri to the sterilisation of water on a large scale. The rays are supplied by a Cooper-Hewitt mercury lamp. The lamp is worked with 3 ampères at 220 volts, and is placed in the bend of a semicircular trough through which the water is passed. At Marseilles the process has been tried with a plant yielding 130,000 gallons per 24 hours, and using 120 watts per 1000 gallons. The crude water always contained some *B. coli*, and the total number of bacteria varied between 30 and 300 per 1 c.c., whilst, in the treated water, *B. coli* was absent and the total number of bacteria was reduced to an average of 1 per 1 c.c. (Modern Methods of Water Purification, Don and Chisholm, London, 1911). See also W. Clemence, *Engineering*, Jan. 27 and Feb. 3, 1911.

Conclusions.—During the nearly 40 years that the systematic bacteriological examination of water has been practised an enormous amount of work has been carried out by a large number of investigators, but notwithstanding the immense multiplication of results it must be admitted that no very surprising novelties have been brought to light since the year 1895. By then all the salient features in the bacteriology of water had been mapped out, and the past 30 years have more especially been occupied in filling in countless details and in confirming over and over again what had already been broadly established.

Thus, already in the earlier period, the methods of bacteriology had been successfully applied to a determination of the value of the most varied processes of water purification natural and artificial, filtration, storage, precipitation, sedimentation, &c. It had been shown how such processes should, in the interests of public health, be continuously watched over and controlled by bacteriological examinations made at frequent intervals. Again, the vitality in water of the principal bacteria associated with water-borne zymotic disease had been investigated, and the results then obtained were substantially the same as those which have been arrived at by the most recent developments in bacteriological technique. In a word, these most recent developments in the methods of bacteriology have served to confirm and emphasise the conclusions which had been generally arrived at by the less perfect methods of the earlier period.

The all-important questions which the water-examiner has to answer are the same to-day as they have been all along: (a) has the water been contaminated with the excreta of man?; and (b) if such contamination has taken place, has the water in its subsequent history been subject to conditions which would ensure the destruction or removal of the pathogenic bacteria which may at any time be present in such human refuse?

To the first of these questions bacteriology cannot give a categorical answer even to-day, because we are not acquainted with any microbes which are absolutely characteristic of human excreta. The greatly increased facilities for the

detection and quantitative determination of the *B. coli*, however, have undoubtedly placed us in a position to ascertain readily whether and to what extent a water has been contaminated with excremental matter irrespectively of whether the latter is of human or animal origin, but it is obvious that this will not, in general, carry us very far, inasmuch as practically all surface water must be more or less so contaminated.

To the second question a similarly qualified answer, again, can be readily given. If the water is free from *B. coli* in a large volume, it may safely be concluded that *a fortiori* it is free from the typhoid bacillus in a similar volume. But should the *B. coli* be found in a small volume, it does not follow that the water may at any time be liable to contain typhoid bacilli, because the discovery of the *B. coli* does not prove that the water has been contaminated by man at all.

Thus with regard to both questions, it is obvious that we are in a much stronger position in the matter of exculpating than in that of incriminating a water. However, the inference that a water free from *B. coli* in a large volume is, therefore, necessarily a safe one, requires a slight qualification in view of the remarkable and interesting revelations which have in recent years been made with regard to what are known as 'typhoid carriers.' Some of these persons suffering from 'ambulatory typhoid' discharge typhoid bacilli in the urine, and it is thus possible that water may actually become contaminated with typhoid bacilli without at the same time receiving any *B. coli*. Although this is not likely to be of frequent occurrence, still its possibility, especially in the case of men working in wells, filter-beds, and service reservoirs, should on no account be disregarded.

Certainly one of the most important advances made in bacteriology during recent years is the careful characterisation of bacteria by means of biochemical tests, and the isolation of particular types of bacteria from such mixtures as are present in water by means of special culture-media, liquid and solid. However, until bacteriologists have agreed upon uniform tests for each particular microbe it is unavoidable that there should be much confusion and that the results obtained by different observers should be difficult to compare. Under these circumstances the interpretation of results by the individual observer is a matter of the greatest importance, and it is needless to say that unless the individual observer has a wide personal experience and a thorough knowledge of the factors affecting the purity of water-supplies of different kinds his interpretation of the results obtained will not only have little practical value but may easily lead to very serious mistakes.

Thus, whilst the outstanding achievement in bacteriological water examination during the past 25 years is the systematisation of tests for detecting the presence in water of specific bacteria, especially *B. coli*, *Streptococci*, and the spores of *B. enteritidis sporogenes*, the different possible sources of these bacteria, and their different hygienic significance according to sources, under any hard and fast application of standards based on the presence of these microbes impossible without liability to serious errors of judgment being committed.

Space has not permitted reference in detail to the spores of *B. enteritidis sporogenes*¹ as an index of faecal contamination. The figures on p. 411 show how much less abundant in faeces are these spores than is the *B. coli communis*. They do not, therefore, form such a delicate test for sewage contamination as does the *B. coli*, and their final identification is much less certain. The water-bacteriologist should, however, not neglect a search for these spores, but should regard the evidence which their presence or absence affords as supplementary to that which is furnished by the *B. coli* results.

In conclusion a word may be said with regard to the relative value of the chemical and bacteriological examination of water. At the present time it is often supposed that the chemical has been entirely superseded by the bacteriological examination, and that the chemical analysis of drinking water can be dispensed with. In reality the two methods of examination supplement each other. In those cases in which the source and general characters of a water supply are well known, the variations in purity from day to day or from week to week can undoubtedly be more satisfactorily watched by means of bacteriological examination. On the other hand, it is often desired by means of a single examination to ascertain the fitness or otherwise of a water for domestic use, and in such cases the omission of a chemical analysis may lead to an entirely erroneous opinion being formed. The ingredients detected by chemical analysis—organic matter, ammonia, nitrates, chlorides, &c.—on which an opinion as to hygienic quality is based, are all much more permanent and uniform features in the composition of the water than are the amount and the nature of the bacterial life which it may contain. The chemical analysis will, therefore, if skilfully interpreted, enable a much better idea of the potability of the water to be obtained than would be possible from a single bacteriological examination.

There are so many factors and considerations which have to be taken into account if an opinion of any real value as to the hygienic quality of water is to be formed, that no knowledge or information which can be gained either by chemical, or by bacteriological examination, or by inspection of source, or by any other available means whatsoever should be neglected.

P. F. F.

WATER-GAS v. GAS, WATER.

WATER-GLASS. *Soluble glass* v. GLASS.

WATER-OF-AYR STONE v. WHETSTONE.

WATER-SOFTENING. Some natural waters require the use of a relatively large amount of soap to form a lather, and are characterised as 'hard' waters. They contain impurities which react with and destroy soap forming a curdy precipitate, and the generic term 'water softening' connotes all processes which remove these impurities, wholly or in part. Certain processes of water purification or treatment not falling strictly within this definition, are nevertheless so related to true water-softening processes that they are most conveniently considered here.

Effects of hardness.—Hardness renders water unsuitable for many domestic and industrial uses. In washing and scouring, hard water wastes soap and discolours fabrics by the deposition of insoluble salts; in the manufacture of worsteds and woollens it decreases the pliancy of the fabric; in tanning it deposits lime in the hides; when heated or evaporated in kettles, calorifiers, boilers, &c., it deposits scale which impairs heat transmission and increases charges for maintenance and depreciation. Bicarbonate hardness hinders the uniform dyeing of fabrics. Even ice prepared by freezing hard water is unsatisfactory, being opaque, or coloured if iron is present, and leaving a dirty sediment on melting (Behrman, J. Ind. Eng. Chem., 1921, 13, 235).

Nature of hardness.—Hardness may be caused by the presence in water of soluble salts of most metals other than the alkali metals; for example, barium chloride is occasionally found as a major impurity causing hardness. But in the great majority of cases hardness is due mainly to salts of calcium and magnesium, and to a lesser degree to salts of iron and manganese.

It is usual to recognise two types of hardness, temporary and permanent.

Temporary hardness due to bases, usually calcium but occasionally iron, present as bicarbonates, is so called because it is removed by boiling the water, whereby excess carbon dioxide is gradually expelled and the less soluble normal carbonate is precipitated. With regard to certain softening processes which depend entirely on this reaction, it is important to observe that at temperatures below 100°C. but little carbon dioxide is removed unless the water be violently agitated, and that even at 100° some 10 minutes' boiling is necessary for its complete expulsion (Paul, Boiler Chemistry, Longmans, p. 94).

Hardness due to magnesium bicarbonate, often regarded as temporary, is less affected by boiling than that due to calcium bicarbonate, normal magnesium carbonate being more soluble than calcium carbonate. On the other hand, at the temperatures attained in boilers, magnesium carbonate is hydrolysed to magnesium hydroxide, which is precipitated and may even be dehydrated to the oxide.

Permanent hardness is that which persists after boiling; it is due to the combined effect of a small quantity of residual normal carbonates and of other salts, chiefly sulphates, nitrates, and chlorides, of calcium and magnesium.

Quantitative estimate of hardness.—Originally hardness was measured and stated in terms of the number of grains of calcium carbonate per gallon of a solution equivalent to the water under test in respect of the quantity of soap required to produce a lather. Hardness corresponding to 1 grain CaCO_3 per gallon (1 part CaCO_3 in 70,000 parts of water) is described as 1 degree (Clark) of hardness. Hardness is now frequently expressed in terms of parts of CaCO_3 per 100,000 parts of water; a quantity evidently equal to $10/7 \times$ the hardness expressed in Clark degrees.

It is convenient to give here a statement (Table I) of the solubilities at about 15°C. of the chief hardening impurities, together with the equivalent concentration of calcium carbonate.

¹ Klein, Local Government Board; Medical Officer's Reports, 1897-8, 1898-9, 1901-2; Klein and Houston, *ibid.* 1899-1900; Hewlett, Trans. Jenner Institute, Series II, 76; Journ. State Medicine, 1904, 12, 102.

in grains per gallon and parts per 100,000, which, evidently, represent the maximum hardness of water which can be caused by each impurity at the ordinary temperature.

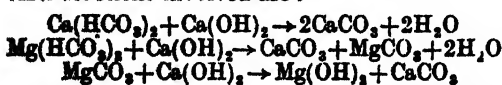
TABLE I

Impurity	Solubility. Parts per 100,000	Equivalent hardness.	
		Parts per 100,000	Degrees (Clark)
CaCO_3 } Dissolved	118	118	82.6
MgCO_3 } as bi-	3100	3675	2570
FeCO_3 } carbonates	abt. 400	345	240
CaCO_3	6.8	6.8	4.8
MgCO_3	abt. 70 ¹	83	58
CaSO_4	198.3	145.5	101.8
Ca(OH)_2	170	230	161
Mg(OH)_2	0.9	1.54	1.08

¹ The solubility of magnesium carbonate varies greatly with the pressure of carbon dioxide; the figure given is for a solution in equilibrium with carbon dioxide at about the partial pressure normally existing in the atmosphere.

Some of the solubility data are uncertain, but the table will serve to give a useful indication of the softening effect of the reactions under consideration. Thus, hardness due to calcium bicarbonate alone, which may in equilibrium with carbon dioxide at atmospheric pressure attain a maximum of 82.6 degrees, can be reduced by boiling to that due to calcium carbonate alone, viz. 4.8 degrees; whilst that due to magnesium bicarbonate which may reach a maximum of 2500 degrees under the above conditions, is, by boiling, reduced only to 58 degrees, equivalent to the solubility of magnesium carbonate.

Water softening reactions.—Temporary hardness is usually removed by the addition of lime, as originally advocated by Clark in 1841, and applied by J. H. Porter in the 'Porter-Clark' process (J. Soc. Chem. Ind. 1884, 3, 51). The chief reactions involved are:



From Table I it appears that the residual hardness in a solution saturated at 15° with calcium carbonate and magnesium hydroxide would be 5.9 degrees. In practice the reactions are not complete and it is difficult to avoid a slight excess or deficit of lime, but the minimum hardness actually attained at 15° is about 3.5

Lime precipitates as hydroxide any magnesium present as sulphate, chloride, &c., but an equivalent amount of calcium remains in solution; lime does not, of course, react with calcium salts: hence permanent hardness is unaffected by the lime treatment.

Permanent hardness due to calcium salts may be treated by addition of sodium carbonate (soda ash), which precipitates calcium as carbonate, leaving in solution sodium salts of the acidic radicals with which it was combined; thus, e.g.



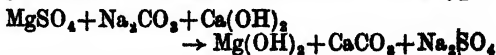
The origin of this use of soda ash is obscure, but it is clear that P. A. Maignen was one of the first to employ it, as a powder with lime and steam (J. Soc. Chem. Ind. 1886, 5, 22). Sodium

carbonate also removes temporary hardness due to calcium bicarbonate:

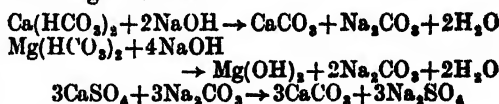


but the method has the disadvantage of leaving sodium bicarbonate in solution and is relatively costly.

Reference to Table I shows that addition of sodium carbonate cannot reduce permanent hardness due to magnesium below the 58 degrees, due to the solubility of magnesium carbonate. Such hardness is best removed by the addition of caustic alkali, or, what is equivalent and cheaper, lime and soda ash in equivalent proportions. The reaction involved is of the type:



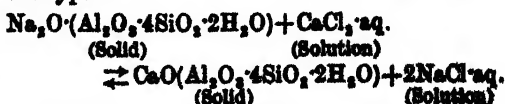
Should a water have only permanent hardness due to magnesium salts the use of caustic soda has the advantage of leaving no residual hardness due to calcium carbonate. In the equally unusual case where the bicarbonate hardness is exactly two-fifths of the total hardness, caustic soda alone will soften the water according to the following reactions:



Certain other reagents merit brief mention. Borax, sodium silicate, and sodium phosphate can precipitate calcium and magnesium as the relatively insoluble borates, silicates, and phosphates; the two former are common ingredients in washing powders, but none of the three is used in industrial water-softening. Barium hydroxide is an effective softening reagent, especially if the impurity in water is chiefly sulphate, but its high cost and poisonous character hinder its general use.

A suspension of barium carbonate in milk of lime has been patented as a softening reagent (H. Reiser, D. R. P. 333994, 1918) and is used in certain plants by Royle; it has the advantage of yielding a water of minimum hardness even where precise adjustment of the quantity of reagent is not attained, but is liable to acquire a coating of barium sulphate, rendering it inactive.

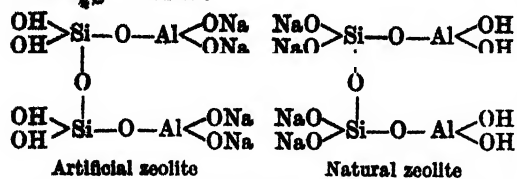
Permutite, or artificial zeolites, form a distinct class of water-softening reagents. They are hydrated aluminosilicates of soda, similar in composition to naturally occurring zeolites, e.g. *analcite*, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Such compounds, in contact with aqueous solutions of metallic salts, enter into reversible reactions of the type:



With dilute solutions of salts of the heavier metals, such as hard water, the reaction is almost complete toward the right; with concentrated solutions of sodium salts, e.g. brine, the reverse reaction largely preponderates. The utility of such reactions in water-softening is obvious, and their application is discussed below.

Though some waters are naturally softened by percolation through strata containing

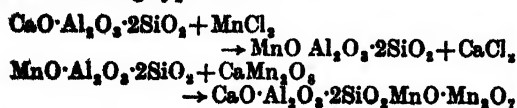
zeolites, these minerals undergo base-exchange but slowly and to a small extent. The artificial zeolites, on the other hand, undergo base-exchange readily and to a large extent, and this has been attributed by Gans to a difference in constitution of the kind indicated by the following formulae:—



Permutit was first prepared by Gans (D. R. P. 174097, 1905) by allowing alkali aluminate free from uncombined alkali to act on hydrated silicic acid, employing heat to complete the reaction. Calcium permutit is formed by treating the product with calcium chloride solution to replace soda by lime.

Numerous methods for preparing similar reagents have since been described, for details of which the patent literature must be consulted. The more important methods consist (a) in fusing together convenient ingredients to yield the desired composition, e.g. 3 kaolin, 6 quartz, and 12 soda-ash (J. D. Reidel, D. R. P. 186630, 1906; see also D. R. P. 200931, 1907); or (b) in hydrating by high pressure steam, with or without the addition of alkali, natural minerals of appropriate composition such as trass, phonolite, leucite, sodalite, &c. (Permutit Filter Co., Eng. Pat. 26094, 1910; see also, re similar hydration of Portland cement, Snelling, U.S. Pat. 1325213, 1919); or (c) in effecting base-exchange by the action of metallic salt solutions upon primary products obtained as above.

Some other base-exchange reactions deserve mention. Sodium permutit removes ammonia from water; if sodium permutit be treated with dilute acid it becomes an acid permutit, which will remove soda and produce an acid water; calcium permutit removes manganese from water. If calcium permutit be treated with a solution of a manganese salt and the resulting manganese permutit be acted upon by a solution of calcium permanganate, reactions of the following type occur:



producing a dark-coloured mass containing both lime and a highly oxidised manganese group. This is, in effect, an insoluble permanganate and can serve either to sterilise water or to eliminate any iron it may contain by precipitation as ferric hydroxide which is retained upon the surface of the filter-bed (J. D. Reidel, A.-G., Fr. Pat. 405900, 1909; R. Gans, Eng. Pat. 21184, 1909). A zeolite in which soda has been substituted by stannous oxide will reduce gold from solutions of its salts and retain it as purple of Cassius. Thus it is evident that base-exchanging reactions are known of the most diverse character and applicable to many purposes.

A number of processes have been described

in which iron is removed from water by aeration effected by allowing the water to flow down towers packed with coke, or by spraying it through nozzles. In this way the iron is oxidised to the hydroxide, which remains in colloidal solution until it is coagulated and removed by the action of the material forming the filter bed. Too much aeration is to be avoided if the water contains a relatively large proportion of lime and carbon dioxide, or the latter may be driven out of the water leaving insufficient to hold the lime in solution as bicarbonate, with the result that calcium carbonate is precipitated and blocks the pipes (Kisskalt. Gas- u. Wasserfach, 1924, 67, 3; J. Soc. Chem. Ind. 1924, 43 B. 230).

Treatment of alkaline and acid waters may be briefly considered. There is no practicable method for the removal of alkali, but various reactions, e.g. addition of calcium chloride or sulphate in the form of a strong solution or as water containing permanent hardness, will serve to convert alkali carbonate or bicarbonate to a neutral salt, but the resultant water will evidently be undesirable as a boiler feed water.

Acid waters derived from moorland catchments may dissolve lead; this tendency may be corrected either by hardening the water with lime or, better, by Thresh's method of adding sodium silicate, which removes plumbo-solvency without increasing hardness.

Artificial hardening, by addition of calcium sulphate, is practised in some cases to render a soft water supply more suitable for use in brewing.

Boiler compositions contain either or both (a) ordinary softening reagents such as lime, soda-ash, and caustic soda, and (b) organic matter, e.g. tan bark, which serves, by mere mechanical action, to prevent the formation of hard scale. Reagents of class (a) may be dismissed with the comment that they are usually dearly bought in the form of boiler compositions and that, in any case, it is unsound to perform water-softening reactions within a boiler. Materials of class (b) are evidently the lineal descendants of the dead pigs our forefathers are reputed to have put in boilers to prevent scale formation (P. G. Jackson, Boiler Feed Water, Griffin, 1919, p. 26).

If a mechanical preventive of scale is desired, undoubtedly the best is pure graphite applied as a cream with water to the clean internal surface of the boiler and subsequently introduced with the feed water at the rate of about $\frac{1}{2}$ lb. per day (Hinchley, Notes on the Economical Management of Small Boiler Plants, Proc. Chem. Eng. Group, (Soc. Chem. Ind.), 1919; but see, for a scientific investigation of the mechanical effect of linseed, Brun, J. Soc. Chem. Ind. 1919, 29, 76; R. Heuss, Zeitsch. ges. Brauw, 1918, 41, 200).

Proportions of reagents.—In the great majority of cases water is treated with a mixture of lime and soda-ash in such proportion that hardness due to bicarbonates and to magnesium is completely removed by lime, and the hardness then remaining by soda-ash. The amount of reagent required for 1000 gallons of water for each grain per gallon of the various impurities is given in Table II (Paul, Boiler Chemistry, p. 99).

If magnesium salts are to be removed as hydroxide the appropriate quantities of both lime and soda-ash should be used. Quantities of reagent calculated from the table are evidently minima, and in practice a slight excess, about 8-10 p.c., should be used, and the treated water should be faintly alkaline to phenolphthalein.

TABLE II.

Impurity (Present in a concentration of 1 grm. per gallon)	Calcium hydroxide required; lbs. per 1000 gallons	Soda-ash (Na_2CO_3) re- quired; lbs. per 1000 gallons
Free carbon dioxide.	0.260	—
CaSO_4		0.111
$\text{Ca}(\text{NO}_3)_2$		0.092
CaCl_2		0.136
MgSO_4	0.095	0.126
$\text{Mg}(\text{NO}_3)_2$	0.077	0.102
MgCl_2	0.120	0.159

Emphasis should be laid on the conclusion, following necessarily from the preceding discussion, that the nature and proportions of water-softening reagents cannot be determined simply upon data of temporary and permanent hardness; for the best results it is necessary to have a complete analysis of the water.

Purity of reagents is desirable in all water-softening processes and essential where the proportion of reagents is adjusted directly or indirectly by weighing.

Commercial *caustic lime* may be of almost any degree of purity. Some samples contain magnesia, some silica and alumina, and in all the content of real lime may vary from 100 p.c. to 70 p.c. or less by absorption of moisture. A much more reliable reagent is calcium 'hydrate,' slaked lime, which, when obtained from trustworthy sources, always contains about 70 p.c. of CaO , will not easily absorb more water, and is a fine powder, convenient for storage and use. If raw quicklime is used, each batch should be tested.

Sodium carbonate is obtainable commercially as the anhydrous salt, soda-ash, and as various hydrates, and may contain impurities such as sodium sulphate or chloride, detrimental to its use in water softening. It should be bought under guarantee or be subject to test before use.

Similarly, *caustic soda* is easily procured in a state of sufficient purity for water-softening; but it should preferably be in the form of 'flake' or powder for convenience in handling, storage, and measurement.

[In the succeeding paragraphs names given in italics in brackets, thus (*Paterson*)], are those of plants or processes which embody the feature under discussion.]

Municipal and domestic water softening and filtration is directed to the production of water free from bacterial contamination and suspended matter, free from colour and from excessive hardness. Owing to its cost, water softening of municipal supplies is practised only in exceptional cases, e.g. with Kentish waters of extreme hardness, derived from the chalk. It is usually effected by an intermittent process in which softening reagents are added to and mixed with a large bulk of water, the precipitate being separated by settlement and decantation; but some small municipal supplies are softened in

large continuous automatic plants of the usual industrial type described below.

Conversely, some large industrial supplies are treated by the intermittent process, using steam to assist solution of reagents and compressed air agitation to ensure their uniform admixture with the water under treatment (*Archbutt and Deeley*). After settlement, the treated water is drawn off by a floating syphon and carbonated by a counter-current of carbon dioxide passed through the outflow pipe (*Proc. Inst. Civ. Eng. 1898, Part 3, p. 404*). Such intermittent systems when properly controlled are probably the most accurate means available for water softening (*E. V. Chambers, J. Soc. Dyers and Colourists, 1918, 34, 240*). They necessitate considerable attention in working and require large tank space, and thus are costly, unless, as in municipal processes, large quantities of water are treated and existing reservoirs can be used.

Domestic water softening is quite commonly practised, and, unless on an unusually large scale appropriate to automatic continuous plant, is also best effected intermittently. Measured bulks of reagent powder are mixed by hand with 5-10 gallon lots of water, the precipitate is allowed to settle and the softened water is withdrawn through a filter (*Maignens*) or by slow decantation (*Wilson-Perrett 'Pukka'*).

One small plant, which may be mentioned here, softens water by heating to about 80°-90°, partly by heat-exchange with treated water, partly by direct heat, the scale being deposited in a tower upon plates removable for cleaning (*Lawrence*). This treatment effectively sterilises water (*Hatch, Proc. Inst. Civ. Eng. 1906*).

Bacteria and suspended impurities are usually removed by filtration. For small domestic supplies this is sometimes effected through porous earthenware filters under pressure, and it is clear that the 'stream-line' filter, which is capable of removing bacteria and even colour from water, could be applied to the purpose (*Hole-Shaw, Proc. Roy. Soc. 1923, 103A, 556*). Wood wool, prepared asbestos wool, cloth and sponges are sometimes employed as filtering media, but practically all large-scale water filtration is effected by beds of sand, preferably quartz sand, carefully graded and supported by a layer of gravel. Filtered water is drawn off either by supporting the gravel layer upon a perforated metal plate or by providing in that layer an effluent pipe system, provided with numerous screened orifices. Wood wool filters are cheaper to install, but the difficulty of cleaning them satisfactorily necessitates periodical renewal, the cost of which must be taken into account.

Large slow sand filters are usually cleaned by laying off units of the filter periodically and removing by hand the top layer of sand. This is continued until the sand bed is so diminished as to require renewal. Rapid sand filters of the gravity or pressure type can easily be cleaned by reversing the flow of water and agitating the sand violently. Agitation is effected in some small plants by hand, in the larger plants by compressed air or by the stream of wash-water itself. A typical illustration is the *Paterson gravity filter*, shown in Fig. 1, in which the steam-jet air-injector A forces a

of compressed air through the manifold strainer system *ss*, thus agitating and cleansing

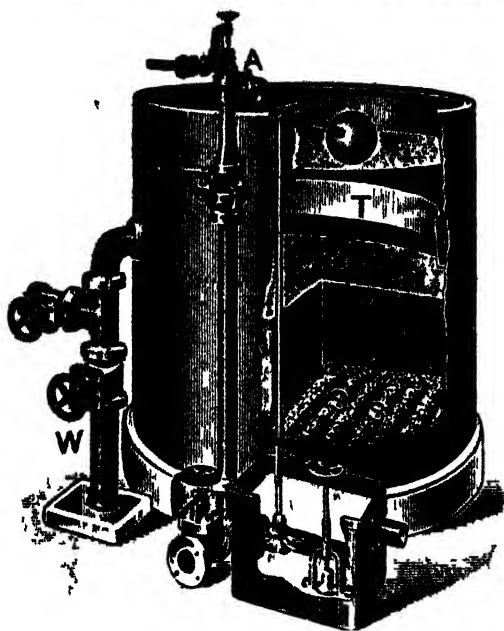


FIG. 1.

the filter bed, whilst the dirty water is drawn off by the annular trough *r* to the water outlet *w*.

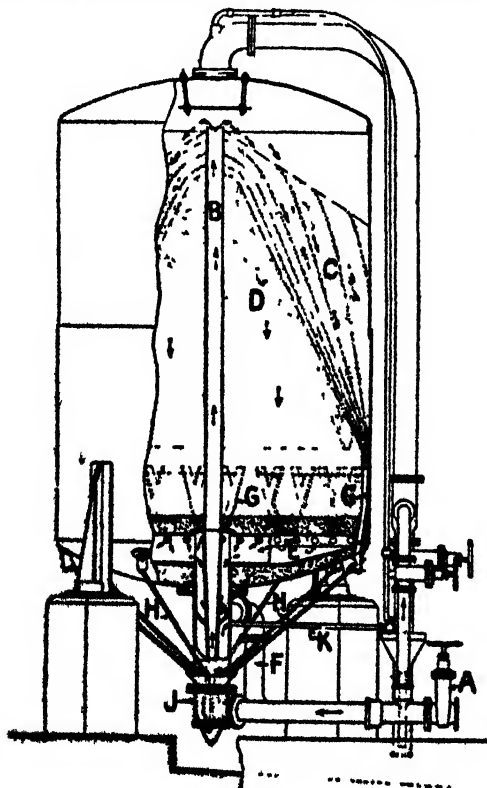


FIG. 2.

The Vickers' drifting sand filter very judiciously effects a partial cleansing of the sand before it is used for filtration, and is adaptable

gravity or pressure filtration on any scale. Fig. 2 illustrates a single unit pressure-filter. In normal operation raw water admitted by the valve *A* enters the filter at *s* and passes first through the loose mass of slowly drifting sand *c*, and then through the stationary sand-bed *b*, to the manifold *x*, and the filtered water outlet *r*. Sand is continuously extracted by the pipe system *g*, and conveyed by the pipes *hh* to the sand-washer *j*, where it is washed by the incoming raw water and a small quantity of dirty water passes away by the outlet *k*, whilst the main flow of raw water carries the cleaned sand back to the filter at *s*. Valves are provided to permit agitation and washing of the whole filter bed when necessary, the advantage of this type of filter being that, under any given conditions, the interval between such washings is much greater than with ordinary filters.

Efficient working of sand-filters depends upon the formation of a superficial film, composed of the suspended matter derived from the water, which is the effective filtering medium. Where the impurities in water are so small in amount, or of such a nature, that this film is not easily formed, filtration is frequently assisted by the previous addition of 'coagulants,' such

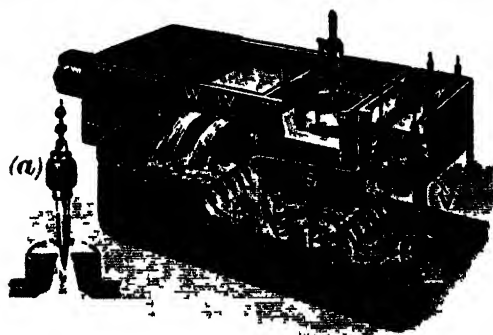


FIG. 3.

as aluminium sulphate. This salt, usually used in the crude form, known commercially as 'alumino-ferric,' is hydrolysed in dilute solution, especially in the presence of bicarbonates, forming aluminium hydroxide, which rapidly coagulates and carries down suspended matter otherwise unfilterable, and also, by adsorption, removes colouring matter present in the water. Precipitation is best effected in a neutral solution (hydrogen ion concentration $p_{H}7$), but is not complete even with the addition of an amount of lime equivalent to the aluminium sulphate (Hannan, Chem. Met. Eng. 1921, 24, 728; 25, 502). Similar results may be attained by the use of the clear 'aluminium hydroxide solution' produced by mixing aqueous solutions of aluminium sulphate (40 grm. in 80 c.c.) and sodium carbonate (10 grm. in 40 c.c.), which, on dilution, precipitates the hydroxide in a form which settles readily (J. W. Coxe, Met. & Chem. Eng. 1923, 29, 279).

Adjustment of the supply of coagulant is effected, in pressure filtration by control of the small acid-resisting pump which delivers it into the plant, and in gravity filtration by float-controlled valves. A typical coagulant supply gear of the latter type is illustrated in Fig. 3 (Peterson), the float *v* controlled by the head of

water at the weirs *w* actuating taper valves *vv* (shown enlarged at *(a)*) so contoured as to permit, for any flow of water, a corresponding flow of coagulant by the *ss* pipes to the trough where baffles *b* cause intimate admixture with the water.

Automatic water-softening plants.—Many types of these plants are in use, differing in the means employed to effect the fundamental operations into which water softening processes are divisible, viz. (1) preparation of reagents, (2) apportionment of reagents to water, (3) mixing, and (4) settlement and filtration to remove precipitated impurities. For the better consideration of the methods to be described, it is desirable to bear in mind the following essential features of an ideal lime-soda softening plant. Preparation of reagents must be conveniently effected, preferably by automatic means, and should be so made and used that they remain of precisely the same concentration until wholly consumed. Measurement of reagents in relation to water must be accurate over long periods and at all rates of flow, and must yet permit of ready and precise adjustment. Mixing must be speedy and thorough. The reaction tanks must be of such capacity that ample time (preferably at least 2 hours) is allowed for completion of the softening reactions before the water leaves the settling tank, and of sufficiently large cross-section to permit proper settling of the precipitate. The filter should be efficient and readily cleansed, but should only be supplementary to efficient sedimentation.

(1) *Preparation of reagents.*—Occasionally reagents are used in the form of a dry powder, usually purchased ready mixed from the manufacturers of the plant or from a firm specialising in the supply of such prepared reagents. In the great majority of cases they are applied as solutions or suspensions in water, which are commonly made by direct weighing and measurement, mixing or solution being effected, in the smaller plants by hand, and in the larger plants by mechanical stirrers or injector agitators, in a tank at ground level (see Figs. 14 and 15), from which they are pumped to a supply tank above the plant.

Sometimes lime is used in the form of clear lime-water prepared in an automatic solutioner, consisting essentially of a vertical tank, having for the whole (*Boyle*) or part (*Harris-Anderson*) of its height the form of an inverted cone (Figs. 16 and 17). By means of a pipe leading nearly to the bottom, the tank is charged from time to time with a sufficient excess of a cream of slaked lime and water, and a stream of water admitted at the apex of the cone flows upward, first agitating and dissolving the lime, and later, as the cross section of the tank increases, depositing excess lime and all impurities, so that clear saturated lime-water overflows at the top. Accumulated impurities are removed from time to time by a sludge cock. The use of saturated lime-water is attended by certain difficulties which must be recognised in order to attain good results. Owing to the small solubility of lime, a considerable proportion of the raw water, sometimes 15–25 p.c., must be by-passed to the lime solutioner, which is, therefore, of considerable capacity. Sometimes the lime, probably because it is of a lumpy character

and unsuited to the process, becomes 'coated' with carbonate and fails to maintain saturation. Lastly, in cases where the temperature of the raw water varies, care must be taken to adjust the proportion flowing to the lime solutioner, so as to compensate for the considerable variation of solubility of lime shown in Table III (Paul, *l.c.* p. 96).

TABLE III

Temperature, Fahrenheit	Calcium hydrate $\text{Ca}(\text{OH})_2$, grains per gallon
32°	132·1
40°	128·0
50°	121·7
60°	115·5
70°	110·9
80°	107·7
90°	103·6
100°	100·0

(These figures do not agree with the absolute solubility given in Tables I and II, but probably correctly represent the variation of solubility with temperature.)

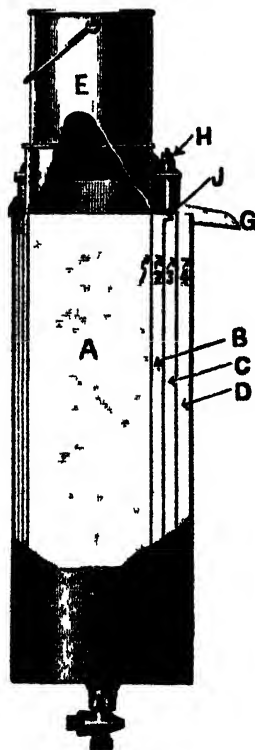


FIG. 4.

One type of plant has a very ingenious solutioner to prepare automatically from solid soluble salts unsaturated solutions of any desired density (*Harris-Anderson*). It consists essentially of three coaxial tubes, 1, 2, and 3 (Fig. 4), contained in a cylindrical tank 4, forming a central chamber *A*, and three annular spaces *B*, *C*, and *D*, all intercommunicating at the bottom. Solid contained in the bucket *a*, having a gauze bottom, dissolves readily in the water in *A*, owing to gravitational convection. Fresh water, introduced at the top of the annular space *B*, mixes at the bottom

with strong solution from A, and flows up the outer space D, to the outlet C. The relatively heavy solution in D balances a greater height of water in A, and the tube 2 is set, by means of the screw and nut H, at such a height that when the density of the solution in D reaches the desired value, water begins to overflow the lip J on tube 2, and, passing down the space C, mixes with the effluent solution and maintains the desired concentration in D.

(2) *Measurement of reagents.*—The numerous methods employed fall into two broad classes.

Of the plants using *clear solutions* of lime and soda, some *prepare* either or both of these as described above, whilst some rely on the *displacement* of the proper amount of a previously prepared soda solution by the quiet inflow of a corresponding amount of water at the top of a

water required to make saturated lime-water, whilst a small cup L, of fixed size, withdraws a smaller proportion of the water to the soda solutioner, the proportion of soda added to the water being controlled by adjustment of the density of the solution as described above.

In plants using lime suspensions, with or without the addition of soda, the commonest

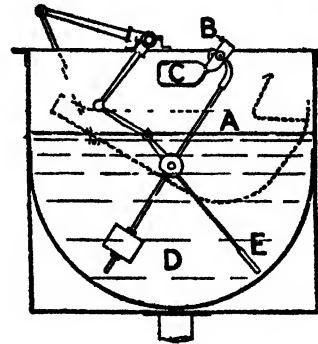


FIG. 5.

'displacement tank,' from the bottom of which a pipe conducts the soda solution to mix with the water under treatment (Figs. 16 and 18). In either case the raw water is divided into one large stream and two smaller streams, of the proper size to make or displace the required quantities of lime and soda solutions. This division is effected by micrometer valves in the base of a common supply tank (Boyle, Fig. 16) or by a turbo-distributor (Harris-Anderson). In this distributor (Fig. 5) a circular tank A, floating on water in B, and free to rotate under guidance by the roller bearings C on the shaft D, receives the whole supply of raw water which flows out tangentially by the orifices E, causing A to rotate: the water is thus distributed evenly over the annular trough G at all rates of flow. Radial partitions, one of which is adjustable, divide off a sector of the annulus, of such size as to separate precisely the fraction of the

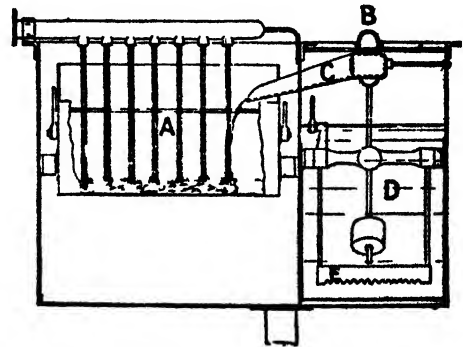


FIG. 6.

measuring device is some form of tipping bucket, actuated by the main flow of water, and actuating cups or scoops which supply a definite quantity of reagent to each charge of water passing. Typical examples of this device in its simplest form occur in the Boby and Beccolegg plants, the latter being illustrated in Fig. 6, where A is the tipping bucket which, after emptying, returns to the normal position

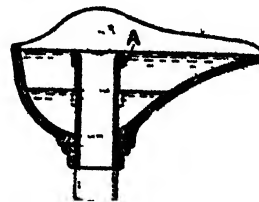


FIG. 7.

shown, and in so doing actuates the arm carrying the chemical scoop A, which discharges into A by a channel C, and agitates the suspension in the chemical tank B by means of the stirrer E. In the Boby plant the contents of the chemical cup (Fig. 7) are variable by vertical screw adjustment of the overflow tube A. Some plants (Lassen-Hort, Paterson, Wilson-Ferris) use double tipping buckets, illustrated by the

Paterson 'Oslameter,' Fig. 8. In the Lassen-Hjort plant the tipping bucket actuates a piston valve supplying reagent.

Special devices are employed in most cases to increase accuracy and decrease wear and tear;

so float in the bucket, which releases the latter when it has a definite content of water; and is buffered by a brake-paddle and springs.

Despite such devices, all tipping buckets are noisy, and in large sizes are impracticable owing to heavy wear and tear. Therefore it is

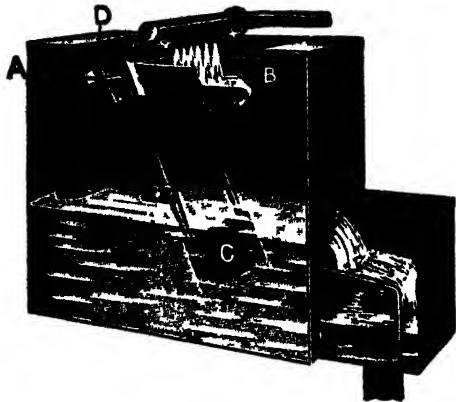


FIG. 8.

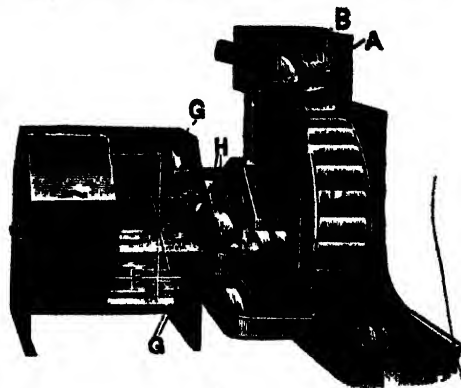


FIG. 9.

thus in Fig. 8, it is seen that the tank has some freedom of movement before it touches the arm A operating the chemical supply gear, whilst an extension lip on the bucket enables a small addition of water finally to overturn it; and the resulting shock is diminished by the brake paddle C, and absorbed by the rubber buffer D. The Lassen-Hjort tipper has a lock, actuated by

customary in the larger plants to sub-divide the main flow of water so that the measuring gear passes but a fraction of the water, whilst the remainder operates stirring gear in the reagent tank. Fig. 9 shows the Paterson bye-pass Oslameter; a dividing plate A at the weir B takes a small fraction of the water to the tipping bucket C, and sends the remainder over the

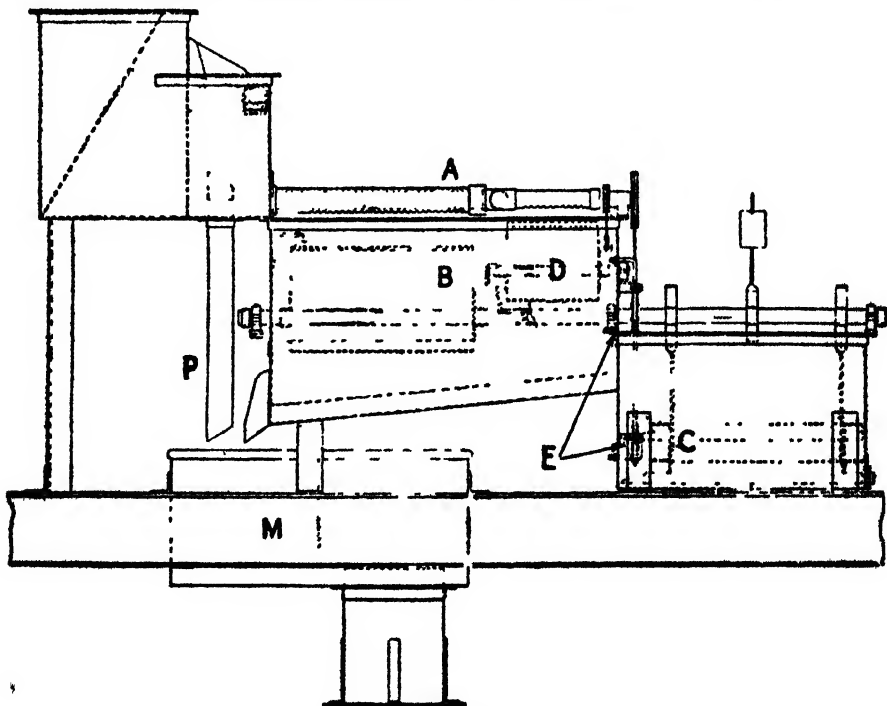


FIG. 10.

wheel D, driving the stirrers in carrying cups X, which maintain a supply of reagent in the measuring cups X. The Wilson-Perrett plant, shown in Fig. 10, passes a large part of the raw water direct to the mixer M

by the main P, and divides the residual flow from the perforated pipes A, between a larger tipping bucket B, driving the paddles C, and a smaller bucket D actuating by wheel and chain the chemical cups X.

A plant made by Wright's Forge and Engineering Co., Ltd. (Fig. 11), passes part of the water from a distributing box A through a bucket wheel B, driving a chain elevator C, carrying chemical scoops D, dipping into the reagent tank M. Another by the same maker (Fig. 12) uses the wheel B to drive by chain and bevel gearing, G, D, a screw M working in an oil-bath which lowers the discharge pipe G in the chemical tank, and so delivers reagent in proportion to the water passing. The Kennicott proportioning gear (Fig. 13) uses a small definite proportion of the raw water to lift the float R in the regulating tank T, whereby the cord C lowers a

vertical cylinder, having a scraper to strike off the powder flush with the top (Tide and Bell).

(3) *Mixing and precipitation.*—Reagents and water usually flow together into the precipitation tank, sometimes along a channel provided with baffles (see e.g. Fig. 3), and are thereby mixed. Liquid reagent is frequently discharged into a tipping bucket as it begins to fill, and is thus agitated by and with the inflowing water, mixing being completed by the very turbulent

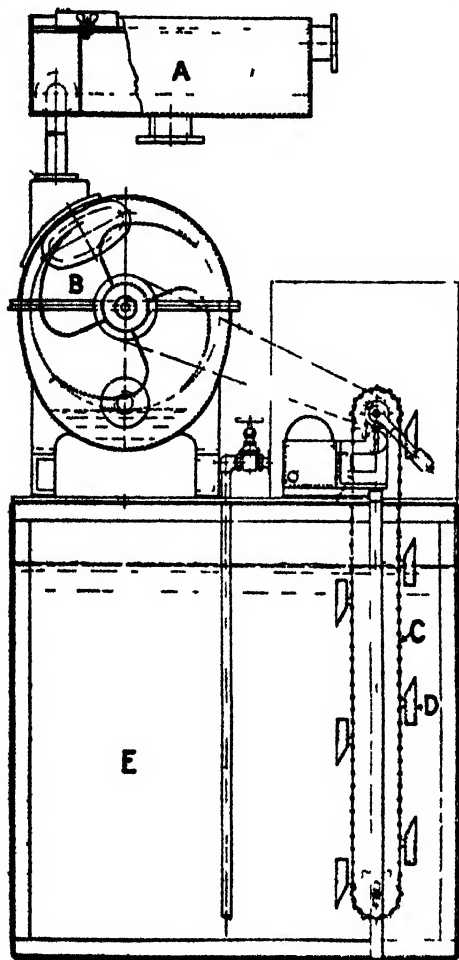


FIG. 11.

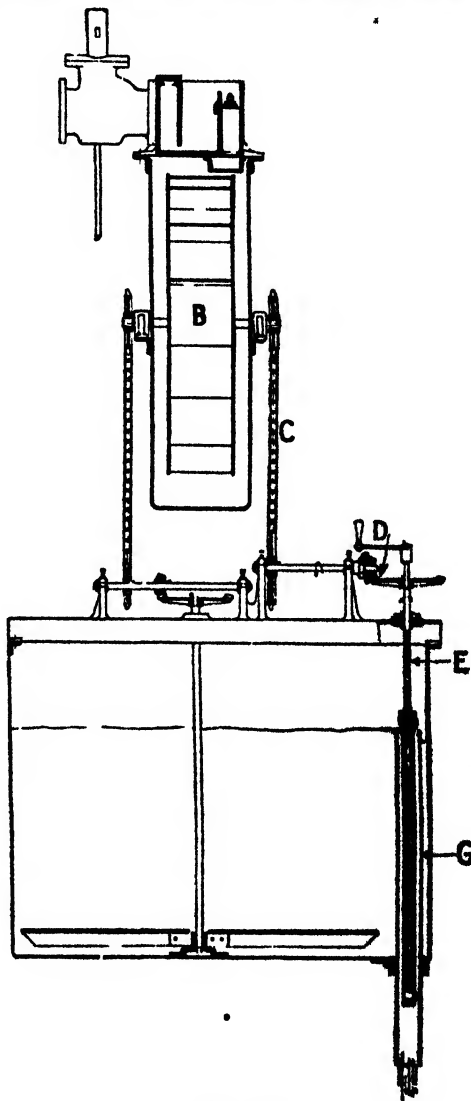


FIG. 12.

slotted discharge pipe F in the chemical tank, the contents of which are agitated by means of a separate water wheel.

In the foregoing plants the proportion of reagent is adjusted by altering the proportion of water passing to the measuring gear, by changing the volume of reagent added or by varying the concentration of the reagent suspension.

Certain plants use a tipping bucket or water-wheel to deliver reagent in the form of dry powder, either from a hopper (*Becco-Logg, Maignane, Bely*) or by continuous rise of a piston in a

outflow when the bucket tips. Some further mixing occurs in most plants by the relatively rapid flow of the water through the channel or pipe leading it down into the settling tank.

(4) *Clarification and filtration.*—Separation of the precipitate is always chiefly effected by settlement, during the slow passage of the water up or along the settling and reaction tank, and completed by filters. These tanks and filters determine the general form and disposition of the plant in one of two commonly occurring types, characterized as 'horizontal' and 'vertical', respectively.

A typical example of the horizontal type, the Laeson-Hjort rectangular softener, is shown in Fig. 14. Water, carrying reagents discharged

by the proportioning gear *a* already described, passes down the reaction chamber *s*, up the first settling tank *c*, and through the first

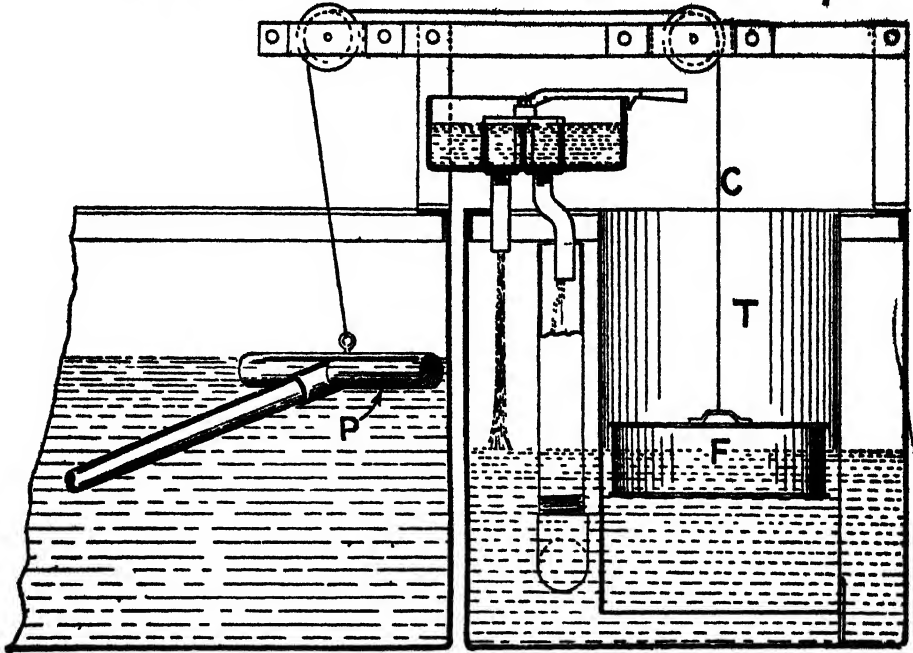


FIG. 13.

wood-wool filter *d*, overflows down channels *ee*, and passes upward through the second tank and filter, *r* and *g*, and finally overflows into

the storage tank *h*, in which a ball-cock *k* maintains a constant level by controlling the raw water supply. Sludge is removed by cocks

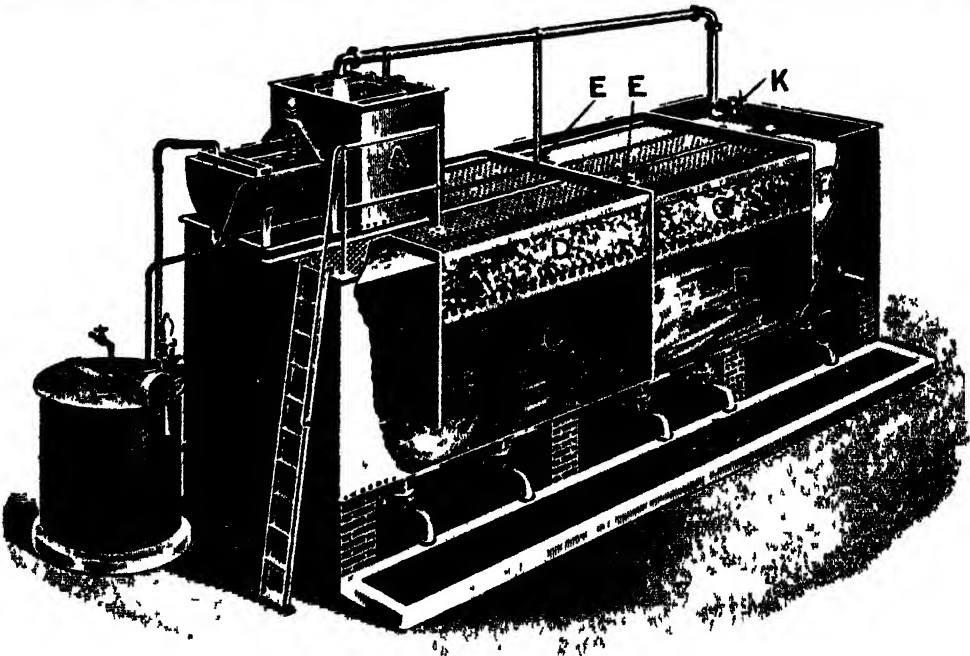


FIG. 14

in this operation being assisted in many plants (*Boyg, Paterson*) by hand agitators.

The vertical type is illustrated by the pattern plant shown in Fig. 15, the mode

operation of which is obvious from the preceding description. Here also a wood-wool filter is used.

Sand filters have the advantage that they

are more efficient and more easily cleaned than wood-wool filters. The Royle plant, shown in

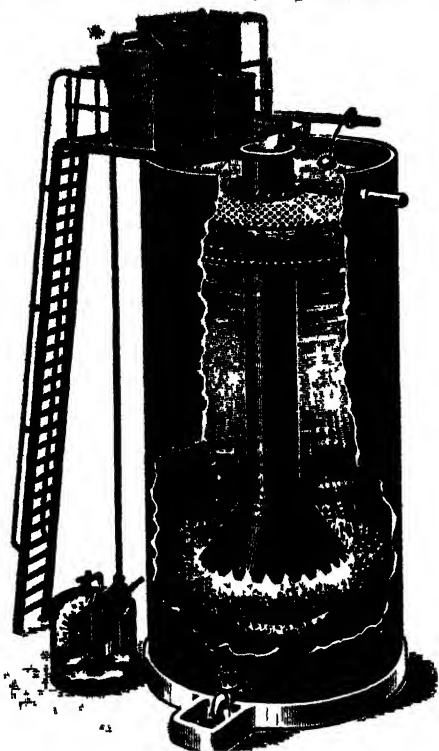


FIG 15

Fig. 16, affords an example of their incorporation in a vertical plant, and is interesting also as

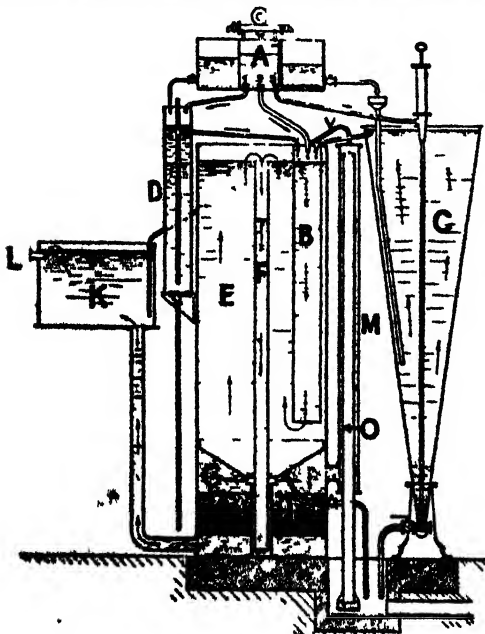


FIG. 16.

_____ an automatic washing device which
media _____ description. Raw water enters the
distribution tank 4, where the three micro

meter valves, 1, 2, and 3, pass the major portion of the water to the reaction tube *z*, a smaller portion to the lime dissolver *c*, and the smallest portion to displace soda solution in the tank *v*. These reagents mix in *z*, with the water which then rises slowly, and is clarified by settlement in *z*, and then overflows down *r* to the filter chamber *g*, passes through the sand filter *h*, rises to the tank *x*, and overflows at *l*. As sediment accumulates on *h*, the head of water in *r*, necessary to maintain the required rate of filtration, increases, and the corresponding rise of water in the outer tube *m* finally sets the syphon *o* in action and causes a heavy back-stream from *x* to flow through the filter, thoroughly agitating and cleansing the filter bed.

External independent filters have the great advantage of ready accessibility; their use is illustrated by the Harris-Anderson plant, shown in Fig. 17, where A is the turbo-distributor.

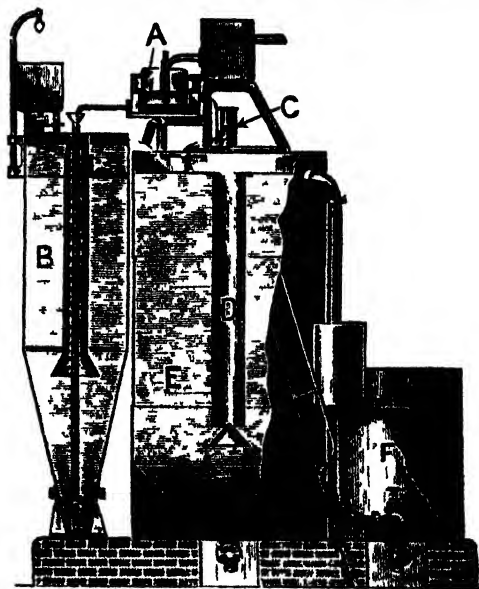


Fig. 17.

B the lime solutioner, and C the soda solutioner, already described, D is the reaction tube, E the settling tank, and F the external filter.

All the foregoing types of plant are open, and thus cannot deliver water at a pressure greater than that due to the height of the outlet above the point of application. Where it is desired to utilise a natural or forced head of water without material loss, a water-softening plant may be enclosed in the manner illustrated by the Royle's plant in Fig. 18, which differs from that of Fig. 16, in that the function of the head tank and micrometer valves in the latter is now performed by the dial cocks 1, 2, and 3, that the tops of C, D, and M are enclosed, that pumps are fitted to charge the reagents into C and D, and that the automatic washing arrangement is eliminated.

By the introduction of waste steam or hot condensates into the mixing chamber (not via the measuring gear), most of the above plants, though sometimes described as 'cold-process' plants, can be used for the hot softening of water. This is frequently advan-

as a means of conserving heat and because softener worked hot will yield water of lower hardness than one worked cold.

There are, however, a number of plants specifically designed to combine the functions of exhaust steam feed-water heating, water softening and oil elimination, of which the

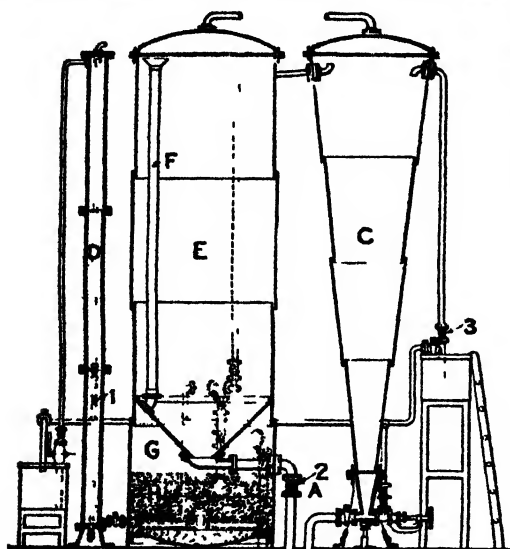


FIG. 18.

shown in Fig. 19 (Royle's) is an example. Some plants rely solely upon heating to soften the water (Lawrence, Erith's Recording Heater), but usually the water is treated also with soda or lime and soda, and if necessary with aluminium sulphate (Erith's, Wright's 'Neptune,' Royle's Type E, Kennicott, Lassen-Hjort, Harris-Anderson).

In Fig. 19 the crude water supply, controlled by the ball-cock A, is distributed in B, and part taken to displace soda and aluminium sulphate solutions in C and D respectively in the usual manner. Water and soda flows down through and over a series of dished plates EE, in parallel current with exhaust steam introduced at F, via an oil-separator G, any excess steam passing to atmosphere by the pipe H. Most of the hardening impurity is deposited on the plates EE, which are easily removable for cleaning. Aluminium sulphate is added in the mixing tube at K, and the water finally passes through a settling tank L and filter M as usual.

Brief reference may here be made to much work that has been done upon the 'degassing' of boiler feed-water, as a consequence of the general recognition of the fact that dissolved oxygen is the essential active agent in the corrosion of boilers and other steam plant. Two methods have been proposed, in various forms, for its removal; depending respectively upon boiling it out at atmospheric or reduced pressure, and upon causing it to combine with iron in the form of scrap-iron, iron-manganese alloys, or couples of iron with zinc or copper (see e.g. Wehner, Eng. Pat. 7272, 1915; Wilson and Anti-Corrosive Eng. Co., U.S. Pat. 1387748, 1921, and Holle, D. R. P. 308288, 1916;

L. and C. Steinmüller, D. R. P. 320898, 1917; Hartung, D. R. P., 368645, 1916; Bailey, Morgan and Met-Vickers' Elect. Co., Eng. Pat. 194342, 1921. For a full discussion see Kastner, Proc. Inst. Mech. Eng. 1921; J. Soc. Chem. Ind. 1921, 40, T. 67).

Zeolite water-softening plants.—These plants make provision for the filtration, or, rather, percolation, of water through a bed of granular zeolite, and for the periodic regeneration of the zeolite by means of brine; they are, therefore, essentially very simple and conform to the type (United Water Softeners, Ltd.) illustrated in Fig. 20. Water enters by a meter A, and, valves 1 and 4 only being open, passes in at the top of the closed reagent tank B, down through the

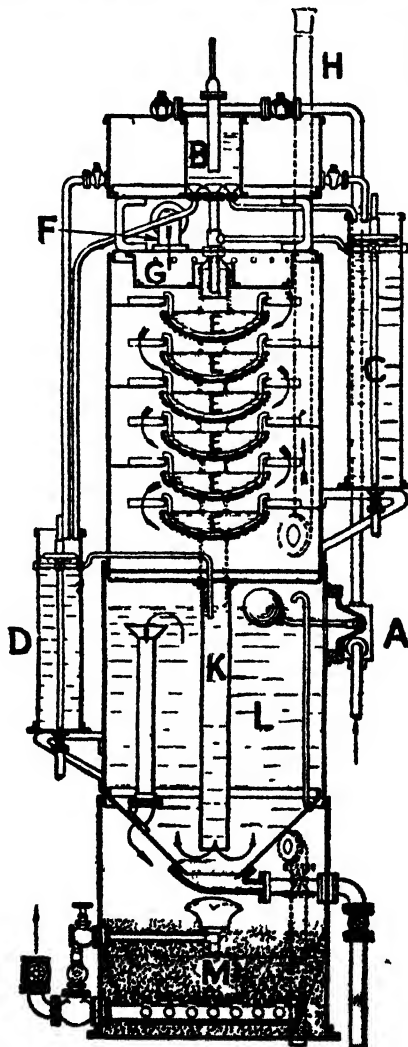


FIG. 19.

bed C of zeolite, supported upon a layer of quartz sand D, and thence to the main. When the meter indicates that the apparatus has treated the maximum quantity of water (calculated with regard both to the quantity of zeolite and to the initial hardness of the water), the cocks are manipulated so as to (1)

the water wholly from the tank, (2) introduce, by means of the steam injector *s*, the proper charge of brine previously prepared in the wooden tank *g*, and (3) to drain and wash the salt from the zeolite bed. This done, cocks 1 and 4 are again opened, all other cocks being shut, and the plant again functions as a water-softener.

Comparison of soda-lime and zeolite processes.—Each process has its peculiar advantages and limitations, which broadly determine its field of use and may be summarised as follows:—

With efficient plant, properly operated, the residual hardness of treated water should be 3–5 degrees for the cold soda-lime treatment, 1–3 degrees for the same process worked hot, and 0–1 degree for the zeolite process.

Dissolved solids are diminished by lime-soda treatment, but increased by zeolite softening,

owing to the substitution of sodium salts for calcium salts.

Treatment of water containing iron or sediment presents no difficulty in the lime-soda process, as these impurities are removed with the precipitate in the normal course of working. Such waters, however, must be freed from iron and sediment before entering zeolite softeners, to avoid the formation of a deleterious coating on the active material.

Cost of plant for lime-soda treatment depends only on the maximum hourly flow of water, whilst for the zeolite process it depends also on the hardness of the water. It is also affected by the fact that stoppages for regeneration of a zeolite plant are more frequent and of greater duration than those for cleaning of a lime-soda plant.

Cost of treatment is about the same for removal

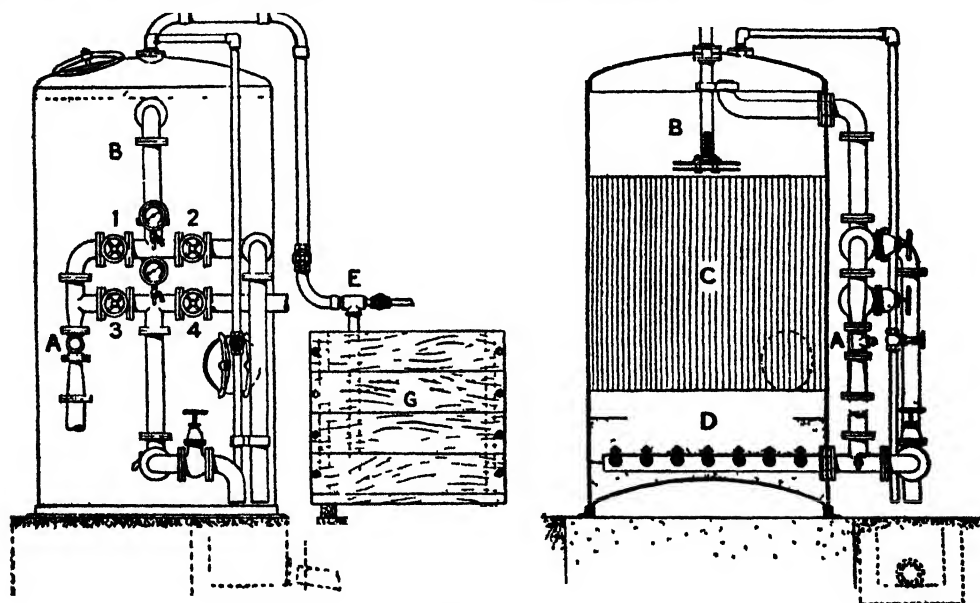


FIG. 20.

of permanent hardness by either method, but temporary hardness is removed by lime at about one quarter the cost of its removal by zeolite.

From the foregoing characteristics it appears that in the textile, dyeing, and laundry industries, where minimum hardness is the first consideration, zeolite softening is the more suitable. In many such cases, where the water contains iron or sediment, and has any considerable temporary hardness, it is advantageous to treat it first with lime in a precipitation softener and then remove residual hardness with zeolite. If this is done, ample reaction space must be provided in the lime softener, as any excess lime may hinder the operation of the zeolite softener and produce a turbid effluent.

The lime-soda process is the better for boiler-feed water, for municipal softening, and for water to be used in ice manufacture. Its suitability for municipal softening is determined by its low cost and by the possibility of applying it in existing installations. For boiler-feed and

ice manufacture reduction of dissolved solids is of primary importance, and this requirement is best met by the precipitation process. Where a raw water contains much bicarbonate hardness, the quantity of alkali bicarbonate produced by zeolite softening may cause serious alkalinity and priming in boilers. (For a fuller discussion of these matters, see Blumenthal, *Zeitsch. angew. Chem.* 1921, 34, 189; and Behrman, *J. Amer. Waterworks Assocn.* 1923, 10, 623; Memoranda by the Chief Engineer to the Manchester Steam Users' Association, 1903, and 1917–18; for a discussion with special reference to the textile industries, see King and Chambers, *J. Soc. Dyers*, 1918, 34, 240–247.)

H. V. A. B.
P. L. R.

WATER STONES v. AGATE.

WATERS, AERATED v. AERATED WATERS.

WAVELLITE. A mineral consisting of hydrous aluminium phosphate $3Al_2O_3 \cdot 2P_2O_5 \cdot 12H_2O$, forming globular or stalactitic masses with an internal radiating structure. The colour is

white, yellowish, or green; sp.gr. 2.32. The mineral usually occurs on the joint faces of slaty rock, and was first observed in the eighteenth century by Dr. W. Wavell in the slates at Filleigh near Barnstaple in Devonshire. Good specimens have also been found in Co. Cork. In larger amounts it occurs in Arkansas and Pennsylvania. At South Mountain in Pennsylvania it has been mined for use as a fertiliser and as a source of phosphorus, used locally for making matches.

L. J. S.

WAX-OPAL v. OPAL.

WAXES, ANIMAL AND VEGETABLE.

These waxes are a group of substances resembling beeswax in their physical properties; they are mixtures of compounds composed of the elements carbon, hydrogen, and oxygen. Waxes of mineral origin, such as paraffin wax, ozokerite, ceresin, and montan wax, are described elsewhere. Physically the waxes come in the series (1) fixed oils, (2) soft fats, (3) tallow-like substances and solid fats, (4) waxes, and (5) resins. The waxes all melt below 100°. The waxes differ from the fats in having little or no greasiness at ordinary temperatures. The greasiness of most of the fats is probably due to their containing some olein (glyceryl oleate) or some glyceryl esters of unsaturated fatty acids. There was an impression in the last century, doubtless produced by Chevreul's work on the fats, that whilst the fats contained glyceryl esters, the true waxes did not, but contained esters of higher members of the $C_nH_{2n}O$ series of acids with alcohol radicles other than glyceryl. As a result of this an unfortunate system was introduced of denying the name of 'wax' to those waxes that are largely composed of glycerides, and of calling them 'tallows.' It serves no useful purpose and has the effect of upsetting the ordinary meaning both of 'wax' and of 'tallow.' By it, on the one hand, Japan wax was to be called Japan tallow and myrtle wax was to be called myrica tallow, because they are both largely composed of glyceryl palmitate; and on the other hand, sperm oil was to be described as a liquid wax, because it was thought to contain very little glyceryl esters. Refined wool fat, a soft unctuous substance, was called wool wax. The inadvisability of attempting to alter the meaning of a word in common use to suit some special scientific classification was

noted out by Gregory in *Nature*, 1911, 87,

Beeswax and most of the vegetable waxes seem to be produced by the integuments of the organisms and not internally, and their value to the plant is to repel water or resist its action and prevent its ingress or egress. Beeswax, similarly, is a very suitable material of which to form the cells for storing honey, as it does not become soft or soppy by the action of the water in the honey.

The chief proximate components of the waxes are: (1) esters of the fatty acids with alcohols containing a high number of carbon atoms; (2) esters of fatty acids with glycerol; (3) free fatty acids; (4) free alcohols containing a high number of carbon atoms; (5) hydrocarbons. With respect to the formulae of compounds containing a high number of carbon atoms, it should be borne in mind that a CH_2 more or less makes such a small difference in the percentage com-

position that the exact formula cannot be settled by a carbon and hydrogen determination, and consequently authors differ somewhat in the formulae they assign to the components of the waxes; such formulae must therefore be regarded as scarcely fixed yet. Another point to be remembered is that authors have sometimes been careless, in that they have stated that substances found in the products of saponification of a wax were present in the wax; thus it has been stated that beeswax contains myricyl (melissyl) alcohol and ceryl alcohol, when the experiments only showed that these were found after saponification. There was no evidence to show that the free alcohols were present, and no doubt those found came from esters in the beeswax.

The waxes, like most natural products, are mixtures of several components, and the isolation of these is a difficult and lengthy task, which has been attempted by comparatively few investigators. In consequence of this and in order to meet the requirements of commerce, it is customary when examining samples of the waxes to determine what may be called their *analytical values*, and from the results to infer their quality and freedom from adulterations. These values are also called the *characteristics* of the waxes; they have been much studied and include the physical determinations of specific gravity, melting point and sometimes refractive index, and also certain chemical determinations, which are explained below under the heading 'Beeswax.'

It has been observed that Japan wax has the peculiarity of showing a lower specific gravity and a lower melting-point when it has recently solidified after having been melted, than when some time has elapsed since solidifying. Other waxes probably possess similar peculiarities.

Text-Books.—Benedikt-Ulzer, *Analyse der Fette und Wacharten*, Fünfte Auflage, 1908. Lewkowitch and Warburton, *Chemical Technology and Analysis of Oils, Fats and Waxes*, 6th ed. 3 vols. 1921–23. Wolff, *Die Lösungsmittel der Fette, Oele, Wachse und Harze*, 1922.

Arjun wax (*White insect wax of India*). About the year 1786 a wax produced by an insect was noticed in Madras by Dr. James Anderson (Correspondence, 1788–1791) and was called by him *White Lac*. It was thought that it might resemble the Insect wax of China, but it is distinctly different. Attention has been drawn to it from time to time, but it seems never to have been utilised. The insect producing it was first named *Coccus ceriferus*, and later *Cero-plastes ceriferus*; it has been found on the arjun or kowa tree, on poplar, mango, tea bushes, and on other trees. The crude wax occurs on the twigs in small mounds of a dull buff colour; it contains some moisture and black matter from which it can be freed by melting and straining. When thus purified it is yellow like beeswax, and hard and brittle like resin. It is partially soluble in cold alcohol, and nearly all of it dissolves in boiling alcohol; when the solution cools it becomes white and opaque. In warm ether it dissolves readily, but not completely. In hot oil of turpentine it dissolves readily, but the liquid becomes white and opaque on cooling. In benzene it is easily soluble with the exception of a little brownish matter. Carbon disulphide dissolves it only partially.

Pearson (Phil. Trans. 1794, p. 383) examined the wax from Madras and found that it melted in water at 83°. He made candles of it, but found that they smoked and gave a resinous odour.

Moore (J. Agric. Hort. Soc. of India, 1874-75, 5, 78) reported on some from Chota Nagpur, that one specimen contained 11 p.c. of moisture, another 13 p.c.; that it melted at 55°; that (probably after drying and melting) the specific gravity was 1.04, and the composition corresponded to the formula $C_{13}H_{22}O$.

Holland (Indian Museum Notes, 1891-93, 2, 93) reported on some from the Central Provinces, that it (the crude material apparently) melted at 60°, and had a specific gravity of 1.04 at 29°.

Balanophore wax occurs in the parenchymatous cells of various species of Balanophores. These are small parasitic plants growing on the roots of various other plants and are found in abundance in Java. They are so rich in wax that they burn with a bright light, and the natives prepare candles by pounding the plants to a paste and coating thin strips of bamboo with this. The wax was named *balanophorin* by Göppert in Nova Acta Acad. Caes. Leopoldinae Carolinae Nat. Curiosorum, 1841, 18 Suppl. 229, where a botanical account of the plants is given. The wax was examined by Poleck (*ibid.* 1847, 22, 117), who found that it was very soluble in ether and also that it dissolved when gently warmed with concentrated sulphuric acid and was precipitated again by dilution. It was examined more recently by Simon (Sitz. Ber. Kaiserl. Akad. Wissenschaften, Wien, 1910, 119 II. b, 1161). Air-dried slices of the plants (the latter had been preserved in alcohol) were reduced to a coarse powder and extracted with hot ether; they yielded about 65 p.c. of crude wax which, when melted and filtered (this took 4 months to accomplish), gave a honey-yellow wax, brittle when cold, but becoming soft when warmed in the hands and capable of being drawn out in fine threads. One part required about 140 parts of 95 p.c. alcohol for its solution, and of the product of this purification one part required about 50 parts of acetone for its solution. Balanophorin was thus obtained as a white amorphous powder. After further purification it was found to melt at 56°-57° to a colourless liquid resembling glycerin, which slowly solidified to a white wax. By analysis it was found to have a composition corresponding to $(C_{13}H_{22}O)_n$, just as Poleck had found. It gave no acid value nor saponification value. When strongly heated no acrolein was given off. Simon succeeded in decomposing it by distillation in a partial vacuum containing carbon dioxide, and also by fusion with potassium hydroxide, and in both cases obtained palmitic acid as a product. An account of other products was to be published later.

Langedorffia hypogaea, another of the Balanophores, which is found near Bogota, in Colombia, yields large quantities of wax, and the stems are sold in the markets and used as candles on saints' days (Hooker, Trans. Linn. Soc. 1859 22, 41). This wax does not seem to have been chemically examined yet.

Beeswax is produced by the common bee *Apis mellifica*, and also by some allied species;

it is not collected from the flowers by the bee, but is the secretion of certain organs situated on the underside of the abdomen of the neuter or working bees, and is used by them in forming the cells of the honeycomb. They are said to consume about 10 lbs. of honey in order to secrete 1 lb. of wax. To obtain the wax the honey is allowed to run out from the comb, which is then pressed to separate as much honey as possible. The adhering honey and other impurities are next removed by melting the mass in hot water; the melted wax floats on the surface, and is strained to remove dead bees and brood. The residue is put in layers with straw, and is pressed to obtain more wax, the straw acting as a filter; this product is known as 'press wax.' The mass then remaining is sometimes extracted with benzene to obtain still more wax, the product being 'extraction wax.' The 'extraction wax' is apt to be impure from the use of artificial comb, and also from substances being extracted from the dead bees and straw; further, wax compositions and adulterated beeswax are also sold under the name of 'extraction wax' (Hirschel, Chem. Zeit. 1904, 28, 212). A common practice is to pare off the capping of the honey cells and then place the comb in a centrifugal machine, which removes the honey and leaves the comb undamaged, so that it can be replaced in the hive to be refilled by the bees, and thus save the honey that they would use to produce fresh wax. In this system the capping only is melted down for wax. Impurities may be introduced into beeswax by the use of artificial combs and foundations for combs made of materials other than beeswax. These are employed to save the honey which the bees would consume in making the wax.

Beeswax is yellow in colour and varies in tint, according to the materials employed by the bees and the care taken in its preparation; sometimes it is brownish, reddish, or greenish. It has a pleasant honey-like smell, which is made more apparent by warmth. When cold it is brittle; at ordinary temperatures it is tenacious; its fracture is dry and granular.

Solubility.—It is insoluble in water. Carbon tetrachloride is said to be the best solvent. Other solvents are: chloroform, carbon disulphide, tetralin (tetrahydronaphthalene), hexanil (hexahydrophenol), benzene, benzine, oil of turpentine, ether (not a very good solvent). The solvent is to be used hot, and in the case of some or all of these, a portion of the beeswax separates on cooling.

As regards ether, Buchner (Chem. Zeit. 1907, 31, 570) allowed beeswax to soak in ether at the ordinary temperature for some time, then filtered the resulting homogeneous paste, and washed it with ether; after getting rid of the ether he obtained from the filtrate 30 p.c. of a fairly soft, deep yellow mass, and from the insoluble residue 70 p.c. of a bright brownish wax considerably harder than the original wax. The soluble portion had an acid value of 40 and a saponification value of 83.8, whilst the insoluble portion had an acid value of 11.6 and a saponification value of 99.1; thus the part that dissolves is richer in acid and colouring matter and poorer in ester than the undissolved part.

Buchner (Chem. Zeit. 1918, 42, 373) also describes the difference in analytical values of

wax obtained from press-residues by using different solvents, namely, benzine, chloroform, and carbon tetrachloride. The esters appeared to be less easily dissolved than the other components, so that light benzine removed less of them than the other solvents, and the extraction wax, when light benzine was used, appeared abnormal.

Cold alcohol dissolves scarcely any; boiling alcohol dissolves a good deal (about 15 p.c. reckoning from the acid value), leaving an undissolved residue from which something is dissolved every time the treatment with boiling alcohol is repeated. All except about 2 p.c. is deposited when the alcohol cools.

Analytical values.—The creation of a systematic plan for examining samples of beeswax is due to Becker, Hehner, and Hübl. Becker (Dingl. poly. J. 1879, 234, 79), following Köttstorfer's plan for butter (Zeitsch. anal. Chem. 1879, 18, 199), determined the saponification value. Hehner (Analyst, 1883, 8, 16) determined the amount of potassium hydroxide required to neutralise the free acid and that required to saponify the whole wax; but he expressed his results in terms of cerotic acid and myricin. Hübl (Dingl. poly. J. 1883, 249, 338) prescribed the determination of the acid value, the ester value, the ratio value, and later for fats and oils (*ibid.* 1884, 253, 281) of the iodine value. The meaning of these terms may be briefly explained as follows:—

Acid value.—This is the number of milligrams of potassium hydroxide required to neutralise the free acids in one gram of the sample.

Saponification value.—When an oil, fat, or wax is boiled with alcoholic solution of potassium hydroxide, not only is the free acid neutralised, but the esters of the various acids are decomposed, potassium taking the place of the alcoholic radicles and forming salts (soaps) with the acids and the alcoholic radicles forming the corresponding alcohols. The number of milligrams of potassium hydroxide used in effecting these two actions for one gram of sample is called the *saponification value*.

Ester value.—If the acid value is deducted from the saponification value the remainder represents the number of milligrams of potassium hydroxide that has been used in decomposing the esters, and is called the *ester value*. Esters were formerly known as compound ethers, so the term *ether value* is sometimes found instead of ester value.

Ratio value.—If the ester value is divided by the acid value, the quotient is called the *ratio value*. It is useful in deciding on the purity of a sample.

Iodine value.—In most cases the oils, fats, and waxes contain unsaturated compounds; these when treated with solution of iodine and mercuric chloride under prescribed conditions combine with a certain amount of iodine. The percentage of iodine thus taken up is called the *iodine value*; it is a measure of the amount of unsaturated compounds in the sample. It differs from the other values in being a percentage and not a number of milligrams.

Total acid number.—Benedikt and Mangold (Chem. Zeit. 1891, 15, 474) proposed a determination of what they called the *total acid number*, but it has not come into general

Instead of 'value' the term 'number' is often used for the above results.

Although these values are a useful guide in judging the purity of a sample, they are not infallible, since it has been found possible, by a judicious mixture of ingredients, to prepare composition waxes which will give the correct analytical values for a pure beeswax.

Buchner value.—To examine samples of beeswax containing such composition waxes, Buchner (Chem. Zeit. 1895, 19, 1422, corrected by Kissling, *ibid.* p. 1682, and improved by Berg, *ibid.* 1903, 27, 753 and 754. and in Benedikt-Ulzer's Anal. Fette u. Wachsarten, 1908, p. 1095) devised a determination giving what is known as the *Buchner value*. The sample is boiled with alcohol, and then after 12 hours the acidity of the liquid is determined.

Weinwurm's test.—This is a test described by Weinwurm in Chem. Zeit. 1897, 21, 519, to detect paraffin or ceresin in beeswax. It uses glycerol and is useful, but not always reliable; see various papers in the bibliography and Benedikt-Ulzer, Anal. Fette u. Wachsarten, 5th ed. 1908, p. 1109.

Long tables giving the recorded analytical values of ordinary yellow beeswax are to be found in the text-books of Benedikt-Ulzer and of Lewkowitsch and Warburton; and Buchner in Zeitsch. öffentl. Chem. 1912, 18, 90, gave the values of some abnormal waxes. Berg (Chem. Zeit. 1903, 27, 752) gives a long table of the values of various waxes. They may be summarised as follows. Some errors have been corrected by the original sources, and 'press wax' and 'extraction wax' are excluded.

	Commonly occurring values lie between	Extreme values are	
		Minimum	Maximum
Specific gravity at 15°.	0.958 to 0.967	0.949 F. (0.941 L.)	0.972 St.
Melting-point . . .	62.5° „ 66.5°	61° St. (60.5° L.)	66.5° Bg.
Acid value . . .	17 „ 22	15.6 I.I.	25.7 Bch.
Ester value . . .	70 „ 82	60.8 Bch.	84.9 Bg.
Saponification value .	90 „ 103	80.8 Bch.	106.5 Bg.
Ratio value . . .	3.2 „ 4.3	2.38 Bch.	5.0 I.I.
Buchner value . . .	1.5 „ 6.1	1.1 M.	7.4 Bg.
Iodine value . . .	6 „ 13	5.6 Bg.	17.12 St.

- Boh.—*Buchner*, Zeitsch. öffentl. Chem. 1912 18, 80.
- Bg.—*Berg*. Beeswax from many places, Chem. Zeit. 1903, 27, 755.
- Bt.—*Bertainchand and Marcille*. 'Note sur la Cire d'Abeilles en Tunisie, 1898; Extrait du Bulletin de la Direction de l'Agriculture, Tunia.' (A pamphlet.)
- F.—*Fendler*. Beeswax from German East Africa, Arbeiten Pharm. Inst. Univ. Berlin, 1904, 1, 203.
- I.I.—Beeswax from Northern Nigeria, Bull. Imperial Institute, 1911, 9, 238.
- L.—*Lidow*. Russian commercial samples, but it is not clear whether adulterated samples were excluded and in the sp.gr. the temperature is not stated, Chem. Zeit. Repert. 1905, 29, 278, from Westnik shirow. wesch-tsch, 1905, 6, 89.
- M.—*Masbaum*. Portuguese beeswax, Zeitsch. angew. Chem. 1903, 16, 647.

Detailed directions for ascertaining the analytical values, for performing tests, and for interpreting the results will be found in the text-books and in the original papers; they have been subjects of much controversy especially those for the saponification value, since many of the waxes are not so readily saponified as the fats.

In deciding on the purity or otherwise of a sample, all the analytical values and the results of tests for impurities must be considered together. The text-books and various original papers and experience give guidance in forming an opinion.

Composition.—The composition of beeswax has received the attention of several investigators, and some account of the leading researches is given below.

Dr. J. F. John (Chem. Tabellen der Pflanzenanalysen, 1814, p. 42) separated beeswax by means of alcohol into a soluble and an insoluble portion. These he named *cerin* and *myricin* respectively, believing them to be the same substances that he had previously obtained from the wax of *Myrica cordifolia* from Cape Colony and had so named; thus making the common mistake of early investigators of identifying compounds from different sources on quite inadequate grounds. The *cerin* and *myricin* from beeswax and from *M. cordifolia*, however, must not now be regarded as identical. The latter wax seems not to have been examined recently and probably would be found to resemble myrtle wax in its composition. In Dr. John's time it was imagined that the number of compounds present in plants and animals was far fewer than are now known, and consequently compounds were believed to be identical if they agreed in a few simple properties. This belief has given rise to some misleading names.

Brodie (Phil. Trans. 1848, Pt. 1, 147; 1849, Pt. 1, 91), using Surroy and other beeswax, found two acids in the *cerin* or portion soluble in boiling alcohol, and named the most important of them with m.p. about 78° *cerotic acid*, giving it the formula $C_{26}H_{54}O_2$; he thought that the other acid was present in the wax in very small quantities; he estimated the wax to contain 22 p.c. of *cerotic acid*. In the *myricin*, or portion nearly insoluble in boiling alcohol, he found an ester of palmitic acid with a wax alcohol $C_{26}H_{54}O$ with m.p. 85°, which he named

melissin, no doubt from *melissa*, a bee. This alcohol is now called *myricyl alcohol*, or better, *melissyl alcohol*, since myricyl is a misleading name, arising from Dr. John's mistake, and very probably there is no myricyl present in the waxes of the *Myrica* group. Brodie also found in beeswax indications of other substances.

Very thorough investigations to find the components of beeswax were made by Nafzger (Annalen, 1884, 224, 225) and Schwalb (*ibid.* 1886, 235, 106); they used Württemberg country yellow wax and employed long series of fractionations. In the part soluble in hot alcohol, the *cerin*, Nafzger found principally *cerotic acid* with m.p. 78°, for which he favoured the formula $C_{26}H_{54}O_2$, or perhaps $C_{25}H_{50}O_2$; he found also some *melissic acid* $C_{26}H_{50}O_2$ with m.p. 89°–90°, and another acid of m.p. 75°–76° in small quantity. The ester portion left undissolved by the hot alcohol, the *myricin*, was saponified, and the product was extracted with hot petroleum ether to dissolve out wax alcohols, &c., thus leaving sodium salts of the fatty acids. From these latter he obtained palmitic acid $C_{16}H_{32}O_2$ with m.p. 61.5°, and satisfied himself that they included no salts of other higher fatty acids such as *cerotic acid* or *melissic acid*. Consequently no esters of such acids are present in the *myricin*, although *cerotic* and *melissic acid* are present in the wax in the free state and are found in the *cerin*. As regards acids of the *oleic* series: from the mother liquor of the *cerin* and from a certain mother liquor obtained in the examination of the *myricin*, he obtained similar yellow acid syrups having the characteristic odour of beeswax. These he believed to contain mixtures of acids of the *oleic* series, the odour being due either to these acids or to some special substance mixed with them. Thus these acids are present both free and as esters.

Schwalb completed Nafzger's work by examining the substances extracted by petroleum ether from the saponified *myricin* and so containing the wax alcohols which had existed as esters in the original wax. In this extract he found not only wax alcohols, but hydrocarbons; the presence of which in beeswax he was the first to discover. He isolated two which he believed to be normal heptacosane $C_{27}H_{56}$ with m.p. 60.5° and normal hentriacontane $C_{31}H_{64}$ with m.p. 68°; he also obtained a soft vaseline-like mass and thinks that other lower paraffins were present. He estimated the amount of the above two in beeswax (not the total hydrocarbons) to be about 5 to 6 p.c. As regards the alcohols produced by the saponification of the *myricin*, he found *melissyl alcohol* with m.p. 85°–85.5° and from it prepared the corresponding *melissic acid* with m.p. 88.5°–89°. He favoured the formula $C_{26}H_{50}O$ for the alcohol and $C_{26}H_{50}O_2$ for the acid. He also found evidence of the presence of lower alcohols in the saponification products, so to identify them he converted the mixture containing them into the corresponding acids and drew the conclusion that one was *ceryl alcohol* $C_{26}H_{54}O$ or $C_{27}H_{56}O$, convertible into *cerotic acid* by heating with soda lime and that another was $C_{24}H_{50}O$ or $C_{25}H_{52}O$. (These alcohols, doubtless, were not present free in the wax, but were produced by the action of their esters with palmitic acid.)

Marie (Ann. Chim. 1896 [7], 7, 145) made a close examination of the product regarded by Brodie as cerotic acid. He found that fractional solution in methyl alcohol was a much better method of separation than fractional precipitation or fractional crystallisation, and that it effected separation into pure cerotic acid and a much larger proportion of melissic acid than had previously been believed to be present. He regarded cerotic acid as being $C_{31}H_{60}O_2$ or $C_{30}H_{58}O_2$ with m.p. 77.5° , the evidence pointing to the first of these formulæ; and melissic acid as being $C_{26}H_{50}O_2$ with m.p. 90° . He obtained from beeswax about 15 p.c. of the pure mixed acids, and in this he found 30–40 p.c. of melissic acid. As regards these percentages, it should be noted that in extracting the beeswax with boiling alcohol to obtain the free cerotic and melissic acids a certain amount of myricin (melissyl palmitate, &c.) dissolves too. In the treatment adopted by Marie, namely, heating the crude mixed acids with potash-lime and potash, the alcohol radicles of the myricin are converted into melissic and cerotic acids, and these are included in his percentages, although they were not present free in the beeswax. What proportion they amounted to is not clearly stated; perhaps it was not large. His object was rather to get cerotic acid than to estimate its amount in beeswax.

Schalkef (Ber. 1876, 9, 278, and 1888; 1879, 12, 696, from Russian Phys. Chem. Soc.) thinks that cerotic acid, melissic acid, and melissin are mixtures of several substances and that in cerotic acid he found an acid with m.p. 91° and formula $C_{34}H_{68}O_2$. Lipp and Casimir (J. pr. Chem. 1919, 99, 263) found in Ghedda wax an acid with this formula, but with m.p. 94.5° – 95° .

Heiduschka and Gareis (J. pr. Chem. 1919, 99, 293) have studied the question of the formulæ for melissyl alcohol and melissic acid obtained from beeswax, and of the formulæ for the similar alcohol and acid obtained from carnaüba wax. They find that the products obtained from carnaüba wax have the formulæ $C_{30}H_{61}OH$ and $C_{29}H_{58}O_2$, whilst those from beeswax contain CH_2 more and are $C_{31}H_{63}OH$ and $C_{31}H_{62}O_2$. They succeeded in preparing from the carnaüba wax alcohol the acid with an added carbon atom, and found that its lead salt was identical with that of beeswax-melissic acid. Analyses of a number of compounds that they prepared also supported these views.

The question of the total amount of hydrocarbons in beeswax can hardly be considered as settled yet. In order to determine it A. and P. Buisine (Bull. Soc. chim. 1890, [3] 3, 872 and 1891, 5, 656), using Dumas and Stas's reaction (Annalen, 1840, 35, 129), heated beeswax with potash and potash lime to 250° . In this way potassium salts of the acids are formed and the alcoholic radicles in the esters are converted into salts of the corresponding acids with evolution of hydrogen; these salts remain undissolved when the product is extracted with ether or petroleum ether, whilst the hydrocarbons go into solution. They found 12.5–14.5 p.c. and that some were unsaturated as the hydrocarbon mixture absorbed 22 p.c. of iodine. Abrams and Hett (J. Soc. Chem. Ind. 1899, 18, 591, from Zeitsch. öfentl. Chem. 5, 91), using Buisine's method, found from 12.7 to 17.5 p.c.

in different kinds of wax. Ryan and Dillon (Sci. Proc. Roy. Dublin Soc. 1916, 15, 107) found, however, that the product, supposed to be nothing but hydrocarbons, obtained from beeswax by a series of treatments, including Dumas and Stas's reaction, really contained a little oxygen; this amounted on an average to 0.8 p.c. It therefore seems that Buisine's method gives results which are too high. Ryan and Dillon suggest that some primary alcohol may be present in the product and also some secondary or tertiary alcohols; for they found that secondary and tertiary alcohols when heated with potash-lime evolve no hydrogen, and that primary alcohols do not evolve the full theoretical amount. The method thus requires further study.

The hydrocarbon, *melene*, found by Rictet and Bouvier (J. 1915, 604) in coal, in *vi*rum-tar, in Galician paraffin, and in the distillation products of beeswax, was assumed to be a solid naphthene, $C_{30}H_{60}$. J. Marcusson and F. Böttger (Ber. 1924, 57, 633) have now found that Indian paraffin wax, which melts at -60° , consists very largely of *melene*. The hydrocarbon can be readily isolated by crystallisation from benzene and then from benzine. It melts, when pure, at 62° – 63° , has $d_{20}^{20} 0.7913$; $d_{20}^{20} 0.9037$; $n_D^{20} = 1.4228$. Its composition corresponds to $C_{30}H_{60}$, and on oxidation with strong hot nitric acid, it gives a mixture of aliphatic acids, whereas naphthenes, under similar conditions, give nitro-compounds. Further, by catalytic oxidation with air in presence of manganese dioxide, *melene* yields solid fatty acids, whilst naphthenes yield polynaphthenic acids; and *melene* is slowly assimilated at 30° by *Bacterium aliphaticum*, which is incapable of attacking naphthenes. *Melene* is therefore a paraffin and not a naphthene (J. Soc. Chem. Ind. 1924, 43, B 457; cf. Funcke, Arch. Pharm. 1921, 259, 93).

In order to discover the cause of the difficulty experienced in saponifying beeswax completely Berg (Chem. Zeit. 1908, 32, 777) investigated the substances, amounting to about 2 p.c., that remain in solution after boiling beeswax in alcohol and allowing the liquid to cool, thus eliminating the crude cerotic acid and myricin. By evaporating the solution and extracting the residue thus obtained with ice-cold petroleum ether, he first separated as insoluble 0.44 p.c. of a brown semi-fluid mass having an intense beeswax odour. In the part that dissolved he found indications of various acids and then cholesterol esters, discovered by the colour test; he believes that 0.6 p.c. of these are present in beeswax, and probably considerably more. Such esters are difficult to saponify and have high saponification values. He saponified them and found cholesterols and several acids which seemed to be acetic, butyric, valeric, and others which were not volatile on the water bath, and included one that possessed the beeswax odour and was unsaturated, as its lead salt was soluble in ether. He did not succeed in making any ultimate analyses; but his work shows what a large number of compounds are contained in beeswax in minute proportions. He also examined in the same way a white wax bleached by permanganate.

Summing up the results of the various re-

searches, it appears that ordinary beeswax is composed chiefly of melissyl palmitate $C_{31}H_{63}O_2$, $C_{31}H_{61}O_2$, with some ceryl palmitate $C_{33}H_{65}O_2$, $C_{33}H_{63}O_2$, and some palmitate of the radicle $C_{16}H_{33}$; these are contained in the part known as myricin, which is very nearly insoluble in boiling alcohol. In the part known as cerin, which is soluble in boiling alcohol, there are present free acids amounting when purified to about 15 p.c. of the beeswax, chiefly cerotic acid. According to Mario, crude cerotic acid contains about 60 to 70 p.c. of cerotic acid $C_{26}H_{52}O_2$, and about 30 to 40 p.c. of melissic acid; but owing to the method he used, some of these acids may have come from decomposition of some of the myricin. There are also indications of the presence of another acid. Hydrocarbons are also present, namely, normal heptacosane $C_{27}H_{56}$, and normal hentriacontane $C_{31}H_{64}$, together amounting to 5 to 6 p.c., and in addition a soft vaseline-like mass has been separated.

Gascard and Damoy (Compt. rend. 1923, 177, 1222, 1442) state that after saponification they have obtained from beeswax the following compounds: (1) Neocerotic acid $C_{25}H_{50}O_2$ (m.p. 77.8°), the same acid that Mario described as having m.p. 77.8° and called cerotic acid. It has the same formula as Carius's hyaenic acid, but they consider that that was not a pure compound. (2) Cerotic acid $C_{27}H_{54}O_2$ (m.p. 82.5°), identical with that obtained from Chinese insect wax, and apparently identical with the acid that Tropsch and Kreutzer (Brennstoff-Chemie, 1922, 3, 49, 177) obtained from montan wax and named carbocerinic acid. (3) Montanic acid $C_{29}H_{58}O_2$ (m.p. 86.8°), apparently identical with the acid that Tropsch and Kreutzer (l.c.) obtained from montan wax and called montanic acid. (4) Melissic acid $C_{31}H_{62}O_2$ (m.p. 90°). They suggest that perhaps the acid that Brodie obtained from myricin is really not palmitic acid $C_{16}H_{32}O_2$, but one with an uneven number of carbon atoms. (5) Neoceryl alcohol $C_{29}H_{58}O$ (m.p. 75.5°). (6) Ceryl alcohol $C_{31}H_{62}O$ (m.p. 80°), identical with that from Chinese insect wax. (7) Montanyl alcohol $C_{29}H_{58}O$ (m.p. 84°). (8) Myricyl [melissyl] alcohol $C_{31}H_{64}O$ (m.p. 87°). The ceryl and melissyl alcohols were the most abundant of the alcohols. (9) Penta-cosane $C_{25}H_{52}$ (m.p. $54.5-54.6^\circ$). (10) Hepta-cosane $C_{27}H_{56}$ (m.p. $59.2-59.5^\circ$). (11) Nona-cosane $C_{29}H_{60}$ (m.p. 63.5°). (12) Hentriacontane $C_{31}H_{64}$ (m.p. $68.4-69^\circ$).

Indications have been found of many minor constituents which have not yet been fully identified: (1) The yellow colouring matter which is very soluble in alcohol. (2) The substances to which the characteristic odour of beeswax is due. (3) Unsaturated acids (their lead salts being soluble in ether), both free and as esters; the odour seems to be associated with these. (4) Various other acids. (5) Cholesterols combined as esters, perhaps with acetic, butyric, valeric, and non-volatile acids. These cholesterol esters amount to at least 0.6 p.c. of the beeswax and very probably more, and perhaps some cholesterols are also present free. (6) It has been suggested that the difficult saponification of beeswax is due to the presence of lactones as well as to the cholesterol esters, since carnauba wax is known to yield a lactone. (7) Buchner (Zeitsch. öffentl. Chem. 1910, 16, 131) says that traces of

glycerides are nearly always present in beeswaxes.

It must be remembered that a substance like beeswax is not of constant composition and that there are many circumstances likely to cause variations such as the breed of the bee and the weather of the year it was produced in. Further, Reid (J. Soc. Chem. Ind. 1915, 34, 462) points out that usually in melting the comb some of the propolis is absorbed by the wax, and that the wax from old pollen-clogged combs is different from that from new combs.

Foreign varieties of beeswax.—In addition to wax resembling European beeswax fairly closely, varieties giving very different analytical values are imported into Europe; they are products of various species of bees other than *Apis mellifica*. About 1896, samples of Indian beeswax were appearing in Germany under the name of *Ghedda wax* and were examined by Buchner; it turned out later that they were products from *Apis dorsata*, *A. indica*, and *A. florea*. He found that they gave values differing considerably from those of ordinary beeswax, although they resembled it in appearance. They were, however, brighter in colour, more plastic, and had a pleasant odour, which was especially noticeable on saponification. This Indian beeswax continued to come on the German market from Bombay. Buchner (Chem. Zeit. 1905, 29, 79) found that it was characterised by a low acid value, a high ester value, and a high ratio value; thus in 36 samples he found the acid value to range from 5.3 to 12.2, but only in four samples was it over 10. The ester value ranged from 75.2 to 111.5, the saponification value from 81.8 to 120.2, and the ratio value from 7.4 to 17.9. Wax of this description appears sometimes to have been called China wax, and may have come from Annam or French Cochinchina as well as from India. Buchner maintains that *Ghedda wax* is a true beeswax (Chem. Zeit. 1905, 29, 79 and 1906, 30, 529), so that the difference in its analytical values must be remembered when judging the purity of a beeswax.

Hooper (Agricultural Ledger of India, 1904, 11, 73) describes the species of bees found in India, and the wax and honey trade there. The wax is derived from *Apis dorsata*, *A. indica*, and *A. florea*, but chiefly from *A. dorsata*; *A. mellifica* does not occur there except as an importation. The wax from the combs of these three species seems to be substantially of the same composition. It differs from European beeswax in having a much lower acid value; in the case of 33 specimens from these three species the acid value ranged from 4.4 to 10.2, with an average of about 7, the ester value from 69.5 to 123.8, the saponification value from 75.6 to 130.5, and the Hübl iodine value from 4.3 to 11.4. The m.p. ranged from 60° to 68° . Some Indian waxes of unknown origin gave higher acid values and other values outside these limits. In the comb the upper part gives a clean white wax and the lower part a dirty and coloured substance; but as a rule these parts are not separated before melting. Turmeric is universally added to give the wax a golden yellow colour, as white wax is not appreciated in the native markets. In one district it is said that oil of *Sesamum indicum* is added.

Hooper (l.c. p. 79) also describes another kind

of beeswax produced in India and Burma by minute stingless bees of the *Melipona* or *Trigona* species, sometimes called mosquito bees or dammar bees. It is of a blackish colour and sticky consistency. In 8 specimens the acid value ranged from 16.1 to 22.9, the ester value from 55.2 to 128.3, the saponification value from 73.7 to 150, the iodine value from 30.2 to 49.6, and the m.p. from 66° to 76°.

Most probably the natives do not keep the *Melipona* wax separate, but mix it indiscriminately with the wax of the three *Apis* species.

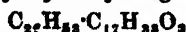
Hooper describes (*ibid.* 1908, 9, [3] 31, Abstract in J. Soc. Chem. Ind. 1909, 28, 664) *Pwé-nyet* (black wax of Burma) obtained from the nests of *Trigona laeviceps* and possibly from those of other dammar bees; it is not always black and seems to be more of a resin than a wax.

In the old records a wax called *Andaques wax* is described as being collected by the Indians in New Grenada (now Colombia), especially by the Tamas tribe, which lives near the Rio Caqueta. It was probably the product of small *Melipona* bees. A sample was examined by Lewy (Ann. Chim. 1845, [3] 13, 453); after purifying it by treatment with boiling water he found that its m.p. was 77°, its sp.gr. at 0° was 0.917, and that it contained 81.66 p.c. of carbon and 13.55 p.c. of hydrogen. It was used locally for making candles for religious worship.

A black beeswax found in the Dutch Indies is described by Blits (Nederl. Tijdschr. Pharm. 10, 35, abstr. in J. Soc. Chem. Ind. 1898, 17, 468), and the wax of a South Brazilian bee, probably of the *Melipona* or *Trigona* species, is described by Gadamer and Hinderer (Arch. Pharm. 1917, 255, 423), who gives its composition as well as its analytical values.

Returning to the Ghedda wax, there is a long paper by Buchner and Fischer (Zeitsch. öffentl. Chem. 1913, 19, pp. 147, 170, and 188) on East Indian or Ghedda wax, and on so-called China wax, which gives 160 analyses by Buchner and 108 analyses by Schulten, of Calcutta. Further information about the beeswaxes of India and Eastern Asia is given by several papers of Fischer (*ibid.* for 1913 and 1914). Recently 23 samples of comb and beeswax from Bengal and Assam, collected under the supervision of District Officers, were examined at the Imperial Institute by Roberts and Islip (Analyst, 1922, 46, 246); they found that neither *Weinwurm's* test nor that of Salamon and Scaber could be relied on.

The composition of Ghedda wax or East Indian beeswax has been investigated by Lipp, with Kuhn, Kovács, and Casimir (J. pr. Chem. 1912, 86, 184; 1919, 99, 243, and 256). They found that the principal components are: one of the ceryl hydroxymargarates



ceryl margarate $C_{25}H_{52} \cdot C_{17}H_{35}O_2$, and ceryl palmitate $C_{25}H_{52} \cdot C_{15}H_{31}O_2$; together with roughly 7 p.c. of hydrocarbons, namely: heptacosane $C_{27}H_{56}$ (roughly 5 p.c.), hentriacontane $C_{31}H_{62}$ (roughly 2 p.c.), and indications of another hydrocarbon which they could not isolate. As in European beeswax, they found some free acids, but only in small proportions, namely, cerotic acid $C_{26}H_{52}O_2$, and an acid $C_{24}H_{48}O_2$, which they named *Ghedda acid*. Its m.p. was 94.5°-95°.

An acid with this formula and m.p. 91° was described by Schalfée (Ber. 1876, 9, 278, and 1888). These two acids are present chiefly in the free state and the other acids as ceryl esters. In the products of hydrolysis they found also, but only in small proportion, a different hydroxymargaric acid and traces of formic, acetic, and butyric acids and of a resinous substance.

White or bleached beeswax.—Most beeswax is bleached before use; bleached beeswax is harder, and candles made from it burn better than those made of yellow beeswax. The bleaching is effected by exposure to light and air or by chemical agents, or by both methods. Chemical agents do not bleach it so thoroughly as does light, so that when they are used a bleaching by light is required to get the results; they serve, however, to shorten the time taken in bleaching.

The wax is first purified by repeated meltings in hot water until it is no longer grey, and the remaining honey is removed. In doing this grey underlayer is cut or scraped off from cooled cake of wax, and is remelted with the next lot treated. If the water used is hard, it is stated (Cheshire, Bees and Bee-Keeping, p. 589) that the cerotic acid of the wax forms an insoluble calcium soap, appearing as a grey spongy material and that thus a waste of wax is occasioned. Rain-water or distilled water should therefore be used, or else the water should be acidified with sulphuric acid. The use of acidified water also checks the formation of emulsions and is recommended for the various remeltings. Old and dirty combs should be soaked in cold water for some time before melting, as the dirt and cocoon skins when wet do not absorb and waste wax as they would if dry.

In order to expose as much surface as possible to the sun's rays, the wax is reduced to thin bands. The melted wax is poured into a box of metal plate, in the bottom of which are several narrow slits or holes. These are directly over a horizontal wooden roller revolving in a vessel containing cold water, which covers half the roller. The wax escapes from the slits in bands, which pass on to the revolving roller and solidify in the water in the form of thin ribbons. These ribbons are removed from the water, spread on canvas stretched over wooden frames, and exposed to the sun; they are sprinkled from time to time with water to keep them moist, and turned over to expose fresh surfaces to the sun. If the sunshine is very powerful, the heat may cause the ribbons to stick together; this can be avoided by watering, but not more than is necessary should be employed, as Heinz (Seifensieder Zeitung, 1913, 40, 1140) thinks that evaporating water vapour checks the oxidising action of the air. The inner portion of the ribbon bleaches more slowly than the outer surface, so to accelerate the bleaching the partially bleached wax is remelted and again made into ribbons, so that new surfaces are exposed; this remelting, however, causes some loss. Wax from different sources bleaches with varying facility, and some varieties cannot be bleached, so samples should first be tried on a small scale.

The addition of a little oil of turpentine to the yellow wax before making it into ribbons reduces the time taken in bleaching, but is said

by Heins to impart an unpleasant odour to the wax. Rectified oil of turpentine free from resin should be used. The bleaching effect of oil of turpentine was noticed by Ostermaier (Repert. f. d. Pharm. 1834, 48, 97). Sometimes a few p.c. of tallow are added to the wax to hasten the bleaching and to diminish brittleness, and this is considered allowable and is not counted as an adulteration.

After a longer or shorter period, depending on the intensity of the sunshine and the temperature, the bleaching is complete; it takes from 10 to 60 days. The wax is then once more melted in hot water, strained, and allowed to solidify in suitable shapes.

When chemical agents are used a mixture of potassium dichromate and sulphuric acid is said to be the best (Heinz, Seifensieder Zeitung, 1913, 40, 1140, 1169, and 1192). The wax is boiled with a solution containing 12 parts of potassium dichromate and 35 parts of sulphuric acid to 100 parts of water and wax. The green chromium compound produced by the reduction of the dichromate is removed by washing the wax with water containing 6-8 p.c. of lactic acid, or containing sulphuric acid. This process has been found effective even with some waxes that were considered unbleachable.

Potassium permanganate solution, followed by sulphurous acid has been tried, but the results were not very satisfactory. Other chemical agents that have been tried or recommended are the use of artificially made ozone, of hydrogen peroxide acidified with sulphuric acid, of barium peroxide of potassium chlorate with sulphuric acid, of a liquid prepared from bleaching powder and soda. The formation of chlorine compounds in the wax is objectionable, however, as hydrochloric acid is liberated when the wax is burnt. Whenever chemicals are used they should be thoroughly washed out of the wax when the bleaching is accomplished.

Another proposed way of decolorizing beeswax is by the use of agents that absorb the colouring matters, such as animal charcoal, fuller's earth, and the like.

The theory of bleaching and the effect of various methods and also the effect of the addition of a little tallow to the yellow wax have been studied by A. and P. Buisine (Compt. rend. 1891, 112, 738, and Bull. Soc. chim. 1890, [3] 4, 465); they found that light is necessary, since, in the dark, yellow wax is not bleached when kept in a current of air or of oxygen or of ozonised oxygen, whilst in sunlight it is bleached even when kept in carbon dioxide or nitrogen or in a vacuum, though much more slowly than in air. In oxygen it bleaches more rapidly than in air, and very rapidly in ozonised oxygen. They noticed that in air-bleaching the colour does not decrease uniformly, but that white spots are seen which increase in size. They think that the colouring matter undergoes total combustion and that the oxidation of the unsaturated hydrocarbons and unsaturated acids induce this combustion, and that is why the addition of tallow, which contains olein, helps the bleaching. Oil of turpentine acts in the same way because it undergoes oxidation. They think it probable that these substances when undergoing oxidation in the light give rise to ozone, and that this under the influence of light burns up the colour-

ing matter; it being known that oil of turpentine exposed to air and light produces ozone, and that tallow, whilst turning rancid, gives an odour like ozone. They found in most cases that the m.p., the acid value, and the saponification value are increased, and that the iodine value and the percentage of hydrocarbons are lowered; decolorizing by animal charcoal, however, caused little change in the values.

Berg (Chem. Zeit. 1902, 26, 605) also records many experiments on the subject; he finds that the acid value is raised and the ratio value consequently lowered, which should be borne in mind when examining a white wax for admixtures. It is not easy, however, to draw general conclusions from his results. In Chem. Zeit. 1903, 27, 754, and 1908, 32, 778, he again treats of white wax.

Medicus and Wellenstein (Zeitsch. Nahr. Genussm. 1902, 5, 1092) examined the bleaching action of potassium chromate and sulphuric acid; they found: (1) that the acid value and the saponification value were considerably increased, but that the ester value was unaltered; (2) that the m.p. was raised 1°; (3) that the characteristic odour of yellow wax was destroyed or volatilised; (4) that no stearic acid could be found by the Fehling-Röttger test either before or after bleaching; (5) that the ester value of some myricin prepared from yellow wax was only slightly increased by bleaching.

Bibliography.—A very full bibliography for the years 1848 to 1891 is given in the U.S. Dept. Agric. Div. Chem. Bull. 13, Pt. 6, 1892, with an account of the contents of many of the papers. An abstract of this is given in J. Soc. Chem. Ind. 1892, 11, 756. The following are papers of 1892 and after, with a few earlier ones. A. and P. Buisine (Bull. Soc. chim. 1890, [3] 3, 867), methods of examination, including determination of the hydrocarbons and of the hydrogen evolved by Dumas and Stas's reaction. Kossel, Obermüller, and Krüger (Zeitsch. Physiol. Chem. 1890, 14, 599; 1891, 15, 321; 1892, 16, 152), use of sodium alcoholate or of metallic sodium for saponifying. Antoushevich (J. Soc. Chem. Ind. 1891, 10, 1014, from J. Russ. Chem. Soc. 1891, 23, 223), analyses of Russian waxes and method of analysis. Forde (Consular Report No. 1304 for Morocco for 1892, p. 17), adulteration with low-class paraffin from candles. Röttger (Chem. Zeit. 1892, 16, 1837), methods of analysis, criticism of Benedikt and Mangold's method. Buchner (*ibid.*, p. 1922), methods of analysis. Benedikt (*ibid.*, p. 1922), defence of Benedikt and Mangold's method. Marie (Bull. Soc. chim. 1892 [3] 7, 111), bromoacetic acid. Gascard (J. Pharm. Chim. 1893, [5] 28, 49), myricyl (melissyl) alcohol from beeswax, carnauba wax and gum-lac, and its derivatives. Buchner (Chem. Zeit. 1893, 17, 918), criticism of Hübl's method, and some extra tests recommended. Kehler (J. Franklin Inst. 1894, 137, 58), detection of adulterants. Parry and Estcourt (Year Book of Pharm. 1893, 370 and Chem. and Druggist, 1894, 45, 645, and 693), adulterants and their detection. Kromer (Chem. Zeit. Repert. 1895, 19, 289, from Pharm. Zeitsch. Russl. 1895, 34, 529), composition of the oil obtained by the dry distillation of beeswax and used as a remedy. Buchner (Chem. Zeit. 1895, 19, 1422), artificial compositions giving the same

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After dilution with 15 c.c. of water, the mixture is slowly acidified with dilute sulphuric acid (1:4) and filtered; 2 c.c. of the filtrate are treated with 20 c.c. of saturated bromine water till colourless, and 2 c.c. of this solution are treated with 0.1 c.c. of alcoholic solution of codeine and 5 c.c. of pure sulphuric acid (*d.* 1.84). After shaking and heating on a boiling water bath for 2 minutes, a fine greenish-blue coloration develops if glycerol is present; 1 p.c. of a glyceride can easily be detected in beeswax by this test (J. Soc. Chem. Ind. 1924, 43, B. 431). Lipp and Kuhn (J. pr. Chem. 1912, 86, 184), composition of Indian (Ghedda) beeswax. Mastbaum (Chem. Rev. Fett-u. Harz-Ind. 1912, 19, 232 and 260), beeswax of Portugal and its colonies; method of examining. Prettner (Prometheus, 1912, 23, 341), origin, preparation, uses, and adulterants. Leys (J. Pharm. 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Candelilla wax is obtained from plants growing wild in great quantities in the dry and desert-like districts of northern Mexico and the southern parts of the United States; they are called 'candelilla' by the Mexicans. It is a recent addition to the waxes in commercial use, attention having been called to the wax on these plants by Sanders in 1905. *Euphorbia cerifera* (Alcooc), *E. antispyphilica* (Zucc.), and *Pedicularis Peronis* (Boiss.) have been given as the plants from which the wax is obtained.

It occurs as an excretion covering all parts of

the plant, except the roots. It can be obtained by boiling the plants with water and skimming off the layer of melted wax; the pieces of plant must be kept from rising by enclosing them in wire cloth or by tying them in bundles and weighting these down. In practice a little sulphuric acid is added to the water when first obtaining the wax, and also when remelting; its action is probably to prevent the formation of an emulsion. Another plan is to subject the plant in suitable containers to live steam, which melts off the wax, and this can be easily separated from the condensed water. It is said that this plan gives a better yield, but that the wax appears softer and contains more water than that obtained by simply boiling out the wax from the plant. The wax can be purified by remelting and straining off plant debris. The yield of wax is from 1 to 5 p.c. In 1918 there were about twenty-five factories producing the wax in the Monterey district.

The wax is hard and brittle, and can be broken down to a powder at low temperatures; when full of air bubbles and water it is opaque and greyish-yellow in colour, but if these are got rid of by melting it is dark brown and translucent. When heated it gives off an aromatic odour. It is only slightly soluble in alcohol, ether, acetone, chloroform, carbon disulphide, gasoline, and oil of turpentine when cold, but is readily soluble in all these when hot; a boiling mixture of three parts absolute alcohol and two parts of 90 p.c. benzene was found to be an excellent solvent. On cooling these solutions become pomade-like masses.

The analytical values that have been recorded vary widely; this may be due to the age of the plant, the time of year at which it was gathered, the mode of preparation, the presence of water in the sample examined, the method of analysis, or even to adulteration. The following are the lowest and highest values found in the literature of the wax: m.p. 65° to 92°; sp.gr. 0.936 to 0.998; acid value 0.03 to 24; saponification value 35 to 104; iodine value 5.2 to 57.6; unsaponifiable matter 65 to 91.2 p.c. There are also variable amounts of dirt, water, and ash. These analytical values vary so much that it may be well to add those of the following authors.

Sanders (Chem. Soc. Proc. 1911, 27, 250) states that a sample of wax prepared in January from plants collected in Coahuila was greenish-white, and contained a considerable proportion of water. When freed from this it was dark brown and gave the following values: m.p. 67.5°; sp.gr. 0.9850; acid value 14.36; saponification value 46.76; iodine value (Hübl) 16.60; unsaponifiable matter 77.00 p.c.; and hydrocarbons 48.60 p.c.; he found hentriacontane and melissyl alcohol (whether free or as ester is not stated).

Lüdecke (Seifensieder Zeit. 1912, 39, 829) gives as normal values: m.p. 68-70° 0.950-0.990; acid value 13-18; saponification value 50-60; iodine value 15-20; unsaponifiable matter 65-75 p.c.; moisture 2 to and dirt 0 to 3 p.c.

Berg (Chem. Zeit. 1914, 38, 1162) gives for a grey crude wax: m.p. 80-88°; acid value 9.8; ester value 44.0; saponification value 53.6; and as the mean of two samples of brown wax: m.p. 68.5°; sp.gr. at 15°/15° 0.986; acid value

11.6; ester value 51.5; saponification value 63.1; iodine value (Wijs) 57.6 after 19 hours standing, 14.5 after 3 hours; unsaponifiable matter 67.5 p.c. Both Berg and Lüdecke used xylene when saponifying.

Composition.—Candelilla wax is remarkable among the waxes for the high proportion of hydrocarbons that it contains, but as in the case of its analytical values the results of investigations as to its composition are discordant. Sanders, in *Anal. Inst. Med. Nacional, Mexico*, for Oct. 1907, recorded the presence of hentriacontane (*J. Ind. Eng. Chem.* 1911, 3, 115). Fraps and Rather (*ibid.* 1910, 2, 454) found hentriacontane with m.p. 68°, and indications of another hydrocarbon with m.p. 85°, and of other substances.

Meyer and Soyka (*Monatsh.* 1913, 34, 1159) found that it contained resin amounting to 18 to 20 p.c., to this they attribute the acid value and the iodine value. They removed most of the resin by repeatedly boiling out the wax with alcohol, allowing to cool and then separating the alcoholic resin-solutions; they then removed from the residue all that ether would dissolve. In the soluble part, after removing the last traces of resin by the charring action of thionyl chloride, they found a hydrocarbon which they believe to be normal dotriacontane $C_{32}H_{66}$, with m.p. 71°, and in the insoluble part they found an oxylactone $C_{30}H_{58}O_2$, with m.p. 88° to 88.5°, identical or isomeric with the lactone of lanoceric acid. They sum up the composition as 18 to 20 p.c. of resin, 74 to 76 p.c. of dotriacontane, and 5 to 6 p.c. of the oxylactone.

Berg (*Chem. Zeit.* 1914, 38, 1162) found: (a and b) about 50 p.c. of two hydrocarbons, one with m.p. 68° and the other with m.p. 84°–85°; (c and d) about 10 p.c. of a semi-fluid mixture of two cholesterols, these were free in the wax, when acetylated they yielded acetates, one a white powder, nearly insoluble in alcohol, the other readily soluble in alcohol on warming; (e) a small quantity of a substance containing oxygen, with m.p. 88°–89°, it was fairly soluble in alcohol, could be acetylated, did not give any cholesterol reaction, and must have been present in the wax as an ester; (f) a very small quantity of a substance containing oxygen, melting with decomposition at 243°, it was readily soluble in alcohol, from which it crystallised in leaflets, it could not be acetylated, it gave a colour reaction with acetic anhydride and sulphuric acid, and may be an ester of a lupeol-like cholesterol.

Buchner (*Chem. Zeit.* 1918, 42, 374) gives the composition as determined by Staempfli as: 50–52 p.c. of a hydrocarbon $C_{31}H_{64}$, with m.p. 68°; 25 p.c. of melissic acid $C_{31}H_{58}O_2$, present partly free and partly as a melissyl ester with m.p. 88°–90°; 10–14 p.c. of melissyl alcohol $C_{31}H_{64}O$, with m.p. 85° (whether free or as ester is not stated); 1 p.c. of another hydrocarbon, with m.p. 85°; traces of a phytosterol, with m.p. over 130°; and 10 p.c. of resinous matter; but none of the experimental evidence is given.

Uses.—Owing to its hardness it resembles carnauba wax. It is especially valuable in making shoe-dreams and polishes, as it imparts to such preparations the power of producing a brighter lustre than any other wax. On the other hand, when mixed with paraffin wax it

has not nearly as great a hardening effect as carnauba wax, and it has little hardening action when mixed with soft wax compositions. For candle making it is considered inferior to carnauba wax, owing to its lower melting-point (given as 65°), and for phonograph records its suitability is considered small. The insulation of telephone cables is another suggested use.

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Cape berry wax. Samples of this wax have been shown at exhibitions in London, and it is capable of being collected in quantities in Cape Colony, but it has not yet come into any extensive use. It is probably derived from one of the species of *Myrica* growing in South Africa, which include *M. quercifolia* (Linn.), *M. cordifolia* (Linn.), and *M. serrata* (Lam.); it is similar to myrtle berry wax in its general characters and in its physical and chemical properties, which were found to be: sp.gr. 0.874 at 99°; m.p. 40.5°; m.p. of the fatty acids 47.5°; mean molecular weight of the fatty acids 236.1; acid value 4.1; saponification value 211.1; iodine value 1.1. It yields a hard white soap, but does not seem to be suitable for candle making (*Imp. Inst. Bull.* 1906, 4, 300). The results of another examination are: sp.gr. 0.9893; m.p. 49°; refractive index at 80° 1.4364; acid value 2.5; saponification value 212.3; iodine value 2.03; unsaponifiable matter 2.51 p.c.; fatty acids 89.7 p.c.; m.p. of mixed fatty acids 48.5°; solidifying-point of these 46.5°; mean molecular weight of these 241.4; it was described as South African berry wax, and was pale greenish-grey with a granular fracture; when melted it formed a greenish-brown muddy liquid, and it was filtered before examination (*Cooking, Chem. and Drug.* 1908, 73, 74).

Berry wax from *M. cordifolia* came into prominence during the war. The plant is grown as a sand-binder in the neighbourhood of Cape Town, Port Elizabeth, and other places. The wax was previously exported to Germany, and

was used for gramophones and for floor polish (J. Soc. Chem. Ind. 1918, 37, 74 R).

Carnaúba or carnaúba wax is derived from the carnaúba palm, *Copernicia cerifera* (Mart.) (*Corypha cerifera*, Linn.), which grows in Brazil, especially in the provinces of Ceara, Rio Grande do Norte, and Piahy. The trunk is 25-35 ft. high with a crown of leaves at the top. The young leaves of about 3 ft. long have a coating of wax on both the upper and under sides, which appears homogeneous to the naked eye. The wax layer is thicker on the upper side, and comes off in scales; on the lower side it is thinner and more adherent. The harvesting extends over the six dry months of the year, and the leaves are cut twice a month, about eight leaves being cut from a palm at a time, those leaves that have reached a certain stage of development being taken, leaving the very young leaves to develop later. If the leaves are allowed to become too old the wax is easily detached, and is lost before the leaves are brought to the ground. The leaves are spread out to dry, and are then slit up with a knife and beaten over a cloth to detach the wax which comes off in scales or as a greyish-white powder. A little water is added to the powder, and it is melted and poured into moulds, in which it solidifies in cakes of about 2 kilos. About 850 leaves give 16 kilos. of wax; about 1.8 kilos. of wax, valued at 1s. 6d., are obtained from one palm. On poor land 1200 leaves, and on good land only 500 leaves are required to give the 16 kilos. In some estimates, however, the yields are not so good as these.

The following table, based on Hambloch's Reports on Brazil, Dept. Overseas Trade, 1919, 1921, and 1922, shows the exportation of carnaúba wax:

Year	Metric tons	Value in £	Value per metric ton in £
1913	3867	439,500	114
1914	3315	324,200	98
1915	5897	505,100	86
1916	4166	398,900	96
1917	3669	443,300	121
1918	4215	1,135,200	269
1919	6200		
1920	3500		
1921	1540	January to June (inclusive)	
1922	2200	"	"

In 1913 Germany took 1710 metric tons; the United States 941; the United Kingdom 687; and France 509. In 1920 the United Kingdom took 1000 metric tons and the United States 2200.

Raw carnaúba wax is of a dirty yellowish or greenish colour, amorphous, hard, brittle, and easy to powder. In its outward appearance it is compact, but penetrated with very many air spaces; it is tasteless, and smells, when fresh, somewhat like fresh hay—i.e. of coumarin; later it becomes inodorous. It is purified by remelting, and has then a greenish-yellow or straw-yellow colour.

Analytical values.—The melting-point is variously given as from 80.5° to over 86°, it increases with the age of the sample, and an old specimen melted at 90°-91°; about 84° seems a common experience; light-coloured specimens have a somewhat lower melting-point than darker ones. The sp.gr. at 15° is 0.978-0.999.

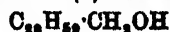
The acid values recorded are from 0.3-10, about 4 being common; the saponification values from 69-88, and even 95; the iodine values from 5-14. In preparing bleached carnaúba wax additions, such as paraffin wax, are made so that the above values do not hold good for it. The wax is not easily saponified. Berg (Chem. Zeit. 1909, 33, 885) recommends the use of xylene as a solvent in order to hasten the saponification and to diminish the risk of oxidation occurring during long boiling with potassium hydroxide.

Composition.—Carnaúba wax is composed mainly of an ester of triacontyl, $C_{30}H_{61}$, with the acid $C_{27}H_{54}O_2$, which is either cerotic acid or an isomer of it. The triacontyl was formerly supposed to be the same as the melissyl of beeswax, but it now appears that melissyl is most probably $C_{31}H_{63}$. Carnaúba wax contains a considerable proportion of triacontyl alcohol $C_{30}H_{61}OH$. In addition there are a number of compounds present in small proportions.

Story Maskelyne (J. Chem. Soc. 1869, 87) found: (a) melissin (melissyl alcohol) both free and coming from an ester; (b) a compound with m.p. 105°, corresponding to $C_{30}H_{61}O_2$; (c) an alcohol with m.p. 78°, corresponding to $C_{32}H_{65}O$, and also other compounds.

Von Pieverling (Annalen, 1870, 183, 344) prepared from this wax melissyl alcohol and examined its products, he also obtained a small quantity of ceryl alcohol $C_{27}H_{54}O$.

A long investigation of the composition was made by Sturcke (Annalen, 1884, 223, 283), employing carnaúba wax with m.p. 83°-83.5°. He found that the principal component was the ester $C_{30}H_{61} \cdot C_{27}H_{54}O_2$, and that there was a considerable quantity of free wax alcohol present. When the wax is extracted with boiling alcohol a considerable proportion dissolves but separates again when the alcohol cools. He found when 1200 grms. of wax were boiled out with 5½ litres of alcohol and the hot clear solution was poured off that on cooling 350 grms. (equivalent to 29 p.c.) were deposited. By repeated extraction small quantities of the ester seem to be removed each time; thus when 10 grms. of the wax were boiled with half-litre lots of alcohol, 350 c.c. of the ninth lot contained 0.295 grm. and of the tenth lot 0.286 grm. By saponifying the wax and separating the products with petroleum ether, &c., and by many fractionations he found: (1) A hydrocarbon with m.p. 59°-59.5° present in small proportion. (2) An alcohol $C_{28}H_{57} \cdot CH_2OH$ with m.p. 76° in small proportion. (3) An alcohol



with m.p. 85.5°-85.7° in large proportion. From this he prepared the acid $C_{28}H_{57} \cdot COOH$ with m.p. 89.9°-90.2°. This alcohol he called myricyl (melissyl) alcohol, but according to Heiduschka and Gareis (J. pr. Chem. 1919, 99, 299) it contains CH_3 , less than the melissyl alcohol $C_{31}H_{63}O$ obtained from beeswax. (4) A dihydroxy alcohol $C_{28}H_{56}(OH)_2$, with m.p. 103.5°-103.8° in small proportion. From this he prepared the acid $C_{28}H_{56}(OOH)_2$, with m.p. 102.5°. (5) An acid $C_{28}H_{56} \cdot COOH$ with m.p. 72.5° in small proportion, isomeric with lignoceric acid. This acid was subsequently

called carnaubic acid by Darmstadter and Edschütz (Ber. 1896, 29, 620) in a paper on wool fat. (6) An acid $C_{22}H_{42}COOH$ with m.p. 78.8° – 79° , either identical or isomeric with the cerotic acid of beeswax, in large proportion. It would not crystallise when it solidified from the melted state, and for this reason he doubted its identity with the cerotic acid of beeswax.

(7) A lactone $C_{19}H_{38} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} O$ with m.p. 103.5° in small proportion. From this he prepared the acid $C_{19}H_{38}(COOH)$, with m.p. 89.5° – 90° .

It should be noted that these products were obtained after saponification. The hydrocarbon, no doubt, was free in the wax, and the $C_{19}H_{38}CH_2OH$ alcohol probably was partly free and partly came from the ester, but the others were not proved to be free before saponification. Besides these Stürcke also noticed, as had von Pieverling, a greenish balsam-like substance with an odour like coumarin, but in too small quantity for examination. Stürcke's results, it should be remarked, do not fully explain the analytical values given above, so further work on the composition is needed.

Liebermann (Ber. 1885, 18, 1979) obtained a substance from the wax by a great many fractional crystallisations with m.p. 92° , which could not be materially raised by further crystallisations; it formed a matted paper-like layer without any lustre; he did not, however, make an analysis of it.

Heiduschka and Gareis's work (J. pr. Chem. 1919, 99, 293) is described above under the composition of beeswax.

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alcohol as solvent. Engler (Chem. Zeit. 1906, 30, 711), the rotatory power. Berg (Chem. Zeit. 1909, 33, 885), xylene as solvent for finding analytical values. Leys (J. Pharm. Chim. 1912, [7] 5, 577), describes a new method of examining this wax and beeswax; he uses a mixture of amyl alcohol and fuming hydrochloric acid to dissolve the wax alcohols and separate them from the hydrocarbons; he found no hydrocarbons in carnauba wax. Lüdecke (Seifensieder Zeit. 1913, 40, 1237, 1274, 1302, 1327), descriptions of the commercial varieties, adulterants (fragments of candelilla wax are sometimes mixed in), detailed methods of finding melting-point, sp.gr., and analytical values. Buchner (Chem. Zeit. 1918, 42, 373) quotes Popp on the formula of melissic acid prepared from carnauba wax (Heiduschka and Gareis do not agree with Popp's formula). Heiduschka and Gareis (J. pr. Chem. 1919, 99, 293) compare melissyl alcohol from beeswax and its derivatives with the alcohol from carnauba wax and its derivatives and find them to differ by CH_2 .

Cochin China wax (*Cay Cay fat*, *Irvingia butter*). This is obtained from the fruit of the Cay Cay tree, *Irvingia Oliveri* (Pierre), a forest tree reaching the height of 100 ft., and growing widely in the east of Cochin China. The fruit is the size of a lemon, the endocarp has the size and shape of an almond with its outer covering, and the kernel, too, resembles in size and shape that of the almond. The fruits are ripe in July, and fall to the ground; they are gathered into heaps by the natives, and left for two months to allow the soft outer parts to decompose; they are then carried to the houses and dried in the sun. They are opened with a strong knife, and the kernels are removed, dried in the sun, and pounded in a mortar. The pulp is placed in a vessel having a bottom of plaited material; this is fixed above water in another vessel, and the water is heated, but not to boiling. When the pulp has become a sticky paste it is wrapped in a mat of rice straw, and submitted to pressure in a crude press, the operations being repeated several times, and the melted wax is either allowed to solidify in moulds or else is cast into candles in bamboo tubes. In the laboratory the dry kernels extracted with carbon disulphide gave 52 p.c. of wax. The wax is of a greyish-yellow colour, and is unctuous to the touch. The purified wax softens at 37° , melts at 38° , and solidifies at 34° (Vignoli, Le Cay Cay, Thèse présentée à l'École Supérieure de Pharmacie de Montpellier, 1886).

Bontoux (Les Matières Grasses, 1908, 1276; J. Soc. Chem. Ind. 1909, 28, 429) found that 100 dry seeds weighed 360 grms. and gave 78 p.c. of shells and 22 p.c. of kernels. The latter, on extraction with light petroleum, gave 60.45 p.c. of wax. The wax had the consistency and texture of beeswax, and was more brittle, with the same conchoidal fracture; its sp.gr. at 40° compared with water at 40° was 0.913; it melted at 39.7° in a capillary tube, and solidified at 31° ; its acid value was 0.86; saponification value 235.3; unsaponifiable matter 0.42 p.c.; iodine value 6.7; Reichert-Meissl value 0.62. The insoluble fatty acids, together with the unsaponifiable matter were 94.0 p.c., their m.p. was 38.8° ; solidifying point (titer test) 36.6° ; neutralisation value 250.2.

and mean molecular weight 224. Two samples of the wax of native origin had nearly the same values, but the acid values were 23.5 and 34.9, which, however, are not excessive, and they contained 0.16 p.c. and 0.19 p.c. of unsaponifiable matter. Bontoux prepared methyl esters, and concluded that the wax was mainly composed of myristin 60-65 p.c., laurin 30-35 p.c., and about 5 p.c. of olein. The wax gives a hard white soap. The production in Indo-China has declined, owing to the introduction of petroleum. A Cay Cay wax is also obtained from the fruit of the tree *Irvingia malayana* (Oliver), which grows in Cambodia. Other references are: Heckel, Annales de l'Institut colonial de Marseille, 1893; Apoth. Zeit. 1898, 169; Crevost, Les arbres à suif de l'Indochine, Hanoi, 1902; Bulletin économique de l'Indochine, Hanoi, 1902; Chem. Zeit. 1903, 27, 43.

Cow tree wax (Milk tree wax). In the north of Venezuela, in the neighbourhood of Caracas and of Lake Maracaibo, and in the valley of Canaguas, there grows a tree (*Brosimum Galactodendron*) called *Palo de vaca* or *Arbol de leche*, which yields a thick milk when incisions are made in its trunk; this is drunk like milk by the inhabitants. This milk, when heated, forms a skin, and if this is removed and evaporation continued, an oily liquid is obtained, together with a fibrous mass. The oily liquid when it has solidified, is a yellowish-white, hard translucent wax; it begins to melt at 40°, and is completely melted at 60°. It is insoluble in water, but is easily dissolved by essential oils. It dissolves in boiling alcohol and separates on cooling; it is saponifiable by caustic potash. It can be used like beeswax for making candles. Humboldt, Ann. Chim. 1817, 7, 182; Boussingault and Mariano de Rivero, *ibid.* 1823, 23, 219; Marchand, J. pr. Chem. 1840, [i.] 21, 43.

Esparto grass wax. In preparing the fibre of this grass for paper making the material reaches the mills in tightly compressed bales. It is there loosened by a special machine and at the same time freed from dust by a strong current of air from a powerful fan. This dust contains from 25-50 p.c. of wax, and in most mills is deposited in special dust collectors. The wax when obtained from the dust is hard, rather brittle, and of a light brown colour, and has the following characteristics: m.p. about 74°, loss of weight at 100° overnight about 1.5 p.c., ash 0.02 p.c., acid value 34.42, saponification value 71.41, iodine value 6.48, unsaponifiable matter (soluble in hot CCl_4) 50.34 p.c., fatty acids 45.69 p.c. The wax is in demand by some manufacturers and commands a good price; but unfortunately the quantity of dust obtainable at any one paper mill is not very large, so the output of wax is not equal to the demand (Budds, J. Soc. Chem. Ind. 1916, 35, 401).

Fig tree wax (Gondang or Kondang or Getah wax, Java or Sumatra wax). This wax is obtained in Java from the milky juice (*getah* in Malay) which runs from incisions made in the bark of the gondang, a wild fig tree (*Ficus variegata*, Blume. = *F. ceriflua*, Jungh. = *F. subracemosa*, Blume.). The juice is boiled with water until the wax separates. It forms a fairly hard cake, cream coloured within, turning brown in the air; it has a conchoidal fracture and can be powdered, but not readily. The

crude wax melts at about 80° to a very viscous mass, which, on cooling, remains viscous for a long time, and from which an aqueous liquid separates. The sp.gr. of the wax after melting is 1.015 at 15°. It softens at 55°, and is only completely melted at 73°. It is soluble in benzene, chloroform, carbon disulphide, oil of turpentine, light petroleum, and boiling ether. Boiling alcohol dissolves it slowly, and the greater part separates on cooling. Cold alcohol keeps in solution a little over 5 p.c. of the wax. By means of boiling alcohol over 70 p.c. of white crystalline purified wax can be obtained, melting at 61°, insoluble in cold alcohol, but soluble in boiling alcohol. Greshoff and Sack (Rec. trav. chim. 1901, 20, 68), by analyses and saponification of the wax thus purified, obtained results suggesting that it is an ester $\text{C}_{22}\text{H}_{44}\text{O}_2$ of an alcohol $\text{C}_{17}\text{H}_{34}\text{O}$ (flococeryl alcohol), with m.p. 198°, and of an acid $\text{C}_{12}\text{H}_{24}\text{O}_2$ (flococeric acid), with a m.p. 57°, this ester is probably associated with some accessory substance; they also think the original wax contains some free flococeryl alcohol.

Vogl (Lotos, published at Prag, 1872, 22, 54) describes Sumatra wax or Getah Lahoe coming from the same tree. Kessel (Ber. 1878, 11, 2112) assigns formulae to components of the wax which differ from the above. Ultée (Chem. Zeit. 1915, ii. 794, from Pharm. Weekblad. 1915, 52, 1097) examined the milky sap of *Ficus variegata*; it contained 35 p.c. of solids, and when coagulated by heating, or by alcohol, or by dilute acetic acid it yielded gondang wax. From this by suitable treatment, including a saponification, he obtained a wax alcohol, the flococeryl alcohol of Greshoff and Sack. This alcohol he identified as being the same as β -amyryn with m.p. 197.5°. (β -amyryn is $\text{C}_{20}\text{H}_{40}\text{O}$ and comes from elemi resin.) In the wax itself he found lupeol acetate with m.p. 190°-197°, but no free β -amyryn.

Insect wax. This is also called *Chinese wax*, *Chinese tree wax*, *Vegetable spermaceti*, and sometimes, but incorrectly, *Japanese wax*; it must not be confused with Japan wax. It is the secretion of an insect *Coccus pala* (Westwood), *Coccus confusus* (Fabr.). The industry of its production is peculiar, in that the insects are bred for the purpose of producing eggs in one district, and these eggs are then transported to another district where the insects are reared to produce wax. The Chien-Chang valley in the prefecture of Nung Yuan Fu (Long. 102° 26', Lat. 27° 54') in the Sze Chuan province of China is the great breeding-ground of the wax insect; it is about 5000 ft. above sea-level. Here the insects are reared on the *Ligustrum lucidum* (Ait.) or large-leaved privet. In March, when the trees were seen by Mr. Hosie, he found numerous brown pea-shaped excrescences attached to the bark of the boughs and twigs. The larger of these were readily detachable, and when opened presented either a whitish-brown pulpy mass or a crowd of minute animals like flour, whose movements were just perceptible to the naked eye. From 2 to 3 months later these had developed in each case into a swarm of brown creatures, each provided with six legs and a pair of antennae; each of these was a wax insect. Two hundred miles to the north-east of the Chien-Chang valley, and separated from it

series of mountain ranges, is the prefecture of Kia-ting-fu (Long. 104° , Lat. $29^{\circ} 34'$), also called Chia-ting-fu, containing the district of Omi and the valley of the Ya river, the headquarters of the wax-producing industry. The scales produced in the Chien-Chang valley are ready for removal by the end of April, and are then full of eggs; they are made up into paper packets, each weighing about 16 oz. Sixty of these packets make a load, and are conveyed by coolies from the Chien-Chang valley to the town of Hung Ya in the Kia-ting-fu prefecture for sale to the farmers. In May thousands of coolies are engaged in the traffic. They travel only at night, in order to avoid the high temperature of the day, which would tend to the rapid development of the insects and their escape from the scales. At the stopping places the packets are opened out in cool places; but in spite of this, each packet is found to have lost on an average an ounce in transit. A pound of scales laid down in Kia-ting-fu, in years of plenty, costs about half a crown; in bad years the price is doubled. In favourable years a pound of scales will produce 4-5 lbs. of wax. In the plain around Kia-ting-fu the plots of ground are thickly edged with stumps of *Frazinus chinensis* (Roxb.), a species of ash varying from 3 or 4 to 12 ft. high, with numerous sprouts rising from their gnarled heads, and resembling at a distance pollard willows. On the arrival of the scales they are made up into small packets enclosed in a leaf of the wood-oil tree. The edges of the leaf are tied together with a rice straw, by which the packet is suspended close under the branches of this ash. A few rough holes are drilled in the leaf with a blunt needle, so that the insects may find their way through to the branches. On emerging from the scales the insects creep rapidly up to the leaves, among which they remain for a period of 13 days. They then descend to the branches, on the underside of which they take up their position, and commence to deposit the wax. This first appears as an under-coating on the sides of the boughs and twigs, and resembles quinine sulphate or a covering of snow. It gradually spreads over the whole branch, and attains, after 3 months, a thickness of about a quarter of an inch. After the lapse of 100 days the deposit is complete, the branches are lopped off, and as much of the wax as possible is removed by hand. This is placed in an iron pot of boiling water, and the wax on rising to the surface is skimmed off and placed in a round mould, whence it emerges as the insect wax of commerce. Where it is found impossible to remove the wax by hand, the twigs and branches are thrown into the pot, so that this wax is darker and inferior. The insects which have sunk to the bottom of the pot are placed in a bag and squeezed of the last drop of wax, and are then thrown to the pigs. Not only the *Frazinus chinensis*, but also the *Liquidum lucidum* is used in the final wax-producing stage of the industry. The wax is used for coating the exterior of animal and vegetable tallow candles, as it serves to hold in the more fusible tallow when the candle is burning; a little is also mixed with the tallow; it is employed to give a gloss to paper, for coating glass, and a polish for furniture and ieda-ware.

(Nature, 1891, 43, 291; Wilson, Chemist and Druggist, 1906, 68, 143; Bull. Imp. Instit. 1924, 22, 64; Pharm. J. 1924, 27, 278).

Insect wax is white and crystalline, resembling spermaceti in appearance, but it is harder and more fibrous; it is brittle, and at 15° can be powdered. Its sp.gr. is 0.970 at 15° (0.926 at 15° , Gehe and Co., Zeitsch. anal. Chem. 1895, 34, 765) and 0.809-0.811 at 98° - 99° ; m.p. 80° - 83° ; saponification value 80-93; iodine value 1.4. It is only very slightly soluble in alcohol and ether, but is readily soluble in naphtha, from which it can be crystallised. Brodie (Phil. Trans. 1848, 159) saponified the wax by melting it with potash, and obtained an alcohol and an acid; the alcohol he named *cerotin*, and to it he assigned the formula $C_{17}H_{34}O$, it is now called *ceryl alcohol*; the acid he considered to be the same as the cerotic acid he had obtained from beeswax, to which he had assigned the formula $C_{27}H_{54}O_2$; the wax he regarded as ceryl cerotate, the ester of this alcohol and acid. Brodie's formulae have been supported by Gascard (*see below*). Marie (J. Chem. Soc. 1897, 72, 1, 318) proposes $C_{26}H_{52}O_2$ or $C_{25}H_{50}O_2$ for the cerotic acid of beeswax; and Henriques (*ibid.* 460) regards ceryl alcohol and cerotic acid from insect wax as $C_{26}H_{52}O$ and $C_{26}H_{52}O_2$, and it is stated that the identity of the cerotic acids from insect wax and from beeswax is not quite certain. Other substances besides ceryl cerotate are probably present.

Gascard (Compt. rend. 1920, 170, 1326) investigated the formulae for the ceryl alcohol and for the cerotic acid obtained from insect wax, and confirmed those of Brodie, namely, $C_{17}H_{34}O$ with m.p. 80° for the alcohol and $C_{27}H_{54}O_2$ with m.p. 82° - 82.5° for the acid; but thought that the acid must be different from the cerotic acid of beeswax that Marie prepared with m.p. 77.5° . The following was his method. He started with insect wax with m.p. 80.5° - 81° , and first purified the ester, ceryl cerotate, by extraction with boiling acetone; the undissolved ester after recrystallisations from benzene melted at 84° . He saponified this by boiling with alcoholic potassium hydroxide. He then added calcium chloride and obtained a precipitate of calcium cerotate; from the filtrate he obtained the ceryl alcohol which, after purification, melted at 79° - 80° . From this he prepared the iodide and found that the percentage of iodine in it corresponded to $C_{17}H_{33}I$. From the iodide he obtained the hydrocarbon which melted at 59.5° ; thus agreeing with Kraft's $C_{17}H_{34}$. As regards the acid, he obtained it from the calcium cerotate and found that it melted at 82° - 82.5° . He also prepared some from the ceryl alcohol by oxidation with potassium bichromate in acetic acid solution; after purification it melted at 81.5° - 82° , and by titration he found that its molecular weight corresponded to $C_{27}H_{54}O_2$. By further purification it melted at 82° - 82.5° , like the acid got by saponification.

Japan wax (Japan tallow, *Banach masu*, Vegetable wax of Japan). This must not be confused with insect wax which has sometimes been called Japanese wax. Japan wax is one of the most important of the vegetable waxes, large quantities being exported from Japan. Before 1854, whilst Japan was closed to foreigners,

except to the Dutch, it came through China and Singapore, and was imported in small quantities coming in small thin cakes, but after the opening of certain Japanese ports to British merchants, it arrived in large quantities and in square blocks or cases of about a picul each (133½ lbs.).

It is derived from the berries of three species of *Rhus* that grow in Japan, namely, *R. succedanea*, L., *R. vernicifera*, De C., and *R. sylvestris*, S. and Z. *R. succedanea* grows in the southern parts of Japan and yields wax only, but *R. vernicifera*, which has a more northerly range, yields a more important product, namely, the well-known Japanese lacquer, which is prepared from its sap, but its berries are also used as a source of wax. *R. sylvestris* is a less important source. *R. succedanea* and *R. vernicifera* also grow in China. The berries of all three are composed of an outer skin, a mesocarp in which is the wax, and a kernel.

In Japan to obtain the wax the berries are reduced to a meal—some authors say that they are previously slightly roasted; the meal is heated by steam in hempen sacks and then quickly squeezed in a wedge press to force out the wax. The residue is again treated in the same way. In the case of *R. vernicifera* the kernel is easily separated and is removed in the course of crushing, but in the case of *R. succedanea* the wax adheres to the kernel in spots, and it is not clear from the accounts of the process whether the kernel is separated or crushed with the mesocarp. The methods, no doubt, vary in different localities. It has been stated that perilla oil is added to obtain the last portions of the wax, but this is denied by Tsujimoto (Lewkowitsch and Warburton, Oils, Fats, and Waxes, 6th ed. vol. ii. 1922, p. 45), who states that a proportion of the kernel oil of *R. succedanea* is added. With respect to this oil, A. Meyer (Arch. Pharm. 1879, [3] 15, 119, 120) found in the cotyledons contained in the kernels of *R. succedanea*, after carefully removing the shells, 36 p.c. (30 p.c. ?) of fat, or 2.65 p.c. on the whole fruit. It was yellowish-green, melted at 30°, was not a drying oil, and dissolved in about 30 parts of alcohol at 30°. Crowe (Consular Rep. for Japan for 1912, p. 43) says that by the use of benzene an additional 10 p.c. of wax can be obtained, and that several works were adopting the system.

The yield is from 15 to 25 p.c. Impurities are removed by melting and skimming off the clear wax. It is bleached by melting it and allowing it to drop through woollen bags into cold water, so as to subdivide it into small pieces. These are exposed to the sun and are sprinkled with water and frequently turned over; the process occupies about 30 days.

The wax is pale yellow and hard with an even or conchoidal fracture; it becomes yellowish brown on keeping, and acquires a white waxy surface. The m.p. varies from 48° to 56°, that usually found being 53°; the wax solidifies again at about 41°, and when recently solidified melts at 42°; it slowly regains the higher melting-point. It is said that on warming it becomes transparent 10°–12° below its melting-point (Schaeffler).

Its specific gravity is close to that of water, and as it contracts and expands at a greater

rate than water, it exhibits the peculiar property of sinking, hovering or floating in water at different temperatures, sinking in cold water and floating in water somewhat warmer. After melting and resolidifying its specific gravity is lowered, it rises again in the course of some months. Thus a sample which hovered at 16.2° was melted and resolidified, it then hovered at 8.0°. Remembering that its expansion is greater than that of water, its specific gravity at 16.2° would be materially less than it was before melting, and it would float in water of that temperature. There is some variation in the specific gravity of different samples.

It is readily soluble in benzene and petroleum-ether and sparingly soluble in cold ether; it is insoluble in cold alcohol, but dissolves on warming and separates again on cooling.

In and after 1900 the following analytical values have been recorded: Acid value, 11.2–32.6; it is very variable, but values between 14 and 20 seem most common. Saponification value, 206.6–237.5; values between 215 and 224 being common. Iodine value, 8.3–15.1. Hubl, in 1884, records the iodine value as 4.2, so it is thought that the method of obtaining the wax has been changed. Part of the iodine value has been ascribed to the use of perilla oil mentioned above, as this oil has a very high iodine value. Ahrens and Hett in some wax prepared from berries obtained from Japan found iodine values of 11.9–12.8, and after bleaching in the sun, of 7.6.

Composition.—Japan wax is chiefly composed of glyceryl palmitate together with some free palmitic acid. Besides these a good many other substances have been obtained from it in small proportions; they may have been free in the wax or may have come from esters. These substances are: (1) About 1 p.c. of janic acid $C_{21}H_{42}O_4$ with m.p. 117°–117.9°; it is normal nonadecamethylene dicarboxylic acid $CO_2H\cdot(CH_2)_{19}\cdot CO_2H$. There is some evidence that the janic acid comes from a mixed ester of glycerol with janic acid and palmitic acid existing in the wax. (2) and (3) Smaller proportions of the two next lower acids, namely,



(4) Five to six per cent. of acids soluble in water, perhaps including suberic acid and isobutyric acid. (5) An odour of cenanthyl aldehyde is given off during saponification. This may be due to the oxidising action of bleaching agents, products being formed from which potassium hydroxide liberates cenanthyl aldehyde. (6) Pelargonic acid. (7) An acid with m.p. 87° and formula $C_{17}H_{34}O_2$ or $C_{18}H_{36}O_2$. (8) and (9) Very small quantities of liquid acids, one insoluble in water and one soluble. (10) and (11) Very small quantities of oleic and stearic acids, perhaps due to some addition made in the course of the manufacture of the wax.

The unsaponifiable matter resembles ointment in appearance, and is recorded as from 0.54 p.c. to 1.63 p.c.; in it have been found: (12) Melissyl alcohol with m.p. 88°. (13) Ceryl alcohol with m.p. 79°. (14) A saturated alcohol with m.p. 65° and with formula $C_{11}H_{22}O$. (15) A phytosterol with a double binding and m.p. 130°; as air-dried it is $C_{27}H_{44}O_2$, the specific

rotatory power is -22.11° , nearly the same as that of the phytosterol of cotton-seed oil. (16) About 60 p.c. of the unsaponifiable matter is a mixture of liquids, unsaturated and containing oxygen.

Uses.—It is only the bleached wax that is exported. It is said to be used for floor, furniture, and boot polishes and in laundry work; but there appears to be some secrecy about its exact use. Added to beeswax it imparts more solidity to the candles and causes them to leave the mould more easily; it is used instead of beeswax for a similar purpose in some rubber factories. Before 1859 the wax or the free acids obtained from it was used for candles and night-lights (Wilson, J. Soc. Arts. 1858-59, 7, 424). Lewkowitsch and Warburton (Chem. Tech. of Oils, Fats and Waxes, 6th ed. vol. ii. 1922, p. 667), however, says that the difficulties of employing Japan wax fatty acids for candles have not yet been overcome. It emulsifies well with water and has been used for currying leather (J. Soc. Chem. Ind. 1898, 17, 167). In Japan it is used for polishing turned wood and cabinet work; unbleached it is used for the candles of the jinriksha men and (unbleached?) in a composition for keeping the women's hair glossy and straight.

Bibliography.—Japan wax, like other substances which are of pharmaceutical interest, has a long bibliography. Kaempfer (Amoenitates Exoticæ, 1712, pp. 791, 794); Thunberg (Flora Japonica, 1784, p. 121); Siebold (Voyage au Japon, 1823-30, published 1838, i. p. 276). These three authors were surgeons in Dutch employ, and thus were enabled to visit Japan when it was closed to other Europeans; they mention the wax and the trees from which it was obtained. Oppermann (Ann. Chim. 1832, 49, 240), percentage composition. Landerer, H. Müller and Buchner (Repert. f. d. Pharm. 1833, 44, 1-34), discussion and experiments as to whether Japan wax is identical with adipocere from dead animals, and whether it is a North American product. Nees von Esenbeck (*ibid.* 1833, 46, 283), commenting on Landerer's work, says that he has seen wax from *R. succedanea* from Japan, and that it is quite the same as that found in commerce. Trommsdorff (J. pr. Chem. 1834, 1, 151), properties and trial as a candle. Brandes (Arch. Pharm. 1841, [2] 27, 288), composition. He thought that Japan wax was composed of the supposed compound ceric acid that Hess (Pogg. Ann. Phys. Chem. 1838, 43, 382) obtained by the treatment of rye-starch with nitric acid. Sthamer and Meyer (Annalen, 1842, 43, 335), composition, distillation, and oxidation by nitric acid. They found that Japan wax is glyceryl palmitate. Hanbury (Pharm. J. 1852-53, [1] 12, 476, and Hanbury's Science Papers, 1876, 60), description and melting-point. Berthelot (Ann. Chim. 1854, [3] 41, 242) suggested that Japan wax perhaps contains a dipalmitin. Simmonds (J. Soc. Arts. 1858-59, 7, 611) and Wilson (*ibid.* p. 424), source and use for candles and night-lights. The Pharm. J. 1859-60, [2] 1, 176), the J. Pharm. Chim. 1859, [3] 85, 368), and the Neues Repert. f. Pharm. (1860, 9, 74) give summaries from various authors. Jackson and Rogers (Proc. Boston Soc. Nat. Hist. 1859-61, 7, 54, 58), properties. Kopp (Rep. Chim. Appliquée, 1860,

2, 142 and 296), discussion of Jackson and Rogers' work; the melting-points were incorrectly reported on p. 142. Blockrode (*ibid.* p. 388), particulars some incorrect, also questioning the identity of the wax examined by previous authors. Simon (Bull. Soc. Imp. Zoo. D'Acclimation, 1862, 9, 596). He was an agent of the Ministre de l'Agriculture and wrote from Nagasaki, giving particulars of the exploitation per 10,000 trees of *R. succedanea* occupying 2 hectares and of the preparation of the wax. Roucher (J. Pharm. Chim. 1872, [4] 16, 20), peculiarities of the melting-point and use in pharmacy for making cerates with olive oil. Ludwig (Arch. Pharm. 1872, [3] 1, 213), particulars. Robertson (Consular Report on Trade of Kanagawa in Japan, 1874, 64; also in J. Soc. Arts. 1873-74, 22, 787; also in Pharm. J. 1874-75, [3] 5, 584), source and preparation. Further particulars about source, preparation and use (J. Soc. Arts. 1873-74, 22, 1000; also in Pharm. J. 1874-75, [3] 5, 425). *Naturalising R. succedanea* in France (Pharm. J. *ibid.* p. 448). Gribble (Arch. Pharm. 1876, [3] 8, 374, from Handels-Bericht of Gehe and Co., Dresden, 1875), preparation written in Nagasaki. Cooke (Oilseeds and Oils in the India Museum, 1876, p. 5), particulars. Simmonds (J. Applied Science, 1877, 8, 55), particulars. Buri (Arch. Pharm. 1879, [3] 14, 403), composition. He saponified and examined the mixed acids and found palmitic acid chiefly, but that others were present, including at least one with melting-point above that of stearic acid, and also an oleic-like acid in small proportion. A. Meyer (Arch. Pharm. 1879, [3] 15, 97), a long paper discussing the work of previous authors and describing the *Rhus* trees with figures of leaves, flowers and fruit of *R. succedanea*, and giving results of a few experiments. Hübl (Dingl. poly J. 1884, 253, 289), iodine value. Eberhardt (Inaug. Diss. Strassburg, 1888), composition. He found the acid afterwards named *japonic acid* by Geitel and van der Want. Rein (Japan: Travels and Researches, 2nd ed. 1888). Rein (The Industries of Japan, 1889, 158-164), an account of the three *Rhus* trees and of the preparation of the wax. Kleinstück (Chem. Zeit. 1890, 14, 1303), peculiarities in the specific gravity. Watt (Dict. Econ. Prods. of India, vol. vi pt. 1. 1892, 499, 500, and Commercial Prods. of India, 1908, 914). Schaedler (Technol. Fette und Oele, 2nd ed. 1892, 80, 870), particulars of the wax and also of its m.p. peculiarities. Hehner and Mitchell (J. Amer. Chem. Soc. 1897, 19, 49, and Analyst, 1896, 21, 330), abnormal behaviour of palmitic acid from Japan wax when mixed with stearic acid. La Wall (Amer. J. Pharm. 1897, 69, 18), starch as an adulterant. Lewkowitsch (Analyst, 1899, 24, 319), analytical values and effect of acetylising. Ball. Bot. Dept. Jamaica, 1900 [2] 7, 37, source and preparation of the wax. Geitel and van der Want (J. pr. Chem. 1900, [2] 61, 151), composition. Eichhorn (Zeitsch. anal. Chem. 1900, 39, 640), directions for finding acid value and saponification value, using amyl alcohol.

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Mexican myrica wax (*Mexican myrtle wax*)

This wax is obtained by the Indians in Mexico from the fruit of *Myrica jalapensis*, and is sold in Mexico city, where it is used for making candles. The tree is known locally as 'arbo de la cera,' and occurs in Vera Cruz, sometimes in dense thickets covering considerable areas. The wax forms a greenish-white layer on the outer surface of the fruit, and is obtained by boiling the fruit in water and skimming off the floating melted wax; it is refined by melting and straining. On examination it gave the following values, which resemble those of Cape berry wax: sp.gr. 0.8763 at 99°; m.p. 43.2°; acid value 4.07; saponification value 214.5; iodine value 2.38. It is considered that it would be suitable for making candles and soap (Olsson-Seffer, Bull. Imp. Inst. 1909, 7, 410).

Myrtle berry wax (*Myrtle wax*, *Laurel wax*, *Bayberry tallow*) is obtained from the wax myrtle, *Myrica cerifera* (Linn.), a shrub growing on peaty soil in North America, and common along the North Atlantic sea coast. The fruit is brown or blackish and the size of a pea; it secretes the wax and becomes covered with a snow-white crust, penetrated by brown or black points of the skin, so that the wax can only be got off as a powder and not in coherent pieces.

Wax is also got from other Myricaceae, namely, *M. caracasana* (Humb. and Bonpl.) in South America, especially in Columbia and Venezuela, and *M. aethiopica* (Linn.) in Abyssinia. See also *Cape berry wax* and *Mexican myrica wax* above.

To obtain the wax the berries are boiled with water, and the fatty mass that floats on the surface is skimmed off and poured into flat dishes; the yield of wax is from 20 to 25 p.c., and a bush yields from 10 to 15 kilos. of berries. The wax which comes from the United States has a deep green colour, probably due to chlorophyll; this colour is bleached to a grey-yellowish tint by exposure to light and air for several years, but the change extends only a few millimetres below the surface.

The statements as to its composition are not concordant. Smith and Wade (J. Amer. Chem. Soc. 1903, 25, 629), however, examined the wax, preparing it by extracting the berries with light petroleum, and concluded that it was mainly palmitin (glyceryl tripalmitate) with some lower glyceride and a small amount of

free acid; they obtained pure palmitin by crystallising four times from light petroleum. The berries they used were picked in September, and the extraction and examination were made in November. The values they record are: sp.gr. 0.9806 at 22°/15.5°, and 0.879 at 99°/15.5°; refractive index at 80° 1.4363; acid value 30.7; saponification value 217; iodine value (Hübl) 3.9; Reichert-Meissl number 0.5. From these they inferred the absence of oleic and volatile acids. They also concluded that no stearin was present. The m.p. in this sample was 48°, as determined by Allen's method (Coml. Organ. Anal. 3rd. ed. vol. ii. pt. i. 34), and the solidifying point was 45°; but it was found that the melting-point rises considerably on keeping the wax. A redetermination in March of the m.p. gave it as 52.5°, a rise of 4.5° in 4 months. A specimen of wax about 4 years old melted at 57° and solidified at 58.3°. Wax from berries obtained in August and extracted in March melted at 55.4°.

Some other observers have found the acid value to be only about 4. It is inferior to beeswax in ductility and plasticity; mixed with beeswax it can be employed for making candles; these are said to give a pleasant smell when extinguished. It could probably be used for soap making. Chittenden and Smith (Amer. Chem. J. 1884, 6, 217) employed this wax as a source for preparing pure palmitic acid.

Some wax prepared in Colombia from the berries of *M. arguta* was examined at the Imperial Institute (Bull. Imp. Inst. 1918, 16, 287) with the following results: m.p. 45°; solidifying point of the fatty acids 46.4°; acid value 21.2; saponification value 216.7; iodine value 1.03; unsaponifiable matter 0.4 p.c.; the wax was yellowish-buff in colour and had a peculiar odour, similar to that of myrtle wax from South Africa (Cape berry wax). It was stated that the wax is employed in Colombia for the manufacture of soap and candles, that the plant is abundant, that the fruit can be gathered cheaply and easily, and that the extraction of the wax is not difficult.

Ocuba wax is obtained from the fruit of a shrub growing in the Pará province of Brasil. It grows well in marshy places, and is found in abundance along the banks of the Amazon river. The fruit encloses a nut covered with a thick skin. The skin extracted by water gives a fine red colour (Ocuba red); after washing with water the nuts are thrown in heaps, crushed to a paste, and boiled, when the wax separates and floats on the surface. The crude wax resembles beeswax, and by purification can be obtained white and suitable for candle-making. 100 kilos. of the seeds give 20-22 kilos of wax. The product is said to be a mixture of wax, fat, and resin, to melt at 40°, and to have a sp.gr. of 0.920 at 15°; it is only slightly soluble in cold alcohol, but is completely soluble in boiling alcohol and ether (Chem. Revue über die Fett- und Harz-Industrie, 1901, 8, 213). See also *Ucububa wax*.

Palm tree wax is the product of a palm tree *Ceroxylon andicola* (Humb. and Bonpl.), which grows on the Andes in Colombia at altitudes of 7900-9700 ft.; it attains a height of 100 ft., and the trunk is coated with the wax, which gives it a white and marble-like appearance.

The wax is obtained by cutting down the tree and scraping off the coating, which is then boiled with water; the wax is thus softened and floats on the surface, and impurities are removed. One tree is said to yield 25 lbs. The wax is made into balls and dried in the sun. Candles are made from it by the addition of a little tallow, and are sold in Carthago. That which is obtained from the Indians is yellowish-white, porous, and friable. When melted it is dark yellow, slightly translucent and fragile like resin. It is partly wax and partly resin, and melts at a temperature a little above that of boiling water; it becomes strongly electric by friction. It is readily soluble in hot alcohol; on cooling the solution becomes a white congealed mass. By using large quantities of alcohol and allowing the solution to cool the waxy part separates and the more soluble resin remains in solution; by repeating this operation several times the wax can be separated from the resin and from a small amount of a bitter substance. Ether also dissolves it, and by evaporation feathery crystals can be obtained. The purified wax melts below the temperature of boiling water, and then resembles beeswax, whilst the resinous matter melts above this temperature (Boussingault, Ann. Chim. 1825, 29, 330; 1835, 59, 19; Seemann, Pop. Hist. of the Palms, 1856, 222).

Bonastre (J. Pharm. Chim. 1828, 14, 349) obtained purified wax by repeated extractions with cold alcohol, and then dissolving the residue in boiling alcohol and filtering. When cold the solution became thick and opaque, like an aqueous starch solution; on standing for some months crystals appeared. On removing the alcohol white silky crystals were obtained; when dried and ground in a mortar it gave luminous sparks. He named this purified wax *cerosylène*, or, according to Boussingault (l.c. 1835, 59, 21), *cérosilène*. Lewy (Ann. Chim. 1845, [iii] 13, 447) found that the wax purified from the resin melted at 72°, and contained carbon 80.73 p.c., and hydrogen 13.30 p.c. Teschemacher (Mem. and Proc. Chem. Soc. 1845, 25) also describes this wax.

A wax obtained from the leaves of *Ceraxylon andicola* was examined at the Imperial Institute. It was a pale straw-coloured powder. After purification it gave the following analytical values: m.p. 93° by the open tube method, as compared with 84° for carnaúba wax, and 70–72° for candelilla wax by the same method; sp.gr. at 15°/15° 1.018; acid value 19.8; saponification value 73.7–104.4, varying with the conditions of the experiment; iodine value 32.8. It was thought that when purified it might be used as a substitute for carnaúba wax (Imp. Inst. Bull. 1917, 15, 182, and 1919, 17, 249).

Peat wax. Waxy substances are obtained when peat is extracted with suitable solvents. By means of benzene or toluene from 1 to 8 parts of crude wax have been obtained from 100 parts of the dry material of samples from different sources. This crude wax was found to contain sulphur, usually amounting to less than 1 p.c. of the wax, but in one case reaching 2.2 p.c. The crude wax consisted of some resinous matter, but principally of a mixture of ester and free acid. The acid or acids obtained by the saponification of the crude wax corresponded in composition to a fatty acid containing

about 22 carbon atoms; the alcohol thus obtained appeared to contain about the same number. No trace of glycerides was found (Kraemer and Spilker, Ber. 1902, 35, 1212). A process was patented in 1903 by Bouchaud-Praceiq (Fr. Pat. 338736) for extracting peat, lignite, &c., with alcohol or ethyl ester, &c., and recovering the wax from the solvent. The wax is said to be hard and to resemble beeswax, and to have a higher melting-point and a sp.gr. above 1.000 (J. Soc. Chem. Ind. 1904, 23, 710).

Zaloziecki and Hausmann (Zeitsch. angew. Chem. 1907, 20, 1141), by extracting peat with alcohol, obtained a dark yellow or brown waxy substance, but the yield was only 10 grms. from some kilograms. It had no sharp melting-point, melting between 80° and 96°; it dissolved very easily in amyl alcohol, and less readily in ethyl and methyl alcohols. In ethyl ether or benzene it dissolved only partially, giving a dark green liquid and leaving a brown insoluble residue. By saponifying the substance soluble in ethyl ether an alcohol was obtained, melting between 124° and 130°, and having a composition and molecular weight corresponding to $C_{20}H_{40}O_4$, and also an acid which began to soften at 145° and melted at 184°, having a composition and molecular weight corresponding to $C_{18}H_{36}O_2$. The part insoluble in ether gave on saponification an alcohol having the same melting-point, composition and molecular weight as the other alcohol, but differing a little in its behaviour, and also an acid which had not melted when 260° was reached, and which had a composition and molecular weight corresponding to $C_{31}H_{62}O_7$. Small quantities of other substances appeared also to be present in the wax, and the above substances are very possibly mixtures.

Pisang wax. This wax occurs as an excretion on the leaves of a species of *Musa*, which grows wild in Java, especially in the uncultivated regions of Tjilatjap and Koenigan. *Pisang* is the Malay name for the banana. The natives obtain the wax by scraping the leaves, throwing the scrapings into boiling water, and then collecting the melted wax. It is said that one stem bears on the average seven leaves (a leaf may be as much as 6 ft. in length), and that 100 leaves yield $\frac{1}{2}$ kilo. of wax. The cakes of wax are white, cream, or slightly greenish in colour, and slightly transparent; the wax is hard with a coarsely granular or crystalline fracture and is very friable. It has been examined by Greshoff and Sack (Ber. trav. chim. 1901, 20, 65), who record the following: sp.gr. 0.963–0.970 at 15°; m.p. 79°–81°; acid value 2–3; it is very hard to saponify, and the saponification value found was 109. Boiling alcohol dissolves very little (about 1 p.c.), and on cooling only retains 0.2 p.c. It is easily soluble in boiling oil of turpentine, amyl alcohol, or carbon disulphide. At 15° petroleum, ether, acetone, and oil of turpentine retain 1 p.c. or less; chloroform and carbon disulphide retain less than 2 p.c. On the basis of ultimate analyses of the wax (previously freed from the part soluble in boiling alcohol), and of the acid and alcohol obtained by saponification, the authors propose provisionally the three following formulae: $C_{21}H_{42}O_4$ for the wax, regarding it as an ester formed from $C_{20}H_{40}O_4$

stearic acid, and $C_{18}H_{36}O$ *pisinoceryl alcohol*. The acid melts at 71° and the alcohol at 78° .

Raphia wax. The raphia palm, *Raphia pedunculata* (Beauv.) or *Ruffia*, which grows in Madagascar, furnishes the fibrous material used by gardeners and known as 'bass'; this is the epidermis of the upper side of the palm leaf. The dull under surface is coated with a whitish layer or bloom, which can be easily rubbed off. After the bass is removed large quantities of the residues are available as a source of the wax. They are spread out to dry on cloths in the open air, but must be sheltered from the wind as the light waxy matter is easily blown away. After drying for 2-4 days a white coating is apparent on the under surfaces of the leaves; this is detached as a powder by shaking or rubbing the leaves between the hands. The powder is collected, freed from foreign matter by sifting, and then put into boiling water when the wax melts and floats on the surface, and earthy impurities settle to the bottom. The melted wax is separated and allowed to solidify. It is yellow to dark brown in colour, and rather harder and more brittle than beeswax. In an experimental trial it was found that ten leaves of medium size ($3\frac{1}{2}$ - $4\frac{1}{2}$ metres in length) weighed 104.5 kilos, and yielded 0.75 p.c. of wax; the yield in practice, however, would be less than this.

Raphia wax in its physical properties resembles carnauba wax but differs chemically; it seems likely to be applicable to the manufacture of candles, polishes, &c., if it can be produced at a sufficiently low cost.

Two specimens were found to have the following properties: m.p. 82° , 83° ; sp.gr. 0.836, 0.832 at $99^{\circ}/15.5^{\circ}$; acid value 4.9, 6.5; saponification value 51.3, 50.3; iodine value 7.7, 10.7 (Bull. Imp. Inst. 1908, 6, 380). It is only slightly soluble in alcohol, ether, acetone, chloroform, light petroleum, and carbon disulphide. It dissolves, but not completely, in boiling alcohol, and separates on cooling. It appears to be mostly composed of an alcohol or mixture of alcohols having a composition corresponding to $C_{22}H_{44}O$, but differing from arachic alcohol (Compt. rend. 1905, 141, 1251; 1907, 144, 594).

In 1918 the raphia wax industry was stated to be still undeveloped, but it was believed that 10 tons would be available annually (J. Soc. Chem. Ind. 1918, 37, 240 R, from U.S. Com. Rep. Apr. 1, 1918).

Rhimba wax. In the Chamber of Commerce Journal, 1901, p. 192, an account taken from the *Moniteur Officiel du Commerce* is given of a product furnished by the Rhimba tree of Madagascar. From the description it appears to be composed of both wax and resin. The wax is said to amount to 14 p.c. The particulars about it are not clearly stated. The wax is said to resist attempts to bleach it.

Snow brush wax. The snow brush (*Ceanothus velutinus*, Douglas) is a shrub from two to six feet in height, which grows in Californian forests; it is considered a nuisance and to involve fire dangers. Scollions and Blakemore made an investigation to see if it could be utilized. Besides obtaining tannin they found that the dried leaves yielded 7.3 p.c. of wax when extracted with gasoline. The wax was greenish in colour,

owing to the presence of a little chlorophyll, and when freed from solvent was brittle with a conchoidal fracture. The crude wax gave the following analytical results: free acid 20.3; saponification number 93.4; iodine value 19.5; Reichert-Meissl number 7.5; sp.gr. at 15° 0.988; melting point 78° - 79° . From experiments made to ascertain the components of the wax, they inferred that it was probably composed in great part of ceryl and melissyl esters of palmitic and stearic acids together with hydrocarbons, free cerotic acid and a small quantity of glycerides (J. Ind. Eng. Chem. 1916, 8, 411, 573).

Spermaceti occurs in special cavities in the head of the sperm whale or cachalot, *Physeter macrocephalus* (Linn.), and also in the blubber; it is held in solution by the sperm oil at the temperature of the whale's body. It also occurs in the bottle-nose whale *Balaena rostrata*, and in some other cetaceans, but not in the oil of the whalebone whales. The spermaceti from *Balaena rostrata* has a slightly higher melting point than that from the sperm whale. The great bulk of the head of the sperm whale consists of dense cellular tissue infiltrated with spermaceti, this is surmounted by the 'case' which holds nearly a ton of very fine oil and spermaceti known as 'head matter.' When removed this head matter is full of spermaceti crystals. The blubber surrounds the whole body in a layer about 18 ins. thick; it is 'tried down,' that is heated to separate the oil from the tissue; on cooling the oil deposits thick scales of spermaceti and becomes semi-solid. The 'trying down' is sometimes done on the ship and sometimes at the factories. At the latter the semi-solid mass undergoes several filtrations and pressings to separate the oil from the spermaceti, which is melted and cast into moulds once or twice during the series of pressings. Finally, the wax is warmed and agitated with a little caustic potash solution to remove the last traces of colour and to neutralise traces of acid, and is cast into blocks forming an almost blue-white glistening semi-crystalline solid (Field, Soc. Arts. Cantor Lectures, 1883). It is said that for some purposes it is best not to free it entirely from the sperm oil.

The sp.gr. at ordinary temperatures is about 0.945, but values as divergent as 0.905 and 0.960 have been given, owing probably to irregularities caused by the crystalline structure. The sp.gr. of melted spermaceti at 98° - 99° is from 0.808 to 0.816 as compared with water at 15° (Kehler, Amer. J. Pharm. 1897, 69, 104). The m.p. is from 41° to 49° , but by repeated purifications it reaches 63.5° . Meldrum (Chem. News, 1916, 111, 37), in order to investigate the phenomena of melting and solidifying points and the rise in temperature on setting, selected spermaceti as the substance, and records numerous experiments on it and also on the effect of impurities such as sperm oil, water, glycerin, and oleic acid. The acid value is from 0 to 1.8; saponification value from 120.6 to 124.6; the iodine value of highly purified spermaceti is 0, but values up to 9.3 (by Wijs' method) have been found, caused, as doubt by the presence of sperm oil (Dunlop, J. Soc. Chem. Ind. 1906, 27, 63). It is insoluble in water, and alcohol dissolves little except the coloring matter; it is soluble in boiling alcohol, ether, chloroform,

carbon disulphide; it separates in a crystalline form from the solution in hot alcohol or ether. Bechmann and Kirschner give a long account of the examination of spermaceti for purity (J. Soc. Chem. Ind. 1921, 40, 89A, from Pharm. Zentralh. 1920, 61, 703, 719, 733).

Spermaceti is mainly composed of cetyl palmitate ($C_{18}H_{38}O_2$). It was examined by Chevreul in 1814, and the purified substance was named by him *cétine*; in 1818 he described the alcohol obtained by its saponification (now known as *cetyl alcohol*) under the name *éthol*, formed from the first syllables of ether and alcohol (Recherches, Chim. sur les Corps Gras 1839, 148). The acid with which the radicle of the cetyl alcohol $C_{18}H_{37}OH$ is combined was found later to be palmitic acid. Although spermaceti has a crystalline appearance, it contains compounds other than cetyl palmitate. Heintz (Pogg. Ann. 1854, 92, 609, 93, 536) believes that it yields on saponification stearic, palmitic, myristic, and lauric acids, and the alcohols $C_{18}H_{37}O$, $C_{16}H_{33}O$, $C_{14}H_{29}O$, and $C_{12}H_{25}O$; he named the first, third, and fourth of these *stéthol*, *methol*, and *léthol* in analogy to Chevreul's *éthol*. These very probably exist in the spermaceti as esters of the corresponding acids. He also found another liquid substance in the products of saponification.

Spermaceti is used for making candles which burn brightly and in pharmacy for making ointments. For candle-making the addition of a few per cent. of beeswax or paraffin is advantageous to remove the brittleness of the spermaceti. Spermaceti candles of prescribed composition and properties were formerly used as the standard for measuring the illuminating power of different lights (Young, J. Soc. Chem. Ind. 1891, 10, 185; Met. Gas Referees, *ibid.* 1894, 13, 65).

Sugar cane wax. A waxy substance is produced by the sugar cane, and is noticeable on the rind of some varieties, especially near the nodes; it is most abundant on the violet cane. It was first described by Avequin (Ann. Chim. 1840, [ii.] 75, 218), who named it *cérose*. Cold alcohol removes some colouring matter, chlorophyll probably, but does not dissolve the wax. The purified wax can be obtained by removing the portion soluble in cold alcohol, then dissolving in boiling alcohol, cooling, pressing, driving off the alcohol, and melting. It is dull yellow, hard, and can be powdered; it is insoluble in water, cold alcohol and cold ether; hot ether dissolves it to some slight extent, and deposits it on cooling in small crystalline grains; boiling alcohol dissolves it completely, and the solution on cooling becomes semi-solid, just as does an alcoholic soap solution. It melts at 82° and solidifies at 80° , and its sp.gr. is 0.961 at 10° . When made into a taper it burns with a fine white flame like wax or spermaceti.

Analyses of the wax were made by Dumas (*ibid.* 225) and Levy (*ibid.* 1845, [iii.] 13, 451) who assigned formulae to it on the supposition that it was a single compound, but from Wijnberg's experiments (Het Rietwas en de Mogelijkheid zijner Technische Winning, 1909; J. Soc. Chem. Ind. 1909, 38, 991, 999) the wax appears to contain cetyl alcohol $C_{18}H_{37}O$, and also a substance of a composition corresponding to $C_{18}H_{35}O$, which is neither an ester nor a primary alcohol,

since it yields no hydrogen when heated with soda lime. Prinsen Geerligs (Arch. v. d. Java-Suikerindustrie, 1893, 1, 67) also examined the wax.

In the manufacture of cane sugar the juice is purified by treatment with lime and heating; the resulting muddy precipitate is filtered off and forms a waste product. Wijnberg proposes to extract the wax from this by the use of benzene or other solvents and utilise it (Fr. Pat. 397843, 1908). He finds that the extract from fresh mud contains a large proportion of fatty matters besides the wax, but that in mud which has been kept for some time the fatty matters undergo a kind of fermentation, and are decomposed and a product is obtained approximating more closely to the wax got by scraping the cane. It is stated that extraction of the wax has been undertaken in Java. The subject is treated of very fully in Wijnberg's book mentioned above. J. Soc. Chem. Ind. 1910, 29, 33, deals with a U.S. Patent and gives analytical values.

W. E. Cross (J. Soc. Chem. Ind. 1915, 34, 845, from Intern Sugar J. 1915, 17, 311) found from experiments that by submitting the raw mill juice to centrifugal action a product containing over 50 p.c. of wax was obtained, and thus by one crystallisation from alcohol gave a pure hard product, melting at 82° .

Ucuhuba wax. An investigation of the wax from the fruit of *Myrsine surinamensis*, Roland, was made by Reimer and Will (Ber. 1885, 18, 2011), who found that the chief component was trimyristin, glyceryl trimyristate. The wax obtained by an ether extraction melted at 45° . An account of the seeds of this plant, obtained from an exhibit of the Pará Province of Brazil, is given by Tschirch (Arch. Pharm. 1887, [3] 25, 619), who says that the seeds are known in commerce as *ucuhuba*. Other references are: Valenta (Zeitsch. angew. Chem. 1889, p. 3); Bolton and Hewer (Analyst, 1917, 42, 35).

About 4 tons of ucuhuba wax were exported in 1920 (Dept. Overseas Trade, Report for Brazil, 1921, p. 19). See also *Oruba wax*.

Oils, Fats, Waxes, and Rosins, by E. E. Bolton and R. G. Pelly. Fats: Natural and Synthetic, by W. W. Myddleton and T. Hedley Barry: E. Benn, Ltd., London. H. H. R.

WEED KILLERS. The best weed killer for the purpose of the agriculturist is generally the hoe in some form or other, aided by the sun and wind. To permit of the ready discrimination, by mechanical means, between the crop and the accompanying weeds is one of the most important advantages of regular drilling or planting. It is only in a few cases that the farmer can derive much advantage from the application of chemical methods of destroying weeds, since, as a rule, any means which will destroy weeds, will render the soil, for a time at least, unfitted for the growth of any plant.

For destroying all vegetation, e.g. for keeping garden paths free from weeds, any general plant poison may be used. Of these there are many; indeed any soluble salt, applied in strong solution, will kill plants by producing plasmolysis. In practice, strong solutions of common salt, 10 p.c., i.e. 1 lb. per gallon; dilute sulphuric acid (1 part in 25 to 30 of water); dilute arsenic

phenol (about 1 oz. commercial carbolic acid to a gallon of water); of sodium arsenite (about 1.5 p.c. solution); or of calcium sulphide (made by boiling 1 part of sulphur with 50 parts of water and 10 parts of quicklime) are often used, the liquid being simply applied to the surface of the walks from a watering pot, which should be well painted on the inside. Sulphides, thiocyanates, and sulphites act as effective plant poisons, and to their presence the poisonous action of fresh 'gas lime' is largely due. Many metallic salts act as plant poisons, even in excessively dilute solution. According to Coupin (Compt. rend. 1901, 654) the weakest solutions of the various salts which had an injurious effect upon the growth of the roots of the seedlings of wheat, contained 1 part of the anhydrous salt and the following parts of distilled water:—

Copper sulphate . . .	700,000,000
Mercuric chloride . . .	30,000,000
Cadmium chloride . . .	10,000,000
Silver nitrate . . .	1,000,000
Zinc sulphate . . .	40,000
Lithium chloride . . .	12,000
Calcium iodide . . .	10,000
Barium nitrate . . .	4,200
Borax . . .	1,000
Manganese chloride . . .	1,000
Calcium bromide . . .	400
Calcium chloride . . .	260

The extreme dilution of the copper sulphate, which can produce a poisonous effect, when applied in solution to the roots, is remarkable. In the presence of soil, however, many of these substances, including copper sulphate, are converted into insoluble and harmless compounds.

But the use of these plant poisons in agricultural practice is limited, owing to the difficulty of restricting their action to the weeds. In some countries, where a particular weed has become a scourge, recourse to these drastic measures is sometimes made, e.g. prickly pear in Cape Colony has been destroyed in many districts by the use of sodium arsenite, or of solutions of arsenical sheep dips, 1 or 2 p.c. solution of the former being sprayed over the uprooted plants, which then die, dry, and can afterwards be burnt.

Of more importance to the farmer is the differential or selective poisoning of weeds, by the use of solutions which, while destroying certain weeds, produce no injurious effect upon the crop itself. The best known of such methods is in the destruction of charlock or wild mustard (*Sinapis arvensis* [Linn.] or *Brassica Sinapistrum* [Boiss.]). The method, due to an accidental observation by Girard in France, in 1897, is to spray the barley or oat field infested with the charlock in the spring, when the charlock plants are about 2 or 3 ins. high, with from 40 to 70 gallons per acre of a 3 p.c. solution of crystallised copper sulphate, best on a still, dry, dull day. Unless rain soon follows the spraying, in which case the result is spoiled, it will be found that the charlock plants quickly blacken and die, while the barley or oats and clover (if that be also present) are uninjured. In addition to charlock, known in various districts as 'ketlock,' 'wild mustard,' 'yellow flower,' and in Ireland as 'preahagh,' other cruciferous weeds, of which

'runches' (*Raphanus raphanistrum*) is the most important, can be killed by the same treatment. Ferrous sulphate in 10 or 12 p.c. solution may be substituted for the copper sulphate, but according to experience in Ireland (Leaflet No. 6, Dept. of Agric. and Tech. Instruction for Ireland, 1901) is not so efficient. Cereals, clovers (and most other *leguminosae*) are uninjured by the treatment, but docks and thistles, although not usually killed, are seriously checked in growth.

Various explanations of this differential action of copper and iron sulphate solutions have been offered. Girard ascribed it to the solution being retained by the rough and more or less horizontal leaves of the charlock, while the smooth erect leaves of the cereals would permit of the solution running off. Against this is the fact that other plants with horizontal leaves, e.g. clovers, suffer little damage. Another possible explanation is that interaction between the metal of the copper or iron sulphate and the sulphur compounds which are characteristic of the *cruciferae*, may take place and lead to the destruction of the plant.

A third and probable theory is that the cell walls of the leaves of charlock are thinner or weaker than those of cereals, and more readily permit of plasmolysis being set up, when they are brought into contact with saline solutions applied to the exterior of the leaves. This view receives some support from the fact, observed by Heinrich (Jahresb. für Agricultur-Chemie, 1901, 351), that 15 or 20 p.c. solutions of sodium nitrate, ammonium sulphate, or potassium chloride—substances which cannot exert any chemical toxic effect—are also effective in destroying charlock. Moreover, the importance of a dull, still, dry day for the spraying, which is always shown in field trials, is in accordance with this explanation, for under such conditions, the droplets of the solution, deposited on the leaves of the plant, would retain their original concentration for a longer period than on windy or sunny days when evaporation would be hastened.

The experience of the Irish Department of Agriculture is that from 50 to 70 gallons per acre of a 3 p.c. solution of copper sulphate, under favourable conditions of weather, is the most effective spray for destroying charlock in cereal crops, and that even when the weed has come into flower, it can be successfully destroyed by this treatment, whilst the cereals and clover are uninjured.

Another example of differential plant-killing is afforded in the use of the so-called 'lawn-sand' for the destruction of plantains and daisies in lawns. The active ingredient in lawn-sand is usually sulphate of ammonia, and to be effective the preparation must be applied in relatively large dressings—usually about 4 oz. per square yard (= 1210 lb. per acre) is recommended. The result is that the flat-leaved plants, e.g. daisies and plantains, wither, turn brown and die, while the grasses, though, perhaps, temporarily injured and browned, recover and afterwards grow vigorously. Lawn-sand is generally applied in March and, after its toxic action on weeds, acts as an efficient nitrogenous manure.

A certain amount of indirect 'weed' killing can be achieved by suitable manuring; thus the

growth of grasses is favoured at the expense of admitted leguminous plants, by repeated applications of nitrogenous manures, whilst the opposite effect is produced by application of calcareous, phosphatic, and potash manures with avoidance of nitrogenous ones. But this method is of limited application, and is rarely of service to the farmer. It may, however, be used in the adjustment of the relative proportions of grasses and clovers in a lawn. But for the destruction of the more important and troublesome weeds of the farm and garden reliance has chiefly to be placed upon the mechanical methods of cultivating the soil at the most suitable season.

H. I.

WEINSCHENKITE. A rare mineral found in the Bavarian Oberpfalz in white matted globular deposits and in radiating needles on brown hematite. Is mainly a hydrated phosphate of yttrium and erbium $\text{PO}_4(\text{Er}, \text{Y})_2\text{H}_2\text{O}$, containing small quantities of other rare earths (Henrich and Hiller, Ber. 1922, 55 [B], 3013).

WEISSENFELS LIGNITE RESINS v. RESINS.

WEISSGILTIGERZ or WEISSGÜLTIGERZ v. FREIBERGITE.

WEHRLITE v. TETRADYMYTE.

WELD is the dried herbaceous plant known as *Reseda luteola* formerly cultivated to a considerable extent in France, Germany, and Austria. Its cultivation in this country has nearly ceased, because not only is the quantity of colouring matter it contains very small, but the carriage of the plant, owing to its bulky nature, is expensive. A special interest, however, attaches to weld, for it is said to be the oldest European dyestuff known, and was used by the Gauls and other nations dwelling north of the Alps in the time of Julius Caesar.

The plant attains a height of about 3 feet, is pale brown in colour, and is sold in sheaves like straw. The colouring matter is disseminated throughout the entire plant, but the greater quantity occurs in the upper extremity and the seeds.

Luteolin, the main colouring matter of weld, was examined by Chevreul (J. Chim. Med. 6, 157; Annalen, 82, 53), who obtained it in a crude condition; its isolation in a state of chemical purity was first achieved by Moldenhauer (Annalen, 100, 180), who assigned it to the formula $\text{C}_{15}\text{H}_{14}\text{O}_6$. It was subsequently investigated by Schützenberger and Paraf (Bull. Soc. Chim. 1861, [i.] 18), who proposed the formula $\text{C}_{15}\text{H}_{10}\text{O}_6$, and purified it in a somewhat novel manner which is worthy of mention. Weld was exhausted with alcohol, the extract evaporated, and treated with water, which threw down a dirty greenish precipitate. This was collected, introduced with a little water into a sealed tube and heated to 250°. On cooling the sides of the tube were found to be coated with golden-yellow needles of luteolin, and the impurities had collected at the bottom of the tube to form a resinous cake.

Hlasiwetz suggested that luteolin had the formula $\text{C}_{15}\text{H}_{10}\text{O}_6$, and was isomeric with the paradiacetin, which he obtained during the fusion of quercetin with alkali (Annalen, 112, 186).

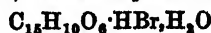
For the preparation of luteolin in quantity, Perkin (Chem. Soc. Trans. 1896, 69, 306, 799) suggests weld extract.

300 grms. of the extract dissolved in 3 litres of water is treated with 180 c.c. of hydrochloric acid (33 p.c.), and the mixture is digested at the boiling temperature for some hours. A quantity of a black resinous substance separates, which is collected while hot, and the filtrate, which contains the colouring matter, is allowed to stand for twelve hours. A brown precipitate of impure luteolin is slowly deposited, and is collected, washed, and dissolved in a little hot alcohol. On pouring this solution into ether, the main bulk of the impurity is precipitated, and the ethereal liquid on evaporation yields a yellow residue, which is crystallised from dilute alcohol. The product in addition to luteolin contains apigenin (Chem. Soc. Trans. 1900, 77, 1315), and the latter can only be removed with certainty by the following method:—

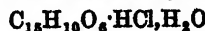
The mixture dissolved in boiling glacial acetic acid is treated with a few drops of strong hydrochloric acid; this causes the almost immediate separation of luteolin as hydrochloride, whereas the apigenin remains in solution. The hydrochloride is collected, decomposed by water, and the luteolin crystallised from dilute alcohol.

Luteolin $\text{C}_{15}\text{H}_{10}\text{O}_6$ crystallises in yellow needles or leaflets, m.p. 327°–329° (Perkin), 327° (v. Kostanecki, Rozycki, and Tambor, Ber. 1900, 33, 3410), soluble in alkaline solutions with a yellow coloration. With alcoholic lead acetate it gives a bright yellow precipitate and with alcoholic ferric chloride a green solution.

Luteolin sulphate $\text{C}_{15}\text{H}_{10}\text{O}_6\cdot\text{H}_2\text{SO}_4$, orange-red needles; *luteolin hydriodide* $\text{C}_{15}\text{H}_{10}\text{O}_6\cdot\text{HI}$, orange prisms; *luteolin hydrobromide*



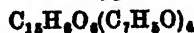
ochre needles; and *luteolin hydrochloride*



(Perkin, l.c.), are readily prepared by the action of the acids on luteolin in the presence of boiling acetic acid. By treatment with water these compounds are quantitatively decomposed into luteolin and acid.

Monopotassium luteolin $\text{C}_{15}\text{H}_9\text{O}_6\text{K}$, fine yellow needles, from luteolin by means of alcoholic potassium acetate, is decomposed by boiling water with separation of luteolin. The sodium compound, $\text{C}_{15}\text{H}_9\text{O}_6\text{Na}$, behaves similarly.

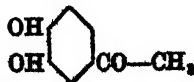
Tetra-acetyl luteolin $\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$, Perkin (also Herzig, Ber. 1896, 29, 1013), colourless needles, melts at 221°–223° (Perkin), 225°–227° (Herzig). *Tetrabenzoyl-luteolin*



colourless needles, melts at 200°–201° (Perkin).

Dibromluteolin $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_6$, yellow needles melts at 305°.

By the action of nitric acid on luteolin Rochleder (Zeitsch. für Chem. 1886, 602) obtained oxalic acid, and with fused alkali *protocatechuic acid* and *phloroglucinol*. Digested with boiling 50 p.c. potassium hydroxide solution, phloroglucinol and *acetyl-catechol* are produced (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1322).—



When methylated with methyl iodide luteolin yields, in addition to luteolin trimethyl ether,

Acetyl-methyl-luteolin trimethyl ether (Perkin and Howard).

Luteolin trimethyl ether $C_{15}H_{12}O_6(OCH_3)_3$, lemon-yellow needles, m.p. 161° – 163° , forms a monoacetyl derivative



colourless prisms, m.p. 156° – 158° , and with alcoholic potash gives a bright yellow crystalline salt, which is decomposed by water.

On hydrolysis with alcoholic potash at 170° the trimethyl ether gives *veratric acid*, and *phloroglucinol monomethyl ether*, which was isolated in the form of disazobenzene-phloroglucinol monomethyl ether, orange needles, m.p. 251° – 252° .

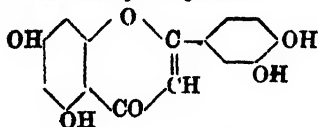
Methyl-luteolin trimethyl ether



melts at 191° – 192° , and the monoacetyl derivative $C_{15}H_{10}O_6(OCH_3)_2(C_2H_5O)$ at 175° – 176° . By means of alcoholic potash *veratric acid* and *methyl-phloroglucinol methyl ether* (identified as disazobenzene methyl-phloroglucinol monomethyl ether, orange-red needles, m.p. 198° – 201°) are produced.

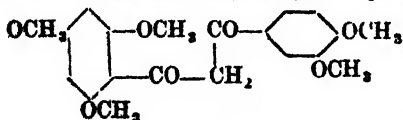
By digestion with boiling hydriodic acid *methyl-luteolin* $C_{15}H_{12}O_6$, yellow leaflets, is formed, m.p. about 307° – 309° , which gives an acetyl compound melting at 235° – 236° .

Perkin (l.c.) assigned to luteolin the constitution of a tetrahydroxyflavone



and the more recent synthesis of this colouring matter by v. Kostanecki, Rozycki, and Tambor (l.c.) has indicated that this formula is correct.

When *phloracetophenone trimethyl ether* is condensed with *ethyl veratrate* it gives 2:4:6:3':4'-pentamethoxybenzoyl-acetophenone



and this by long digestion with boiling hydriodic acid (sp.gr. 1.96) is converted into luteolin.

Though luteolin when digested with alcoholic potash and ethyl iodide in the ordinary manner gives only a triethyl ether, owing to the presence of an hydroxyl in the ortho position to the carbonyl group, when an excess of the reagents is employed, luteolin tetraethyl ether



colourless needles, m.p. 153° – 155° , can readily be obtained (Perkin, Chem. Soc. Proc. 1912, 28, 323). Though quercetin pentamethyl ether on nitration readily gives the 6'-mononitro derivative (Watson, Chem. Soc. Trans. 1914, 105, 333), luteolin tetraethyl ether yields in similar circumstances only the tetranitro compound $C_{15}H_8O_6(NO_2)_4(OEt)_4$, colourless prisms, m.p. 155° .

On the other hand, the introduction of only one nitro group can be effected by nitrating mono-bromo-luteolin tetraethyl ether (see below) (Perkin and Watson, *ibid.* 1915, 107, 197). Bromine (4 molecules) in acetic acid yields *bromoluteolin tetraethyl ether perbromide*

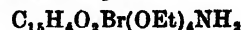
$C_{15}H_8O_6(OEt)_4Br_4HBr$, orange-yellow prisms, m.p. 161° (decomp.), and this on boiling with water gives *bromoluteolin tetraethyl ether* and *tetrabromoluteolin tetraethyl ether*.

With bromine (1 molecule) in acetic acid solution, *bromoluteolin tetraethyl ether hydrobromide* $C_{15}H_{10}O_6(OEt)_4Br \cdot HBr \cdot C_2H_5O$, pale yellow hair-like needles, is obtained, which when boiled with water gives *bromoluteolin tetraethyl ether* $C_{15}H_{12}O_6(OEt)_4$, colourless hexagonal plates, m.p. 183° , whereas by brominating luteolin tetraethyl ether with 2 molecules of the halogen in acetic acid solution in presence of sodium acetate, *tetrabromoluteolin tetraethyl ether*, colourless crystals, m.p. 111° – 114° , is formed.

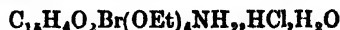
Bromo-6'-nitroluteolin tetraethyl ether



pale yellow rhombs, m.p. 170° – 171° , on reduction in alcoholic solution with stannous chloride and hydrochloric acid, gives *bromo-6'-amino-luteolin tetraethyl ether*



yellow prisms, m.p. 165° – 169° . This forms the hydrochloride



bright yellow needles, which when dried over soda lime become scarlet and melt at 187° (decomp.); with *stannic chloride* it forms the salt $(C_{15}H_{10}O_6NBr)_4H_2SnCl_6$, crimson prisms. By means of sodium nitrite the amino hydrochloride yields in the usual way, crystalline *bromoluteolin tetraethyl ether diazonium hydrochloride*, and from this by boiling with water *bromo-6-hydroxy-luteolin tetraethyl ether*

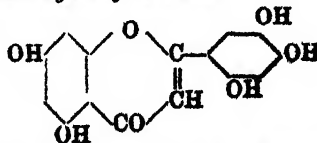


yellow needles, m.p. 255° , the acetyl derivative of which crystallises in white needles, m.p. 270° – 272° , is produced.

This latter, probably owing to its insolubility, is not readily attacked by hydriodic acid (D 1.7), the first product of the reaction being apparently *bromo-6-hydroxy-luteolin diethyl ether*



the acetyl compound of which melts at 213° . The more drastic action of the hydriodic acid, employing also acetic anhydride, gave a small quantity of a compound crystallising in yellow needles, soluble in alkaline solutions with a yellowish brown colour, and which was probably an impure 6-hydroxy-luteolin—



The acetyl compound melted at 250° – 256° .

When air is aspirated through alkaline solutions of luteolin (and also those of chrysin and apigenin), oxidation does not occur. This property, according to Perkin (l.c.), distinguishes the colouring matters of the flavone from those of the flavonol class, which are readily oxidised by this treatment.

It has already been stated that weld contains a second colouring matter, *isochrysin* (v. PARSLAY).

Dyeing properties of weld.—The importance of weld as a dyestuff in silk and wool dyeing has greatly diminished in consequence of its low colouring power compared with quercitron bark, flavin, and old fustic. This in one respect is unfortunate, because, of all the natural yellow colouring matters, it yields the purest and fastest shades. In conjunction with aluminium and tin mordants it gives very bright pure lemon-yellow colours, and these do not change to an olive or reddish tint as in the case of other vegetable yellows. With chromium and iron mordants weld gives yellowish and greenish olives respectively. For yellow, wool and silk are mordanted with alum and tartar in the usual manner and dyed subsequently in a decoction of weld with the addition of chalk to the dye bath. Weld alumina yellow is to some extent still employed in this country for certain army cloths and braid. For silk dyeing, weld extract is manufactured in small quantity, and is used for the production of yellow and olive colours.

A. G. P.

WELDING (*Soude*, Fr.; *Schweiessen*, Ger.) is the joining of two pieces of metal under the hammer at a sufficiently high temperature.

WELSIUM. The name given by Eder (*Akad. Wiss. Wien. Ber.* 1920, 129, 421) to an element supposed to exist between terbium and dysprosium, of which he has tabulated more than 300 lines between $\lambda 6546$ and 3038 .

WESELSKY'S DYES v. OXAZINE COLOURING MATTERS.

WESTFALITES. Explosives consisting of mixtures of ammonium nitrate and resin, with or without potassium nitrate, v. **EXPLOSIVES.**

WETTER DYNAMITE, WETTEREN POWDER, v. EXPLOSIVES.

WHALE OIL is obtained from the blubber of various species of the genus *Balaena*, viz *Balaena mysticetus*, Greenland or 'right' whale (northern whale oil); *Balaena australis* (southern whale oil); *Balaenoptera longimana*, *Balaenoptera musculus* (common rorqual, the largest of all known animals), *Balaenoptera borealis* (northern or Rudolph's rorqual) finback oil, finner-whale oil, humpback oil; *Neobalaena marginata* (Australian whale), *Rhachianectes glauca*, Cope (Japan). Other cetaceans, the zoological species of which have not been determined yet, or which are identical with the foregoing species, are known as bowhead whale, Californian grey whale, orca or killer whale, beluga or white whale; these are chiefly caught by American whalers in the Northern Pacific. The northern whale oil is the 'train oil' of commerce proper; but this name has become a generic name, and has been extended to all other 'blubber oils' included in this group and even to fish oils (see **OILS, FIXED, AND FATS**).

The blubber of whales caught in the northern sea of Europe was, in the early days of the whaling industry, 'tried' on board the whalers; but in consequence of the low yield, and also of the low quality of oil thus obtained, the whales are now brought into the 'trying' stations situated in Finmarken, on the Lofotes, Faro, Shetland, Hebrides, and in Iceland.

To a large extent the American whalers still try the blubber on board ship and deliver the whale oil into the refineries of New Bedford, Mass., on the east coast, and of San Francisco

Columbia the most modern methods (see below) are now in vogue.

During recent years a very extensive whale oil industry has sprung up in the whaling grounds adjacent to the South African coast, especially to that of Natal. The whale, killed by a gun-shot, is blown up with air so as to float the carcass, which is brought immediately into the trying stations, when the whale is hoisted on to a working platform where the blubber is stripped clean from flesh, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting pans, and 'boiled' with steam. Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, known in commerce as 'Whale Oil No 0'; it is of a pale yellow colour, and has but a faintly fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are 'water-white,' and are free from volatile fatty acids. On further boiling, the second quality—'Whale Oil No 1'—runs off, it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified while depositing 'stearine,' which is filtered off, pressed in hydraulic presses, and sold as 'whale tallow,' or 'whale stearine,' for soap making.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is 'tried down' in a digester under a pressure of 40-50 lbs. The oil classed as 'No. 2 oil' is thus obtained. This oil has a brown colour and a strongly developed fishy smell; its proportion of free fatty acids is considerably higher than in 'oil No. 1'. In some stations 'whale oil No. 2' is made from the blubber residues only, and does not contain any oil from the flesh. Hence it represents a superior article to the 'No. 2 oil.'

The bones are worked up in the same manner, and yield a still inferior quality of oil. Such oil ('whale oil No. 3') is darker still, has a more strongly developed odour, and a high percentage of free fatty acids. 'Whale bone oil' of commerce is, however, not exclusively made from the bones, except in those cases where the product is sold under guarantee as 'bone oil.'

All these operations are carried out with the greatest rapidity and precision recalling the routine of the Chicago packing houses which have served as a prototype for the arrangement of a modern whaling station.

In the old whaling stations where the carcass cannot be handled so expeditiously, the oil remains for a longer or shorter time in contact with the flesh, which rapidly undergoes putrefactive changes. The oil suffers in consequence and becomes dark, and is more objectionable as regards smell and free fatty acids than the preceding qualities. This oil is known in the trade as 'carcass oil,' 'whale oil No. 4.'

The residue remaining after the removal of the oil is worked up for manure, 'whale manure.'

This process is carried out in Newfoundland (at Balena) Pacific coast, and South Africa, where the Government has established several new plants. The carcasses of the whales are there completely used up in the manufacture of oil, 'stearine,' bone meal or bones, and other articles of commerce.

If the whale is landed in a perfectly fresh state, cattle meat can be prepared from the fresh meat, as is being done in Iceland and in the Faro Islands, and in South Africa. Some fresh meat is also consumed by the inhabitants locally (Iceland and Faro Islands).

The 'right whale' oil is of better quality than the 'southern whale' oil. The 'finne whale' oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coasts of Norway and Newfoundland, as also to a small extent on the Asiatic coast of Russia, and the coast of Japan. For the chemical characteristics of whale oil, see OILS, FIXED, AND FATS.

Doherty (J. Roy. Soc. N.S. Wales, 1922, 46, 266) obtained the following values for oils from Pacific whales: sp. gr. at 15.5°, 0.9182-0.9232; $n_D^{15.5}$, 1.471-1.476; acid value, 0.75-5.8, sapon value, 192-199; iodine value, 95-119.

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited 'stearine' consists to a large extent of palmitin. The iodine value of a sample of pressed cake examined in the author's laboratory was 37.9. Volatile fatty acids are absent. About 10 p.c. of clupanodononic acid can be isolated from whale oil in the form of its octobromide.

According to Milligan, Knuth and Richardson, who separated the fatty acids by fractional distillation of their methyl esters, a specimen of whale oil fatty acids had the following composition: myristic acid, 4.5; palmitic, 11.5; palmitoleic, 17.0; stearic, 2.5; unsaturated acids (mainly oleic), 36.5; unsaturated acid C_{22} , 16; unsaturated acids, C_{23} , 10; unsaturated acids, C_{24} , 1.5; and unsaponifiable matter, 0 p.c. (J. Amer. Chem. Soc. 1924, 46, 157). E. I. Armstrong and T. P. Hilditch (J. Soc. Chem. Ind. 1925, 44, 180) found in a S. Georgia whale oil that the unsaturated acids comprised myristoleic acid, 1 to 1.5 p.c.; palmitoleic acid, 15 p.c.; oleic acid, 35 p.c.; and highly unsaturated acids with 20 and 22 carbon atoms.

Whale oil is not infrequently adulterated with resin oil, the detection of which is simple. For the recognition of seal oil reliance is mainly placed upon the taste.

The 'water-white' and 'pale' brands of whale oil are used as burning oil, and very extensively in soap-making. The lower qualities are employed for leather dressing. For the characteristics of glycerol from whale oil, see Cocks and Selway (J. Soc. Chem. Ind. 1918, 7, 126 T).

Whale oil is also used as a batching oil or putty, for tempering steel, and as a lubricant or screw-cutting machines. In the hydrogenated form (see HARDENED OILS) it is sometimes used as a substitute for margarine on the Continent. Hydrogenated whale oil yields about 0.9 p.c. of unsaponifiable matter and 0.04 p.c. of cholesterol. The unsaponifiable matter, after removal of the

cholesterol, is optically active $[\alpha]_D^{20} = +5.7$. When crystallised from acetone, whale oils yield a larger quantity of insoluble glycerides than do animal fats, and the glycerides remaining soluble in this solvent have a high iodine value (Buttenberg and Angerhauser, Zeitsch. Nahr. Genussm. 1919, 38, 199).

WHEAT. *Estimation of Rye Flow in Wheat Flour.*—J. König and F. Bartchat (Zeitsch. Nahr. Genussm. 1923, 46, 321) have thoroughly investigated chemical methods for the estimation of wheat and rye flours when present in admixture, and show that the diastase method proposed by several workers (e.g. Amberger, Analyst, 1922, 47, 73), methods dependent on the gluten content, on the solubility of the non-glutenous protein, or on the protein soluble in 20 to 70 p.c. alcohol are not trustworthy for the analysis of the mixed flours. It is shown, however, that the percentage of the total protein soluble in saturated solution of calcium sulphate is constant for each flour, and independent of the actual amount of protein in any particular sample of the flours. Ten grams of the flour are moistened in a 500 c.c. flask with the saturated calcium sulphate solution at the room temperature (0.22 gm. in 100 c.c.), made up to the mark and shaken in a machine for one hour, after which the nitrogen is estimated in 100 c.c. of the clear filtrate and expressed as percentage of the total nitrogen in the flour. Treated in this way, wheat flour shows 29.1 p.c., and rye flour 51.5 p.c., so that the proportion of the two flours may be interpolated from the following table.

Wheat.	Rye.	P.
100	—	29
90	10	31
80	20	33
70	30	35
60	40	38
50	50	40
40	60	42
30	70	44
20	80	47
10	90	49
—	100	51.5

The average experimental error with the method is about 5 p.c., but may be exceeded in the case of flour of unusually high acidity (Analyst, 1924, 49, 187. See also CEREALS, vol. ii. p. 130).

A modification of Fleurent's method for the determination of the baking value of flours has been proposed by Braun (Ann. Falsif. 1924, 87, 269; J. Soc. Chem. Ind. 1924, 43, B 782). The ratio of gliadin nitrogen to gluten nitrogen is used to indicate the quality of the flour.

WHEEL ORE v. BOURNONITE.

WHEATSLATES v. WHEATSTONE.

WHEATSTONE (*Corticeus*, Fr.; *Wetzstein*, Ger.), **OILSTONE**, and **HONESTONE**. Hard, fine-grained rocks, usually highly siliceous in character, used for sharpening or whetting edged tools and also for grinding metals. Rocks of several different kinds are suitable for this purpose, such as hornstone, hornfels, lydian stone, quartzite, sandstone, slate, phyllite, schist, &c. (q.v.). They must possess an evenness of grain and texture combined with a certain degree of friability. If the stone is too hard and tough to wear by friction it becomes

glazed and chipped, and does not present cutting surfaces. At the same time the stone must have a certain degree of firmness and must wear evenly. The cutting power sometimes depends on the presence of minute grains of garnet, rutile, or magnetite distributed through the stone. The chemical composition of materials answering to such a description naturally varies between wide limits, but, as a rule, silica predominates. The following analyses are of I, Novaculite, 'Arkansas stone,' from Arkansas (sp.gr. 2.648). II, Novaculite, 'Ouachita stone,' from Arkansas. III, Novaculite, containing quartz and sericite, from Marquette, Michigan (also P_2O_5 , Li_2O traces). IV, Oilstone (turkey-stone) from Asia Minor. V, Belgian razor-hone from Recht (also P_2O_5 , 0.16, S 0.18, organic matter 0.02; sp.gr. 3.22). VI, Whetstone from Cambrian slates at Lausenstein, Bavaria (also organic matter 1.56).

	I.	II	III	IV.	V.	VI
SiO ₂	99.50	99.49	76.99	72.00	46.52	40.81
ThO	—	—	—	—	1.17	—
Al ₂ O ₃	0.20	0.13	13.92	3.33	23.54	35.57
Fe ₂ O ₃	0.10	0.06	0.45	—	1.05	1.88
FeO	—	—	0.77	—	0.71	—
MnO	—	—	trace	—	17.54	trace
CaO	0.10	0.04	0.32	13.33	0.80	0.27
MgO	0.05	0.08	1.12	—	1.13	0.25
K ₂ O	0.10	0.10	3.65	—	2.69	10.63
Na ₂ O	0.15	0.10	0.60	—	0.30	1.72
H ₂ O	0.10	0.14	2.35	—	3.28	1.03
CO ₂	—	—	—	10.33	0.04	0.28
	100.20	100.20	100.13	98.99	99.13	100.00

The *novaculite** of Arkansas is one of the most important whetstones. It is found over a wide area in the vicinity of Hot Springs, occurring as bands a few inches to 15 ft. in thickness, interbedded with sandstones and shales of Lower Silurian age. It has a homogeneous, finely granular structure, and is white with a faint bluish tinge. It is brittle and breaks with a conchoidal fracture; sp.gr. 2.648 (Arkansas stone). Under the microscope it is seen to consist of an aggregate of quartz grains with an average diameter of less than 0.01 mm. The stone is rendered more or less porous by minute rhombohedral cavities, representing crystals of calcite or dolomite which have been dissolved out; and it is on the presence of these cavities that the cutting action partly depends. In the trade two varieties of Arkansas novaculite are distinguished: namely, the more compact 'Arkansas' stone in which the cavities form 0.17-0.25 p.c. of the bulk of the stone; and the more porous 'Ouachita' (or Washita) stone, in which the spaces amount to 5 p.c. The latter has the dull appearance of unglazed porcelain; it is the more abundant and obtainable in larger masses, and is also more in demand. The average of several analyses shows 99.50 p.c. SiO₂, of which 2.2-7.2 p.c. is soluble in a caustic potash solution, and 0.44-1.14 p.c. in a solution of potassium carbonate (L. S. Griswold, *Whetstones and the novaculites of Arkansas*, Ann. Rep. Geol. Survey Arkansas, for 1890, 1892, vol. iii.; W. C. Phalen, *Oilstones of Arkansas*, Min. Res. U.S. Geol. Survey, for 1911, 1912, 2, 843).

The Belgian razor-hones (anal. V) occur as

* This term is now often restricted to the Arkansas novaculite, although it was introduced by E. Kirwan in 1784, from the Latin *novacula*, a sharp knife or stone.

fine-grey slates or phyllites of Gedinien (Devonian) age, and are quarried at several places in the neighbourhood of Vielsalm and Salm-Château in the Ardennes. They are micaceous slates containing innumerable minute garnets (A. Renard, Mem. Acad. Belgique, 1878, 41). The German razor-hones from the neighbourhood of Ober-Ammergau in Upper Bavaria consist of a very compact, pale-coloured quartzose clayey limestone, and occur as beds in Jurassic limestones. They are very brittle with a splintery fracture, and are composed of CaCO₃, 83.57, FeCO₃, 2.67, clayey matter 7.63, quartz 5.96=99.85 (C. W. Gumbel, Geogn. Beschreib. Bayern, 1881, 1). The celebrated Turkey oilstone (anal. IV) is also calcareous, containing SiO₂, 70-75, CaCO₃, 20-25 p.c., with often a little alumina. It is obtained in the interior of Asia Minor and exported from Smyrna. Two varieties are distinguished, the white and the black, the latter being slightly the harder.

In England several stones of a more or less similar character are obtained at various places; e.g. the Charley Forest stone or Whittle Hill hornstone, which is a fine-grained, siliceous, slaty rock worked in Leicestershire. The Welsh oilstone is a somewhat similar material from near Llyn Idwal in North Wales. Devonshire oilstones are obtained from the metamorphosed slaty rocks in the neighbourhood of Tavistock. From Scotland come the Water-of-Ayr stone, snake stone, and Tam o' Shanter hones.

The coarser grained *scythe stones* are made of certain kinds of sandstone. Those from Pike in New Hampshire are the most celebrated, being exported to all parts of the world. This material is a fine grained, thinly laminated, micaceous sandstone (W. C. Phalen, *The scythe-stone industry in New Hampshire*, Min. Res. U.S. Geol. Survey, for 1909, 1911, 2, 616). Scythe-stones have been long worked near Blackdown in Devonshire, and are known as 'Devonshire batts.' They are made from siliceous concretions embedded in sand, probably of Upper Greensand age. Similar scythe-stones are also made at Penzlewood, near Stourton in Wiltshire.

In preparing whetstone for use, the blocks as quarry dressed are sawn into small rectangular slabs with a lapidary's disc charged with diamond powder, and then smoothed down on an iron plate charged with emery. Tools for special purposes, as used by dentists, engravers, watchmakers, jewellers, &c., are ground to the required shape.

Wheels made of Arkansas stone are used for fine metal grinding; and powdered whetstone is used as an abrasive material by instrument makers. See also ABRASIVES.

References.—On whetstones generally s. L. S. Griswold, l.c.; G. P. Merrill, *The Non-metallic Minerals*, 2nd ed., New York, 1910. L. J. S.

WHEWELLITE. Hydrated calcium oxalate CaC₂O₄·H₂O, crystallised in the monoclinic system.* It forms small, water-clear crystals which are often twinned in heart-shaped forms resembling those of calcite. There are perfect cleavages, and the material is very brittle; sp.gr. 2.46; H.=2½. The refractive indices and double refraction, $\alpha=1.4900$, $\beta=1.5532$,

$\gamma=1.6497$, $\gamma-\alpha=0.1597$, for sodium-light, are very nearly the same as those of calcite (viz. $\epsilon=1.4862$, $\omega=1.6585$, $\omega-\epsilon=0.1713$). The crystals could therefore be used for the construction of Nicol prisms for polarising apparatus if only they were found of sufficient size or if such could be produced artificially. The mineral is found in coal mines, but at only a few localities, namely, Burgk and Zwickau in Saxony, and Brüx and Schlan in Bohemia. It occurs, together with calcite, dolomite, barytes, &c., in small fissures in the shales and sometimes in the coal itself. Crystals have also been found in a metalliferous vein with tetrahedrite and ankerite at Urbeis in Alsace, and under similar conditions at Freiberg in Saxony. L. J. S.

WHISKEY. The term 'whiskey,' applied to the national beverage of Scotland and Ireland, only came into common use in the latter part of the eighteenth century, and is derived from the Celtic 'uisque-beatha' or 'usquebaugh,' meaning 'water of life,' no doubt in reference to its stimulating properties. A similar signification is seen in the terms applied to strong alcoholic liquors in other countries, as 'aqua vitæ,' and 'eau de vie.' Burns employs the three terms 'aqua vitæ,' 'usquebaugh,' and 'whiskey' synonymously.

The introduction of the manufacture of alcohol into Europe is, as the word suggests, due to the Arabs, but in the grape-growing countries of the south, the spirit is naturally produced chiefly from wine, and in the north, from different kinds of grain, the different materials used giving rise to the distinctive flavours characteristic of the spirits of different countries.

In Scotland the manufacture of whiskey was a subject for legislation as early as the sixteenth century, and extracts from the statutes show that 'aqua vitæ' was not the exclusive product of malted barley, but that unmalted grain was also used in the early days of spirit distillation in Scotland, and this has been the practice in Ireland up to the present day.

In 1805, during the Napoleonic wars, and owing no doubt to the possibility of a shortage in the supply of grain for food, the use of grain for the manufacture of spirits was prohibited throughout the United Kingdom.

In both Scotland and Ireland the pot-still was used prior to the invention of the patent continuous still by Aeneas Coffey in 1831, since when the patent still has been increasingly employed for the manufacture of spirit from a mixture of malt and unmalted grain, and known locally as 'whiskey.' About two-thirds of the potable spirit made in Scotland and Ireland at the present time is of this description. The spirit produced from other materials as molasses, rice, starch, potatoes, dates, currants, &c., is almost invariably distilled from a 'patent still,' and is used chiefly for industrial purposes. When *malt only* is used the whiskey is produced in Scotland chiefly, and in Ireland exclusively, from pot-stills. At the present time (1926) there are 9 distilleries in England; all of which are patent-stills only. In Scotland, out of 124 distilleries, 9 use patent-stills and 115 pot-stills only. In Northern Ireland, only 4 distilleries are at present working, and of these 2 use patent-stills and 2 pot-stills only. In the Irish

Free State, out of 14 distilleries, 2 use patent-stills, one both patent and pot-still, and the remainder pot-stills only. Of the latter, 10 are at present 'silent,' i.e. not working.

In 3 of the distilleries in England, 6 in Scotland, and 2 in Northern Ireland, yeast is manufactured on a large scale as a commercial product. In some instances, yeast is the principal product of manufacture—the spirit produced at these distilleries being really a 'by-product.'

The different characters of the various kinds of whiskey are due to the presence of small amounts of secondary products, sometimes referred to as 'impurities' or 'by-products' (as esters, higher alcohols, &c.), rarely exceeding in the aggregate one-half p.c. of the ethylic alcohol present, but sufficient to impart a distinctive flavour and aroma to the spirit.

These differences in character depend mainly upon (a) the kind and relative proportions of the materials used in the wash; (b) the methods of mashing and fermentation employed; and (c) the type of still used and the manner in which it is worked.

For the processes of mashing, fermentation, and distillation employed in the manufacture of ordinary alcohol, and for a description and diagram of Coffey's patent still, see article ALCOHOL.

This is known as 'silent' or neutral spirit, but grain spirit, distilled from patent stills, when intended for potable purposes, is not so highly rectified as to be deprived of its 'whiskey' character.

In the manufacture of pot-still whiskey in Scotland, barley-malt is practically the only material employed in the mash, whilst in the Irish pot-still distilleries the mash consists of a mixture of barley-malt with unmalted barley or other grain. The proportions vary with a view to securing particular flavours in the whiskey, but a typical mash consists of about four-fifths barley (malted and unmalted), and one-fifth of wheat, oats, and rye, the proportions decreasing in the order of enumeration. Maize is generally excluded from the pot-still whiskeys.

Besides the formation of sugar by the action of diastase during the mashing process, other substances, the exact nature of which is not thoroughly understood, are obtained in solution, from which the secondary constituents of the finished whiskey are both directly and indirectly derived. According to Bell (Select Committee of the House of Commons on British and Foreign Spirits, 1800-1) some of the essential oils naturally existing in the malt and grain, and the empyreumatic and creosotic bodies with which the malt becomes impregnated during the process of drying over peat, anthracite, or coke fires, pass through the operations in a more or less chemically unchanged condition, thus imparting distinctive characters to the whiskey, particularly when the ordinary pot-still is employed for the distillation.

Similarly during the process of fermentation, the conversion of the sugar into ethyl alcohol is accompanied by other chemical changes resulting in the formation of substances which also influence the flavour of the finished whiskey. Of these the principal are the higher alcohols,

WHISKEY.

which have been shown by Ehrlich and others to be due to the splitting up of certain nitrogenous substances (amino acids) produced by the peptonising action of the malt in the mashing process. The ultimate result is affected by the special nature of the yeast, the temperature at which it works, and the time occupied in fermentation.

The simplest form of pot-stills employed in Scotland are heated by direct fire, and have no special means of rectification. The long neck of the still, however, although originally designed simply to prevent particles of the boiling mash being mechanically carried over by frothing or spraying, incidentally has the further important practical use of effecting considerable rectification.

The pot-stills sometimes have their rectifying power increased by means of perforated plates placed transversely in the neck of the still, or by the use of 'purifiers,' pipes or circular vessels cooled by water and fitted between the neck of the still and the condenser.

Some stills are heated by means of steam-jackets or coils instead of direct fire, and this difference in the method of heating is said to have an important influence on the flavour of the whiskey. Certain empyreumatic bodies are thought to be generated by the open fire method, but according to Bell, Schidrowitz, and Thorpe, these are more probably derived from the peat or coke used for heating the malt kilns.

In the manufacture of Scotch whiskey, two distillations only are usually made, first from the 'wash still' from which the whole of the volatile constituents are collected as 'low wines'; and second, from the 'low-wines still,' the distillate from which is collected in three fractions, viz. (1) 'foreshots,' (2) clean spirit or 'whiskey,' and (3) 'feints.' The first and third fractions are added to the low wines of the next distilling period, and so on throughout the distilling season, the residue left in the wash still ('pot ale'), and that in the low-wines still ('spent lees') being run to waste.

The whiskey is generally run off at a strength of 11-25 overproof, but in the Lowlands, where a third distillation or 'rectification' is generally made, the strength of the whiskey distillate is from 40 to 54 overproof.

In Ireland the pot-stills are generally much larger than in Scotland, having sometimes a capacity of 20,000 gallons. The head of the still is shorter, and the still for low wines and feints is provided with a 'lyne arm,' or long pipe which passes through a tub of water, the liquid thus condensed between the head of the still and the worm being conveyed by a 'return pipe' to the body of the still. By this means a considerable degree of rectification is effected.

Three distillations are the rule for Irish pot-still whiskey, and the fractions are more numerous than in the manufacture of Scotch whiskey, consisting of strong low wines, weak low wines, strong feints, and weak feints. The middle or 'whiskey' fraction is also run off at a higher strength than in the Scotch process, viz. from 24 to 30 overproof.

The point at which the collection of foreshots is stopped and that of whiskey commenced, as well as that at which the running of whiskey ceases and the collection of feints begins, is determined by the judgment and

experience of the distiller, but various simple devices are employed for testing the distillate at different stages, as glass floats or hydrometers, specific gravity beads, and samplers for testing the distillate by dilution with water and observing whether the mixture is opalescent or clear.

Scotch whiskeys may be divided into the following five principal classes: (1) Highland malts; (2) Lowland malts; (3) Campbeltowns; (4) Islays; all made from malt in pot stills; and (5) grains, a name given to patent-still whiskeys. *Irish whiskeys* have no corresponding classification, all the 'self' or non-blended whiskeys being sold under distinctive names.

The secondary products, and therefore the character of the spirit, are considerably affected by the strength at which the whiskey is run off. Some of these products (especially esters) suffer partial decomposition in both the wash and low wines stills, whilst others, of higher boiling-point, remain in the stills and are run to waste with the pot ale and spirit lees. More than two-thirds of the secondary products are lost in this manner, only from 10 to 30 p.c. passing into the finished whiskey. (For the recovery and utilisation of the esters left in still residues, see art. RUM.)

It has not yet been found possible to trace any definite relationship between the commercial characteristics of various pot-still whiskeys and their composition as ascertained by analysis, for the reason that the secondary constituents are not individually identified by chemical analysis, but are assessed in groups consisting of members of the same family though in varying proportions, e.g. acids, aldehydes, esters, and higher alcohols.

There is some reason to believe, from the researches of Guareschi and Mosso (on behalf of the Italian Government), Vaughan of Michigan University, and Husz of Sweden, that other bodies may be present due to decomposition of albuminous matter in the grain and having alkaloid properties. They are alleged to be largely accountable for the deleterious effects of spirit drinking, but, if present, they occur in such minute quantities as to elude identification hitherto.

Husz attributed the unusually deleterious character of the spirits drunk in Sweden in a certain year to the use of unsound grain, and Lombroso has shown that an alkaloid having an action like strychnine is generated in decaying maize. Lauder Brunton, whilst attributing much of the harmful effects of new spirit to furfural, also supports the theory that these effects may be partly due to the presence in minute quantities of alkaloidal bodies, especially in potato spirit.

Schidrowitz has determined the percentage of nitrogen in new pot-still whiskeys with the results shown below, but failed to detect the least trace of substances giving alkaloidal reactions. The nitrogen is calculated as NH_3 , and expressed as grams per 100 litres of absolute alcohol—

Highland malts	0.09-0.12
Lowland malts	0.11-0.30
Campbeltowns (malt)	0.08-0.14
Grains	0.03-0.14
American rye whiskeys (matured)	0.25-0.30

No definite evidence was, however, obtained by the Royal Commission on Whiskey, &c., that the deleterious effects attributed to the consumption of spirits are directly due to the presence of poisonous secondary products, and the bulk of the medical evidence was to the effect that the actual amount of the secondary products is so small compared with that of the ethyl alcohol, that the physiological effects produced by them must also be extremely small in comparison with those due to the ethyl alcohol itself. It would appear to follow, therefore, that whiskey derived either from pot or patent still has much the same toxic effect if taken in the same quantity and at the same alcoholic strength.

At the same time, since many substances are known to produce marked effects on the digestive system merely as a result of the sensation produced by their *flavour*, this plays an important part from a dietetic point of view, and the more agreeable flavour of a mature whiskey may exert a favourable mental effect which promotes the

activity of the digestive processes, whilst the unpalatable flavour of new 'silent' or neutral spirits may tend to interfere with digestion apart from the direct effect due to the alcohol itself.

The methods usually employed for the estimation of the different groups of secondary constituents are given in detail in the Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, 1908-9, vol. ii. App. Q. xii. Thorpe; see also vol. i. App. F. Schidrowitz.

The following tables give the results of analyses of various kinds of whiskey by Schidrowitz, Tatlock, and Thorpe, expressed in all cases as parts by weight in 100,000 parts by volume of absolute alcohol (e.g. grams per 100 litres).

Schidrowitz and Kaye's results of analyses of 100 samples of the principal classes of *Scotch pot-still whiskey* are summarised in the following table, showing the minima, maxima, and averages—

No. of samples	Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Average total 'impurities'
39	Highland malts .	10-83	33-185	112-235	4-66	1-6-6.3	292
16	Lowland malts .	6-60	27-87	82-228	8-54	0-5.2	255
16	Campbeltowns .	12-100	53-140	160-259	11-85	2.4-8.0	335
5	Islays .	15-36	40-86	155-200	17-40	3.8-5.2	294
24	Grains .	3-69	20-55	33-80	trace-17	0-0.9	120
100	Average .	30.9	60.6	143	18.6	3.2	252

ANALYSES OF IRISH POT-STILL WHISKEY (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
A. New .	7	34	145	12	5.5	203
„ 13 years' plain wood .	29	38	185	68	3.3	323
B. New .	6	28	233	8	4.1	279
„ 13 years' plain wood .	32	47	264	21	4.4	368
C. 14 years' sherry .	87	87	226	32	4.5	436
D. Mature .	67	59	147	16	2.6	291
Average .	38	49	200	26	4.2	317

SCOTCH PATENT STILL WHISKEYS (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
New whiskey .	4	25	65	2	—	96
4 months' sherry wood .	24	26	31	4	0.07	85
2 years' plain wood .	14	25	100	5	trace	144
2 years' sherry wood .	58	40	44	7	0.15	149
Average .	25	29	60	4.5	0.05	118.5

WHISKEY.

IRISH PATENT STILL WHISKEYS (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
Distillery A—new	17	25	38	—	—	80
" " 2 years	21	41	50	—	trace	112
" " 2 years	10	24	48	3	trace	85
Distillery B—new	3	19	52	—	—	74
" " 1½ years	9	25	46	1	trace	81
Distillery C—new	—	33	50	11	—	94
Average	10	28	47	2.6	trace	87.6

The following analyses by Tatlock show the maxima, minima, and averages obtained from 75 samples of Scotch and Irish malt-pot-still whiskeys, grain patent still, American, and blended whiskeys—

	High-lands, 31 samples	Low-lands, 9 samples	Islays, 4 samples	Campbell-towns, 2 samples	Irish, 2 samples	American, 4 samples	Grains, 7 samples	Blends, 16 samples
Esters—								
Maximum	154.16	85.80	78.05	85.62	44.22	119.52	50.90	92.05
Minimum	45.01	34.52	48.31	61.42	38.42	111.06	22.04	33.56
True average	83.06	66.19	61.51	73.52	41.32	115.99	33.26	58.96
Higher alcohols								
Maximum	190.40	240.66	161.70	206.70	169.10	177.34	68.47	111.25
Minimum	73.51	103.49	130.20	139.58	154.93	102.55	32.47	48.71
True average	144.61	140.40	144.55	173.14	162.01	156.99	45.32	80.76
Volatile acids								
Maximum	89.06	39.86	32.41	56.35	49.23	132.11	32.93	100.13
Minimum	21.76	4.70	17.11	31.16	4.55	65.24	2.86	13.12
True average	41.78	17.35	25.86	43.75	26.89	99.43	16.67	40.61
Aldehydes—								
Maximum	35.06	33.59	31.74	33.54	21.12	32.85	12.95	26.00
Minimum	3.21	4.70	19.82	32.45	4.34	17.01	1.59	1.26
True average	19.48	20.42	28.40	32.99	12.73	26.53	7.66	9.29
Furfural—								
Maximum	7.34	5.85	6.29	3.77	3.02	3.86	0.50	3.17
Minimum	1.58	2.65	3.25	3.23	2.73	1.95	0.10	0.43
True average	4.18	4.39	5.02	3.50	2.87	3.00	0.25	1.63
Total secondary products—								
Maximum	382.35	314.81	294.09	385.98	269.62	452.92	130.38	267.64
Minimum	218.94	218.52	225.94	267.84	222.04	328.76	68.04	106.22
True average	294.41	282.03	265.37	326.91	245.83	396.80	102.08	191.23

The results of analysis of 7 samples of high-class whiskeys as supplied by Government contractors for hospital use are given in the following table (Thorpe):—

Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
7 years	28.2	9.6	90.0	175.5	2.7	306.0
" "	28.2	9.6	87.9	175.5	2.7	303.9
" "	28.2	9.6	90.0	175.5	2.7	306.0
10 years	24.3	12.1	92.1	877.1	3.5	1009.1
" "	31.5	9.8	93.0	300.0	3.3	437.6
" "	32.0	0.8	114.0	456.1	3.3	616.1
" "	41.0	12.1	124.5	578.9	3.1	759.6
Average	30.6	10.4	98.8	391.2	3.0	534.0

Results of analyses of 5 samples of spirits made in Germany and sold as cheap whiskey in Hong Kong are given on p. 466.

Samples A and B consisted of 'silent' spirit, with an admixture of pot-still whiskey for the purpose of imparting the genuine flavour of whiskey. They are very similar to what is usually sold as 'whiskey' in public houses in England. Samples C, D, and E consisted of highly rectified 'silent' spirit coloured and flavoured to imitate whiskey. The fusel and impurities were much less than is usually found in genuine Scotch and Irish pot-still whiskeys of high commercial quality, while furfural and other aldehydes were practically absent, and there was no evidence that the spirits contained anything of a deleterious nature apart from the alcohol itself.

'Pot-still' and 'patent-still' spirits (The Royal Comm. on Whiskey and other Pot-still Spirits, App. Q. vi., vii., viii.). "An examination

Secondary products	A	B	C	D	E	Average
Volatile acidity (as acetic acid)	50.7	63.7	10.5	14.0	7.0	29.2
Furfural	1.5	1.2	Nil	Nil	Trace	0.5
Aldehydes (as acetic aldehyde)	1.8	2.1	Trace	Trace	Trace	0.8
Esters (as acetic ester)	87.5	109.5	15.0	7.8	3.6	44.7
Higher alcohols	225.7	205.4	20.4	22.6	33.2	101.4
Total secondary constituents	367.2	381.9	45.9	44.4	43.8	176.6

of the following tables, giving the results of the analyses of a number of representative samples of both kinds of spirits, shows very

clearly the broad distinction between the 'pot-still' and 'patent-still' spirit.

There is always a much larger amount of the

SPIRITS FROM POT STILL DISTILLERIES (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New	16.9	9.2	77.4	407.2	2.9	513.6	Speyside.
2	6 years	52.2	19.6	93.9	472.1	1.9	639.7	"
3	New	13.2	5.4	63.2	471.4	2.9	555.1	Banffshire.
4	7 years	53.6	32.2	91.0	371.4	1.9	550.1	"
5	New	9.8	9.8	63.1	490.0	2.8	575.5	"
6	"	15.0	21.8	63.8	451.6	4.2	556.4	"
7	7 years	30.1	41.6	92.0	490.5	3.6	627.8	Islay.
8	"	46.0	43.2	99.0	563.2	3.6	755.0	"
9	New	17.0	33.6	72.9	410.9	3.5	537.9	"
10	4 years	37.5	34.8	81.4	453.0	3.3	610.0	Campbeltown
11	10 years	47.3	10.0	98.8	322.8	5.7	484.6	Highland.
12	New	3.3	50.2	102.8	522.6	3.1	682.0	Irish.
13	6 years	32.6	55.9	86.4	771.2	2.9	949.0	"
14	New	1.7	26.3	73.7	861.4	2.2	965.3	"
15	"	1.7	8.7	73.0	729.8	0.1	813.3	"
16	8 years	17.5	10.5	30.0	894.7	3.1	955.8	"
17	New	4.2	7.0	13.6	701.7	1.1	727.6	"
18	6 years	21.0	12.2	35.0	789.0	1.4	858.6	Irish.
19	New	1.4	4.6	75.9	336.9	Nil	418.8	"
20	1 year	5.2	7.0	106.6	571.9	"	690.7	"
21	New	1.4	11.5	46.1	857.9	8.5	925.4	"
Average		20.4	21.7	73.3	567.3	2.8	685.3	

PATENT STILL GRAIN SPIRITS (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New	1.9	9.6	30.8	39.0	Nil	81.3	Scotch Distillery
2	7 years	19.0	10.8	35.0	21.8	0.1	86.7	"
3	"	36.9	12.0	47.9	21.1	0.3	117.2	"
4	New	1.9	4.7	41.1	97.8	Nil	145.5	"
5	4 1/2 years	15.6	14.1	46.4	81.3	"	157.4	"
6	New	3.8	trace	22.8	14.0	"	40.6	"
7	3 months	5.2	"	45.6	42.0	"	92.8	"
8	New	3.5	"	12.2	28.0	"	43.7	"
9	7 years	40.0	3.3	22.8	57.8	0.3	124.2	Irish Distillery.
Average		14.2	6.1	33.8	44.6	0.1	98.8	

PATENT STILL SPIRITS OF HIGH STRENGTH (Thorpe).

Description	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
British spirit from molasses . . .	1.2	35.1	62.5	84.0	Nil	182.8
British spirit from grain, highly rectified . . .	1.2	trace	11.1	21.2		33.5
British spirit from molasses, highly rectified . . .	1.2	3.5	7.3	63.0		75.0
British spirit crude, from molasses .	2.5	97.3	187.7	20.9		308.4
Foreign spirit imported from Hamburg . . .	1.2	Nil	5.5	10.4		17.1
Foreign spirit imported from Hamburg . . .	1.2	Nil	9.1	20.9		31.2
Foreign spirit imported from Stettin . . .	1.2	2.2	7.2	83.7		94.3
Average	1.4	19.7	41.5	43.4		106.0

secondary constituents in the 'pot-still' spirit. Speaking generally, the percentage of every one of the secondary constituents usually determined is greater in the 'pot' than in the 'patent' spirit, but the most marked differences are in the 'higher alcohols' and 'furfural.' 'Patent' spirit contains no furfural when new, although after storage in wooden casks it is sometimes found to contain traces of this substance, but always in much smaller amount than in 'pot still' spirit, in which it is never absent. The low percentage of the 'higher alcohols,' and the absence of all but mere traces of furfural render it a comparatively easy matter to distinguish 'patent' from 'pot-still' spirit. But the variations in the amounts of the secondary constituents in both classes of spirits renders it less easy to estimate the exact proportion of each kind of spirit present in mixtures. Comparing the 'pot-still' spirits among themselves it will be observed that there are considerable variations in both the total amount and in each constituent of the secondary bodies. The Scotch whiskeys generally show a somewhat less total amount than the Irish, and the Speyside, Banffshire, and Highland samples have a rather smaller amount than the Islay and Campbeltown samples. The latter, as well as most of the Irish samples, are mainly 'blending' as distinguished from 'self' whiskeys.

The differences between new and old 'pot still' whiskeys, so far as shown by analysis, are mainly in the increased amounts of the volatile acids and aldehydes, and to a less extent of the esters found in the old spirit when stored in wooden casks. The higher alcohols and furfural appear to remain very much the same. Any changes that occur in 'patent' spirit are of a similar kind.

'Pot-still' whiskey is almost always stored in sherry casks, or in other well-seasoned wooden casks that have formerly contained similar spirit. A large proportion of the increase in the secondary constituents which occur in spirit stored in such casks takes place in the first few months, and is due to a process of extraction of these products absorbed in the wood of the casks from former spirits. This

absorption is to some extent selective. The ethyl alcohol slowly diffuses through the wood of the cask and passes into the air, leaving some of the esters and higher alcohols behind in the wood, which thus becomes more or less charged with the secondary constituents, according to the length of time and other circumstances attending the storage of spirit in the warehouse.

Probably also, especially when the casks are empty, there is some production of acids, aldehydes, and esters by the slow oxidation of alcohols in the wood of the casks.

A comparison of the ordinary 'patent' spirits with British and foreign spirits of high strength which are not usually stored in wooden casks, but in metal drums or vats, shows that the latter spirits contain still less of the secondary constituents, and that the slight changes which occur in ordinary patent spirits do not take place in these high strength spirits. These spirits are used mainly for technical and industrial purposes, and are often of very great purity, although made from molasses, potatoes, and beetroot sugar residues, or other materials not employed for making spirits intended for consumption in this country.

Maturation or ageing.—In addition to the changes above referred to in the secondary constituents due to storing in casks, there are other changes due to the presence of substances not included in the ordinary analysis of spirits, but which have much to do with the difference in flavour of new and old whiskeys. Thorpe, for example, found indications of pyridine bases, allyl alcohol, and allyl aldehyde derived from the peat used as fuel in malting, and acrolein, due either to the fat in the wash extracted from the grain or possibly from the soap which is occasionally added to the contents of the still to prevent frothing. Schidrowitz found in new pot-still whiskey distinct evidence of the presence of pyrrole, phenolic bodies, an alkaline substance (probably an ammonium salt), sulphuretted hydrogen, sulphurous acid, and a trace of nitriles. All of these are readily changed on exposure to air and moisture, as in storage in casks. The pyrrole probably resinifies, the phenols interact with aldehydes, acids, and

Description	Total acid	Esters	Alde- hydes	Furfural	Higher alcohols (A-M)	Total
New rye whiskeys (19 samples)—						
Average	11.4	50.6	17.8	2.4	266.4	348.6
Maximum	28.2	132.8	86.0	5.2	378.4	
Minimum	2.6	8.8	0.0	0.0	187.0	
Old rye whiskeys (76 samples)—						
Average	147.6	137.0	27.6	4.6	352.0	661.8
Maximum	312.4	287.4	47.2	14.0	585.8	
Minimum	72.8	60.0	4.4	0.8	146.6	
New Bourbon whiskeys (18 samples)—						
Average	16.4	45.0	7.8	1.7	229.4	300.3
Maximum	39.2	112.8	36.2	12.8	343.4	
Minimum	3.6	1.8	0.0	trace	70.6	
Old Bourbon whiskeys (75 samples)—						
Average	137.6	103.6	19.4	3.8	287.2	551.6
Maximum	203.8	209.0	46.4	16.2	517.0	
Minimum	69.4	39.0	7.2	1.4	50.4	

Adulteration of whiskey.—Under Sect. 10 of the Licensing Act, 1921, whiskey (like brandy and rum) may not be sold below a strength of 35 p.c. under proof unless the fact of dilution is notified, and the great majority of prosecutions under the Act for the adulteration of whiskey are on account of dilution with water below the legal limit of strength. For the method of calculating the degree of dilution, see art. BRANDY.

Sometimes a neutral or 'silent' spirit made from substances other than grain (as potatoes, beet-sugar residues, &c.) is mixed with sufficient genuine whiskey to give it a more or less whiskey character, and such adulteration is best detected by expert tasting ('degustation') combined with a determination of the secondary constituents and a comparison of the relations which they bear to each other.

Amongst the various substances alleged to have been used for the grosser forms of adulteration may be mentioned creosote, fusel oil,

methylated spirit, sulphuric acid, and salt. Traces of copper, tin, and lead have been found as accidental impurities derived from the still and other apparatus employed.

In consequence of representations made as to the deleterious character of the whiskey sold in public-houses in the poorer class districts of the larger towns in England, Scotland, and Ireland, and at fairs and markets, particularly in the west of Ireland, an investigation into the matter was made some years ago by the Excise Authorities. Nearly 100 samples were taken from all parts of the United Kingdom and analysed in the Government Laboratory, but, apart from the fact that most of these consisted mainly of plain patent-still spirit, no evidence of the presence of the deleterious adulterants above referred to could be found.

The results of analyses (showing the maxima, minima, and averages) are summarised in the following table (Thorpe):—

	Volatile acid	Alde- hydes	Esters	Higher alcohols	Furfural	Total
England (38 samples)—						
Maximum	25.1	22.5	127.9	310.5	1.9	370.7
Minimum	1.4	2.2	30.1	11.2	Nil	67.0
Average	7.3	9.0	52.2	95.8	0.7	165.0
Scotland (23 samples)—						
Maximum	18.0	23.8	85.7	179.6	1.6	260.6
Minimum	1.2	1.7	30.8	43.7	Nil	77.8
Average	6.1	10.5	47.2	88.2	0.5	152.5
Ireland (30 samples)—						
Maximum	54.6	37.2	71.5	649.2	4.2	767.3
Minimum	1.4	2.4	29.5	32.2	Nil	73.3
Average	8.2	11.1	47.8	232.0	1.2	300.3

There is no legal definition of 'whiskey' in the United Kingdom, but numerous suggestions were made by witnesses before the Select Committee on British and Foreign Spirits in 1890-1, and the Royal Commission on Whiskey and other Potable Spirits in 1908-9, differing

essentially in principle and depending chiefly upon the point of view of the witness.

The strictest definition suggested was that 'whiskey' should be manufactured in a pot still exclusively and from certain prescribed materials grown in the country, as malted barley alone in

the case of 'Scotch' whiskey, and malted barley with unmalted grain (barley, wheat, oats, or rye) in the case of 'Irish' whiskey.

Others would admit patent-still spirit, restricting, however, the materials to cereal grains (including maize), and the saccharifying agent to the diastase of malt, whilst in a few cases the extreme view was held that no restriction should be imposed either on the materials used or the process of distillation.

Since much of the barley used in both Scotland and Ireland is of *foreign* growth, the definition of Scotch and Irish whiskey cannot well exclude the use of foreign grain, and therefore maize (which came into use in 1846 immediately after the repeal of the Corn Laws) is not excluded in the manufacture of 'whiskey.'

With respect to the blending of patent-still spirit made from grain with pot-still spirit, it was held that since whiskey (consisting as it does of alcohol and water, with certain by-products derived from malt and grain) does not cease to be whiskey when diluted with water, so the addition of patent still spirit, also made from grain, does not remove the mixture out of the category of 'whiskey.'

After full consideration of all the evidence the Royal Commission of 1908-9 arrived at the following conclusions and definitions —

(1) That the term 'whisky' having been recognised in the past as applicable to a potable spirit manufactured from (a) malt, or (b) malted and unmalted barley or other cereals, the application of the term 'whiskey' should not be denied to the product manufactured from such materials.

(2) That no restrictions should be placed upon the processes of, or apparatus used in, the distillation of any spirit to which the term 'whiskey' may be applied as a trade description.

(3) *Definition* — 'Whiskey' is a spirit obtained by distillation from a mash of cereal grains saccharified by the diastase of malt, that 'Scotch whiskey' is whiskey, as above defined,

distilled in Scotland; and 'Irish whiskey' is whiskey, as above defined, distilled in Ireland.
J. C.

WHITE ANTIMONY. *Valentinite v. ANTIMONY.*

WHITE ARSENIC. *Arsenious oxide v. ARSENIC.*

WHITE COPPERAS. *Native ferric sulphate or coquimbite $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.*

WHITE IRON PYRITES. *Ferric sulphide or marcasite FeS_2 , v. IRON.*

WHITE LEAD v. LEAD; also PAINTS and PIGMENTS.

WHITE LEAD ORE v. CERUSSITE

WHITE METAL v. TIN.

WHITE MUNDIC. *Mispickel v. ARSENIC.*

WHITE PRECIPITATE. *Mercuric ammonium chloride v. MERCURY.*

WHITE SAPPHIRE v. CORUNDUM.

WHITE VITRIOL. *Zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ v. ZINC.*

WHITING v. CHALK.

WILKITE A rare mineral consisting of tantalate and titanate acids, zirconia, silica, cerium, and yttrium earths, thoria, uranic oxide, ferrous oxide, &c., and of interest in containing scandium (Sc_2O_3 , 1.17 p.c.) in relatively large amount. It is a black, brown, or yellow, amorphous mineral resembling euxenite or yttrioantalite in appearance, and has been found, together with monazite, in a feldspar quarry at Impilala, Lake Lagoda, Finland. It supplied the material for Crookes's work on scandium (Proc. Roy. Soc. 1904, A, 80, 516, Phil. Trans. 1908, A, 209, 15). Orthite from the same locality has also been found to contain 0.8-1.0 p.c. of scandia (R. J. Heyen, Sitz. Ber. Akad. Berlin, 1911, 379). More recently, a mineral containing scandium as an essential constituent has been described (v. THORVALLITE). L. J. S.

WILD RICE. A comparison between wild rice (*Zizania aquatica*) and cultivated rice gave the following analyses for wild rice —

No.	Moisture. p.c.	Ash. p.c.	Protein. p.c.	Ether Extract. p.c.	Fibre. p.c.	Starch p.c.	Soluble carbohydrates as dextrose. p.c.
1	7.74	1.09	13.36	0.46	1.39	65.26	2.08
2	7.85	1.38	13.97	0.89	1.41	61.60	3.69
3	8.93	1.17	14.62	0.72	1.94	60.47	2.33
4	7.83	1.25	14.40	0.66	1.29	62.03	2.93

Although these results show a high proportion of proteins in wild rice, both these and the mineral salts present are of a variety unsuitable for dietetic purposes. There is just sufficient vitamin A to prevent xerophthalmia, but not enough to promote growth. Wild rice is somewhat superior to the cultivated variety as regards its content of vitamin B, but still is not an adequate food (C. Kennedy, J. Agric. Res. 1924, 27, 219; Analyst, 1924, 49, 342).

WILKITE v. THAUMASITE.

WILKITE. A mineral consisting of zinc orthosilicate Zn_2SiO_4 , crystallising in the rhombohedral system (with parallel-faced hemihedria). It is abundant at Franklin Furnace,

and Sterling Hill in New Jersey, where it is mined, together with zincite and franklinite, as an ore of zinc (Zn 55.5 p.c.). Here it is usually massive, but a few clear prismatic crystals of a pale amber-yellow colour, and up to 6½ cm. in length, have been found. Some of these have been cut as gem stones. Portions of the better coloured or clearer massive material is also suitable for cutting as gems. The mineral has also been found at a few other localities, but only in sparing amounts. It varies considerably in colour, being yellowish, apple-green, flesh-red, &c.; the lustre is vitreous to resinous; sp. gr. 4.0-4.1; H. 5½. *Troostite* is a variety containing up to 10 p.c. of MnO replacing the zinc.

oxide, and found as large rough crystals at Franklin Furnace. When struck with a hammer or when exposed to the emanations of a radium salt, the mineral displays a brilliant green phosphorescence. Crystals of willemite have been obtained artificially, and have also been observed in slags and in the muffles of zinc furnaces.

L. J. S.

WILLESSEN FABRICS AND PAPER v. CELLULOSE.

WILLOW BARKS v. TANNINS.

WILLYAMITE v. ULLMANNITE.

WINE. Wine, strictly speaking, is the fermented juice of the fruit of *Vitis vinifera*. The term *British wines* is applied to beverages made after the manner of wine from substances other than the juice of fresh grapes.

The vine is cultivated for the manufacture of wine in the middle and south of Europe, the northern and southern extremities of Africa, some of the western parts of Asia, the islands of the Atlantic, portions of America—from the Potomac in the north to the centre of Mexico in the south—in California, and in Australia. The number of varieties is very large; but experience shows that the vines employed in particular districts should either be indigenous to those districts or be improved varieties of the indigenous strain. Thus, European vines when tried in America were but partially successful; whilst, on the other hand, American vines transplanted to the Gironde degenerated and yielded no potable wine. The vine grows on chalky, silicious, aluminous, and magnesian soil, best along the borders of rivers, and on ground which, though not itself soaked with water, can constantly attract it from the subsoil.

Vintage and vinification.—The methods of procedure vary with the character of the wine—i.e. whether white or red wine is to be produced. The practice as regards the period of ripeness at which the grape is gathered varies considerably; thus, in the case of champagne, where the greatest attainable paleness is desired, the grapes are gathered before the point of fullest maturity, whereas the wines of Burgundy are vintaged when the grapes produce the deepest colour. Wines from imperfectly-ripened grapes require longer time to mature after manufacture, and, theoretically speaking, the grapes should hang until excessive dryness or danger of frost threatens; but other and conventional considerations, such as colour, have to be taken into account. In exceptional instances, as in the Sauterne district, those berries only are cut out of the bunch which have attained the desired point of ripeness; but the common practice is to gather all the grapes carried by the vines, the vintagers either separating immature and spoiled berries as they proceed, or carrying the whole bulk to a kind of specialist, who performs this part of the labour. Whichever course may be taken, the selected fruit is carried to the press house, and the question then arises whether the stalks are to be removed or pressed with the grapes. In the case of white wines the almost universal practice is to leave the grapes upon the stalks, for the reason that the resulting liquor is almost at once separated from the marc, and before the astringent principle of the stalks can be communicated to it, whereas red wines must be allowed to remain upon

the marc for some time, and the stalks are removed. The commonest mode of separation is to cause the grapes to pass through a series of sieves, by which the stalks are retained. The grapes are now crushed, either by being trodden underfoot in vats or by being passed through machines furnished with grooved rollers, the one thing to be avoided in either case being the bruising of the seeds and stalks if these have not been removed. The next process is pressing. The machines employed for this purpose were formerly boxes, so made that the must was expelled through apertures by superincumbent pressure exerted by a screw; but latterly centrifugal machines have been employed, with a saving of labour and time. In white wines the must is separated as much as possible from the marc before pressing; whilst in the preparation of champagne the grapes are not crushed at all previous to being placed in the press. In pressing grapes for the manufacture of champagne the pressure is so regulated that the juice is separated into four fractions; generally, 4000 kg. of grapes yield a first fraction (cuvée) of 20 hectolitres of juice, second and third fractions of 3 hl. each, and a fourth fraction of 2 hl. The first fraction is the most valuable and yields a wine containing a relatively higher quantity of total acids and free acids (tartaric and malic acids); the presence of these acids increases the resistance of the wine to 'sickness' and to the action of bacteria. The keeping qualities of the wine are also due to the fact that only very small quantities of nitrogenous substances, phosphates, and potassium salts are present. The other fractions of the juice are less valuable, and the wines prepared from them are more readily attacked by micro-organisms (E. Manceau, Ann. Falsif. 1923, 16, 517; J. Soc. Chem. Ind. 1924, 43, B. 227). According to L. Mathieu (Chimie et Industrie, 1923, 10, 847), white wines are liable to the same causes of turbidity as red wines, but the effect is more marked, as a slight haze, imperceptible in a coloured wine, completely destroys the limpidity of the colourless wine. The author classifies turbidity—under which heading he includes all degrees of haze, from the pale bluish fluorescence due to the most minute particles, to actual cloudiness with visible particles—under two headings: (1) normal, i.e. arising in the actual constitution of the wine, such as bacterial infection, cloudiness caused by chilling or heating, or by oxidation of resinous substances or the mutual interaction of the constituents of the wine, and (2) accidental, i.e. caused by some irregularity or oversight in the manufacture or manipulation. As in the case of other wines, one of the most fruitful causes of trouble is the presence of iron in more than insignificant traces. This may arise from the use of unprotected iron vessels. The rigid exclusion of iron vessels, unless the metal be protected in some way from the attack of the acids of the fruit, is essential (J. Inst. Brewing. Abstr. 1924, 30, 234). In the case of red wines the colour is obtained by allowing the juice from the crushing to ferment, after which it is stirred with the grape husks, whereby the requisite amount of colouring matter is dissolved. So much of the must as can be drawn off by this means is run off by that means, and the marc is pressed

the two portions of the must are then added together. The proportion of must depends upon whether the stalks are removed or not; in the former case it is about 95–97 p.c. of the whole, in the latter it may only be 70 p.c.

The following is a summary of analyses by König of a large number of musts of different origin:—

	Specific gravity	Water	Nitro- genous p.c. matter	Sugar	Acid	Other non-nitro- genous matter	Ash
Minimum	1.0690	51.33	0.11	12.89	0.20	1.08	0.20
Maximum	1.2075	82.10	0.57	35.45	1.18	11.62	0.03
Average	1.1024	74.49	0.28	19.71	0.64	4.48	0.40

Fermentation.—The natural fermentation of grape juice is due to the action of various yeasts (*Saccharomyces Ellipsoideus*, *S. Pastorianus*, *S. Marzianus*, &c.) existing on the skin of the grape, and to 'Zymase' and other enzymes present in the juice. Sergent and Rougebief (Compt. rend. 1924, 178, 732; J. Soc. Chem. Ind. 1924, 43, B. 207) have drawn attention to the dissemination of grape yeasts by insects. They concluded from their experiments that certain insects, particularly *Drosophyla*, play an important part in spreading the yeast. White wines are generally fermented at a temperature of 10° or 12° in barrels with only the bung-hole open for the escape of carbon dioxide. Red wines are generally fermented in vats open at the top, on account of the bulk caused by the retention of the husks and the necessity of stirring, an operation variously performed during or at the completed period of fermentation, according to the district. The higher the temperature the sooner the fermentation is finished; at low temperatures a moderate fermentation takes place, which becomes more violent as the liquid becomes warmer, and reaches a maximum at 27°. By the employment of high temperatures a must rich in sugar can be converted into a wine feebly alcoholic, sweet, and yet having tasting properties. Medium musts are best fermented at from 20° to 24°, and this temperature is reached when the fermentation begins at 15°. When fermentation is completed—i.e. after 10 to 14 days—the liquor has become clear, the yeast cells and other suspended matters are deposited at the bottom of the vessel, and the 'young' wine is racked off and allowed to rest for some weeks.

The young wine slowly loses its sugar by after-fermentation, and albuminous substances, colouring matters, together with the acid potassium tartrate, and calcium tartrate, separate out, forming a crust known as *argol* or *argal* (q.v.; also TARTARIC ACID). It is then racked again into clean casks (which are often 'sulphured' before use), fined, if necessary, with isinglass or white of egg, and occasionally with dried blood or with potassium ferrocyanide. When clear it is racked again and sometimes pasteurised before being bottled or stored in casks to mature.

Influence of the 'marc' on wine.—By allowing the skins and stones of ripe grapes to remain in contact with the must, the resulting wine is said to improve in bouquet, &c., and is less liable to become stale and ropy. In order to redden wine with the skins of black grapes the temperature of the wine should be between 15° and 17°. Bad grapes impart to white and red wines a brown colour. Such wines soon become

turbid. Bad grapes and mildewed skins, as well as bad casks and puncheons, precipitate the red colouring matter, so that the wine becomes pale. The following are some of the cases in which the treatment of wine with 'marc' has been successful: Wine which is muddy and cannot be clarified by the ordinary fining agents; wine in which a fining agent has been used which failed to sink to the bottom; wine which has become weak and flat; wine which is assuming or has assumed a black colour; wine having a barrel taste or a by-taste; wine which is 'corked'; wine remaining after casking off; and wine which is obtained by pressing the lees. In cases where the fermentation of new wine has been checked suddenly, the addition of marc prevents the separation of yeast (J. Nessler, Chem. Zentr. 1882, 265; Chem. Soc. Abstr. 1882, 1014). Wines from pressed marc have a greater content of extract, tannin, ash, total and ammoniacal nitrogen, phosphoric acid, sulphate, and chloride than wines from the vat (Hugues, Ann. Falsif. 1925, 18, 347; J. Soc. Chem. Ind. 1925, 44, B. 936).

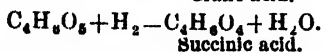
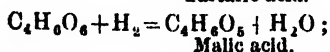
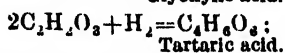
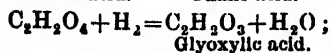
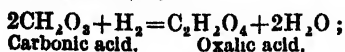
Composition.—Wine contains alcohol, glycerol, acids, salts, extractive matter, and those principles which give to it its particular colour, special flavour, smell, or bloom (*bouquet*, *Blume*). Whilst some of the constituents can be accurately isolated and described, others can only be detected by the smell.

The principal alcohol is ethyl alcohol. In rare instances some butyl alcohol, and in others amyl alcohol, together with ethylene glycol and isobutyl glycol (Henniger) are present. The quantity of alcohol in natural wines from grapes varies from 6 to 12 p.c. by weight, or from 13 to 26 p.c. proof spirit, but these limits are extended in exceptional cases. The quantity of glycerol is usually from 7 to 14 p.c. of the alcohol present.

The principal acids present are tartaric, malic, and tannic acids, due to the original grape juice, and carbonic, formic, acetic, and succinic acids as products of fermentation. These greatly aid in the preservation of the wine by preventing the formation of fungi. Traces of propionic, butyric, and cenanthic acids also occur in wine, together with acetaldehyde and possibly some of its homologues. Salicylic and boric acids have also been found as natural constituents of wine. As regards the origin of the fixed vegetable acids of wine, H. Brunner points out (Chem. Zentr. 1877, 4) that malic, succinic, glycollic, and oxalic acids—which are found in unripe grapes, together with tartaric acid—may either be formed by direct building up of the molecules in the plant, or their formation may be partly direct and partly indirect.

Tartaric acid occurs mainly as the dextro-variety; lævo-tartaric acid is only of comparatively infrequent occurrence. If tartaric acid is not found—as, for example, in certain samples of sherry—its absence is probably due to its removal by 'plastering,' to which reference is made later on. The amount of free acid in sound wine, reckoned as tartaric acid, varies between 0.3 and 0.7 p.c. (inclusive of volatile acid, which should not exceed 0.15 p.c.); a greater amount than this imparts sourness to the wine.

It can be demonstrated in the laboratory that the first reduction products of carbonic acid are formic and oxalic acids, and that, from the latter, we can (by the action of hydrogen) pass successively through glyoxylic, tartaric, and malic, to succinic acid, and all these acids have been found in the grape in its various stages of growth. The principal reactions may be represented as follows:—



The characteristic smell of wine is said to be due to cenanthnic and other esters. These esters probably confer the bouquets which distinguish one vintage from another. Among them are acetopropyl, butyl, amyl, capryl, butyro-ethyl, caprylo-ethyl, capro-ethyl, and pelargo-ethyl, and the tartaric esters.

According to Jacquemin (Compt. rend. 110, 1140), the characteristic bouquets of wines are due to the special characters of the yeast used in each district. One and the same must fermented with the yeast obtained from several different districts gave wines having the bouquet characteristic of the district from which the particular yeast had come.

Babo states that the bouquet of the wine from Riesling grapes is produced by the action of frost; wines from other grapes also possess a like bouquet if the grapes are frozen. Rommer (Bull. Soc. chim. [in.] 2, 297) fermented the juice of an inferior grape and of hot-house grapes respectively with yeast cultures obtained from the Champagne, Côte d'Or, and Baxy districts, and found that in each case the wines had the bouquet of those from which the yeast has been derived. Certain of the odoriferous principles are no doubt in the nature of essential oils, which have not hitherto been isolated owing to their small amount and extremely unstable character under the influence of heat and air. In order to retain the bouquet, wines should be bottled as soon as they have attained their maximum bouquet.

According to Berthelot, the amount of the esters in wine is, after a certain time, a constant quantity independent of the nature of the alcohols and acids, but a function only of their relative amount: If A be the percentage weight of alcohol in the mixture, a the amount of alcohol equivalent to the total free acid contained in one litre of wine, on the assumption that it is acetic acid (46 alcohol = 60 acetic acid), y the proportion p.c. of a present as ester in one litre of wine when the alcoholic strength of the wine is A , and x be the amount of alcohol present in the compound ethers of one litre of wine; then

$$y = 1.17A + 2.8$$

$$x = \frac{y \times a}{100}$$

The alcohols other than ethyl alcohol present

are left out of the account, but as they are insignificant in amount the error is trifling. This formula affords a mode of judging of the age and genuineness of wines, except in the case of very young wines, or wines which have been recently fortified, the esters in these cases being less than that required by the formula. The maximum esterification is reached in from 4 to 6 years. The alcohol obtained by the decomposition of all the esters rarely exceeds 0.06 p.c. of the wine. (For Thudichum and Dupré's method, *v. their Treatise on Wine*, 203.)

Sugar in wine.—The sugars occurring in must and in wine are dextrose and levulose. Cane sugar is never naturally present in must, but it is sometimes added, as in the case of champagne, but even then it is rapidly transformed into invert sugar. Glycerol is formed as a by-product of the growth of yeast during the process of fermentation, and is accompanied (amongst other changes) by the decomposition of sugar. For every 100 parts of sugar which disappear, from 3 to 4 parts of glycerol are produced. After complete fermentation the sugar seldom reaches 0.5 p.c., but when fermentation is arrested by the addition of alcohol, as in the liqueur wines of France and Spain made from dried grapes, and the sweet wines of Hungary, the sugar may be as much as 20 p.c. or more. In some wines—as *e.g.* Sauternes and sweet Rhine wines—sugar occurs in the form of inositol.

The colouring matters in wine are due to two sources. In white wines—which range from an almost colourless liquid, as champagne, to the deep yellow sherry—the colour is derived from the oxidation of the so-called extractives contained in the juice, which, as was before explained, is separated from the husks as quickly as possible. The grapes of some of the best red wines yield an almost colourless juice if pressed before fermentation, and it is only by the joint action of alcohol and acid upon the husks, stalks, and seeds during fermentation, that the red colour is extracted from the marc. Mulder separated the colouring matter contained in red wines by means of lead acetate, and found it to consist of a substance which was bluish-black in colour and amorphous in structure. It is only sparingly soluble in alcohol, insoluble in water, ether, chloroform, carbon disulphide, oil of turpentine, oil of olives; but soluble in solution of tartaric acid or cream of tartar, and in alcohol containing a trace of acetic acid, the saturated solution showing a blue colour; more acetic acid turns the solution red. It is soluble also in alcohol containing tartaric acid, exhibiting a red colour, but neither of these acids renders it soluble in ether or chloroform. The colour of wine, consequently, depends both upon the amount of colouring matter and the amount of free acid contained in it, as the violet colour becomes redder in proportion to the quantity of free acid acting upon the blue colouring matter.

The colouring matter precipitated by hydrochloric acid—in which it is deposited slowly at the ordinary temperature, but more rapidly on boiling—has been examined by Terrell (Bull. Soc. chim. [ii.] 44, 2). The precipitate always contains a substance resembling ulmic acid, from which the colouring principle may be dissolved

out by alcohol. Thus obtained it forms brittle varnish-like scales, insoluble in water and ether, but readily soluble in alcohol, forming a brownish-red solution with a slightly yellow tinge. Acids change this colour to an intense red, while alkalis give a green coloration, which changes rapidly to a brownish-yellow on exposure to the air (*cf.* O. Griessmayer, *Dingl. poly. J.* 123, 531; *Chem. Soc. Trans.* 1887, 368).

The generally held view that the browning of wines is due to unsound grapes is not correct. The presence of stalks in the fermenting mash contributes appreciably to browning. Very acid wines are particularly prone to browning. The browning is most probably due to the oxidation of tannin-like substances of phenolic character by the action of oxidases or by auto-oxidation, or probably by both processes. It can be prevented, at least to a considerable extent, by immediately pressing the grape mash, but this course is not always possible in practice (H. Müller-Thurgau, A. Osterwalder, and H. Haller, *Landw. Jahrb. Schweiz*, 1923, 37, 215; *Chem. Zentr.* 1923, 74, [iv.] 1010; *J. Soc. Chem. Ind.* 1924, 43, 109).

The browning of wines, which is not only accompanied by a discoloration, but also with a strong turbidity and an unpleasant flavour, can be arrested by the use of sulphur dioxide in the form of potassium metabisulphite, which is added to the juice in the cask before fermentation. The yeasts can withstand without risk quantities of sulphur dioxide towards which *Bacterium gracile*, which effects the decomposition of malic acid at the close of the fermentation, is sensitive. The inhibition of the decomposition of the acid, whether it be temporary or complete, is mainly dependent on the quantity of free sulphur dioxide. Further, the duration of time during which the sulphur dioxide remains in the free condition must be borne in mind, as combination proceeds at different rates with different juices, and therefore the action of the same quantity of sulphur dioxide is not always identical. The commencement of the decomposition of the acid is, moreover, influenced not only by the number of acid-decomposing bacteria present, but also by the nature of the juice and its chemical composition, *e.g.* the content of tartaric acid. From very extensive experiments it was found that the addition of 2-4 grms. of $K_2S_2O_5$ to a hectolitre did not in any case hinder the decomposition of the acid. With 5-6 grms. inhibition was produced with juices rich in tartaric acid, and by the addition of 7.5-8 grms. of $K_2S_2O_5$ to different juices a slight retardation was observed. Quantities of 10-14 grms. of $K_2S_2O_5$ per hectolitre, corresponding with an initial content of free sulphur dioxide of 28 mg. and more per litre, produced complete inhibition of the decomposition of the acid (H. Müller-Thurgau, A. Osterwalder, and H. Haller, *Landw. Jahrb. Schweiz*, 1923, 37, 241; *J. Soc. Chem. Ind.* 1924, 43, B. 109).

The colouring matter of red wines may be estimated with sufficient accuracy for technical purposes by the method of Cari Mantrand (*Bull. Soc. chim.* 1906, [iii.] 35, 1017), by precipitating with lead acetate, decomposing the precipitate with sulphuric acid, filtering, and weighing the residue from an evaporated portion of the

filtrate. The extracted colouring matter may be concentrated and preserved in glycerol for use in confectionery, &c. The maximum amount found was 17.2 grms. per litre in Algerian wine.

According to Willstätter and Zollinger (*Annalen*, 1915, 408, 83; 1916, 412, 195) the colouring matters of wine, *viz.* oenidin and oenin, are derivatives of delphinidin. Oenidin, which has been isolated from the black Italian grape, is the dimethyl ether of delphinidin, and oenin is the monoglucoside of oenidin.

The pigments present in two varieties of American grapes, namely, Norton (*Vitis californica*, *V. labrusca*) and Concord (*V. labrusca*), have been examined by the methods of Willstätter and Zollinger (*Annalen*, 1915, i, 295; 1917, i, 47). The same anthocyanin chloride, $C_{22}H_{22}O_{11}Cl_3H_2O$, has been isolated from both varieties. On hydrolysis, it yields dextrose and an anthocyanidin chloride, $C_{17}H_{15}O_7Cl_3H_2O$. The substances are identical in composition with the oenin and oenidin chlorides obtained by Willstätter and Zollinger from European grapes (*V. vinifera*), but they differ from these substances in that the anthocyanidin contains only one methoxyl group, whereas oenidin contains two. The colour reactions are, moreover, different. The anthocyanin gives with ferric chloride in aqueous solution a purple colour which quickly fades to light brown, and in alcoholic solution an intense blue which changes to purple and finally to wine-red; the anthocyanidin gives with the same reagent both in aqueous and alcoholic solution a momentary purple colour fading to an almost colourless or faintly yellow solution. Evidence of the presence of a diglucoside has also been obtained (R. J. Anderson, *Bio-Chem. J.* 1923, 57, 795; *J. Chem. Soc.* 1924, 126, i, 251).

Some additional colour is imparted to white wine by the tannin extracted from the oak casks during maturing. On the other hand, the natural colouring matter of red wine is reduced by the operation of fining as well as on ageing.

Caramel is frequently used to colour white wines (*e.g.* brown sherry), and occasionally boiled must is added either to the juice before fermentation or to the finished wine. (For foreign colouring matters, *see* below.)

Tannin is derived from the grape skins and stalks, the juice itself being practically free. It is sometimes added, however, to champagne and other white wines to prevent 'scuddiness' or turbidity. The natural tannin of grapes is decomposed by acids or by fermentation into glucose and an acid which is not gallic acid.

The albuminous substances in the grape, which set up the ferment, ought by that action to be removed in the yeast when the fermentation is properly carried out, and should not exceed 4 parts per 1000 of wine, unless the latter has been 'fined.' The albuminous matter is also reduced by 'plastering,' and in old wines it is thrown out together with tannin and colouring matter. In imperfectly fermented wines a certain amount remains, and, in the case of white wines, may again render them liable to fresh fermentation. In red wines this danger is obviated by the presence of the tannin of the

husks, which preserves the albuminous matter from change.

The small quantity of ammonia which is present in grape juice, or is formed during fermentation out of albuminous substances, is, for the most part, precipitated during fermentation as magnesium-ammonium phosphate; a small amount, however, remains, and in some wines is accompanied by minute traces of trimethylamine.

Under the term '*extractives*,' some chemists include all matters other than water, alcohol, and volatile acids; others only those substances which are not volatile up to 100° or 110°. The latter would, however, exclude glycerol, which is properly included amongst the extractives. The composition of certain constituents of the extract which contribute to the smell and taste of the wine is still very obscure. The extractives are, of course, abnormally increased by plastering and addition of sugar (*v. infra*).

The mineral constituents of wine, as found in the ash, are potash, soda, and lime as phosphates, chlorides, carbonates, and sulphates, traces of iron, magnesia, and silica, and occasionally alumina, lithia, and manganese. In pure natural wines the ash rarely exceeds 0.3 p.c., but may be much higher in wines which have been plastered, or to which alkalis have been added to reduce their acidity.

As regards the amount of alcohol, a very comprehensive set of tables, embracing the results of the examination of 133 wines, is given by Thudichum and Dupré (Treatise on the Origin, Nature, and Varieties of Wine, 128-304), from which the following *résumé* is compiled:—

	Strength of wines in degree of proof spirit
German wines, 35 samples . . .	16.2-26.3
French wines, 22 samples . . .	18.0-36.2
Spanish wines, 22 samples . . .	26.7-47.7
Sicilian wines, 6 samples . . .	35.5-31.3
Portuguese wines, 14 samples . .	21.9-46.5
Hungarian wines, 10 samples . .	19.2-22.4
Greek wines, 8 samples . . .	17.8-36.1
Cape wines, 7 samples . . .	36.1-52.7
Atlantic Islands, 3 samples . . .	38.2-31.1
Elba wines, 1 sample . . .	34.99
Australian wines, 5 samples . .	23.5-40.1

Sugar solution wines.—Musts which are too thin, and deficient in sugar, are sometimes concentrated by evaporation (as in Portugal) or, more frequently, a solution of sugar is added. The latter process was first sanctioned by the French minister, Chaptal, and is known as '*Chaptalising*.' A similar process (applied chiefly to acid musts), and known as '*Gallising*,' from its inventor Gall, is also practised in Germany. The must of bad years, which contains a deficiency of sugar and an excess of acid, is mixed with sugar, preferably cane sugar, so as to bring the amount of sugar in the liquid to about 20 p.c., and to reduce the amount of acid to about 2 p.c. Frequently, however, commercial glucose is used, and its addition can frequently be detected in the finished product by its dextrorotatory polarisation (*cf.* Fresenius and Grünhut, *Zeitsch. anal. Chem.* 1921, 60, 188).

The acidity of natural wine can also be

reduced, as suggested by Liebig, by the addition of neutral potassium tartrate, which throws down the free acid, if present as tartaric acid, as acid potassium tartrate. Wine deficient in alcohol and containing much acid may often be improved by adding to it the pressed residue of a succeeding vintage (*cf.* J. Nessler, *Bied. Zentr.* 1884).

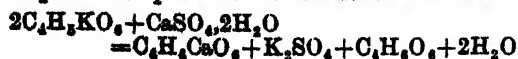
A considerable quantity of wine is now made by covering the marc with an aqueous solution of sugar, and allowing the mixture to ferment. The sugar solution contains 18 grms. per litre for every degree of alcohol which it is desired to obtain, and 250 grms. of marc are used for each litre of solution. Analyses of wines prepared in this way by Girard, and of other samples found in commerce, prove that these wines have an approximately definite composition. When they contain from 9 to 10 degrees of alcohol, the proportion of soluble matter, cream of tartar, tannin, and colouring matter is much less than in the ordinary vintage wines. The amount of solid matter varies from 14 to 18 grms. per litre; the amount of cream of tartar is about 2 grms., but not less than 1.6 grm. per litre; whilst the proportion of tannin and colouring matter varies considerably with the nature of the marc. Girard concludes that those wines constitute a highly useful beverage, and can be produced at a very low cost (*A. Girard, Compt. rend.* 95, 227; *Chem. Soc. Abstr.* 1882, 1335).

Plastering of wine.—The practice of adding gypsum or plaster of Paris to must, either before or after fermentation, which prevails in Spain, Portugal, and the South of France, is said to have for its object the reduction of the amount of the water in the juice, and the production, consequently, of a must relatively richer in sugar. The fermentation is much more rapid and complete, and it is alleged that the wine keeps longer when it has been plastered, and that the colour is richer and more lasting. This explanation leaves something to be desired, because the sacrifice of other constituents of juice than water due to absorption by plaster is entirely out of proportion to any gain by the absorption of the water, and the result desired could be attained either by the addition of sugar or the evaporation or freezing out of water. It is probable that the reason for the practice, although unknown to those who employ it, is that gypsum precipitates some albuminous matters which injuriously effect the wine. An obvious advantage to the wine-maker is that it clarifies the wine rapidly and so enables it to be brought sooner to market.

The plaster of Paris, in the form of powder, is either thrown upon the grapes before they are crushed, or added to the must after fermentation has commenced, or even to the finished wine, and the chemical changes that take place vary accordingly. The quantity used is generally from 1 to 2 kilos. to every 100 kilos. of fruit, although sometimes it reaches as much as 10 kilos.

According to Griessmayer, when gypsum is added to the must, it forms, with the tartar present, neutral calcium sulphate and free tartaric acid, which latter reacts on the sulphate, forming bitartrate and acid calcium sulphate. to Borntraeger (*Annali. Chim. Applic.*

1919, 12, 1), the reaction between calcium sulphate and potassium bitartrate is as follows:



It was shown by Bussy and Buignet that the system ($\text{K}_2\text{SO}_4 + \text{C}_4\text{H}_5\text{O}_6$) is converted into $\text{KHSO}_4 + \text{C}_4\text{H}_5\text{KO}_6$. The ash of such wine is neutral, and does not give off carbon dioxide when treated with hydrochloric acid. When gypsum is added to the finished wine, the alcohol prevents its solution, but it carries down many impurities. Kayser (Bied. Zentr. 1881, 632) made experiments which confirmed these conclusions, and states that from the proportions of the ash to the extractive matter, it is possible to declare with certainty whether the wine has been plastered as must or as finished wine; in the first case the ash is disproportionately high, in the other it remains normal. Kayser also states that by the interaction of KHSO_4 and KH_2PO_4 , free phosphoric acid is formed together with neutral potassium sulphate, the former producing the bright colour of plastered red wines. The main change, however, appears to be a decrease in the tartrates and an increase in the proportion of potash and sulphates.

The injurious effects attributed to plastered wines have been the subject of investigation by several commissions appointed by various foreign governments. The most exhaustive inquiry yet made on the hygienic aspect of the subject was by a commission appointed by the French War Department owing to complaints made by the French army in Algeria, where many cases of illness were said to be due to the use of plastered wines. The symptoms are said to be colic, and slight vomiting. The acid potassium tartrate acts towards many reagents in the same manner as free sulphuric acid, and when introduced into the system may have the effect of reducing the alkalinity of the blood.

In view of the inconclusive nature of the evidence, the Commission recommended the maintenance of the regulation forbidding the sale of wines containing more sulphate than that corresponding with 2 grms. of potassium sulphate in the litre, and this limit has been also adopted in Germany, Switzerland, and other countries.

The attempts to 'de-plaster' wine are, from a hygienic point of view, more injurious than the plastering, owing to the use of poisonous barium and strontium salts.

Wine is liable to be affected by a number of injurious ferments, and is especially subject to acetous fermentation, due to *Mycoderma aceti*, which principally attacks the alcohol with production of acetic acid, whilst *Mycoderma vini* attacks principally the cream of tartar and extractive matters. The action of foreign ferments may frequently be prevented by the process devised by Pasteur, which consists in heating the wine for some time to about 70° in absence of air. The bouquet, and in some cases the colour, is thus found to be improved. The heating must be quickly performed, and, as far as possible, out of contact with air.

Numerous substances are employed for the preservation of wine by chemical means as *abrazol* or *asaprol* (the calcium salt of β -naphthol sulphonic acid), *benzoic*, *boric*, and *cinnamic*

acids, *fluorides*, *formaldehyde*, *saccharin*, *salicylic acid*, *sulphurous acid*, and *sulphites*. It should be noted that of these, boric acid, fluorine, and salicylic acid may be present in minute quantities as natural constituents of the wine (*v. infra*).

Sulphuring is carried out either by burning sulphur, sometimes placed on strips of paper, linen, jute, asbestos, &c., in the casks, or by addition to the wine of sulphurous acid or one of its salts. For small works the use of aqueous sulphurous acid or potassium metabisulphite, $\text{K}_2\text{S}_2\text{O}_5$, is most convenient, and in large works that of liquid sulphur dioxide. The colouring matter of red wine is at first bleached by sulphur dioxide, but with proper sulphuring the wine later assumes a more vivid red colour than the non-sulphured wine. In the wine the sulphur dioxide is converted partly into sulphuric acid and into compounds with acetaldehyde and dextrose, the rest remaining in the free state—sulphites are blood- and stomach-poisons, but they are readily and rapidly changed in the human body. Most German wines contain less than 200 mg. of total or 50 mg. of free sulphur dioxide per litre, but with choice wines, which require repeated sulphuring to bring their slow fermentation to a close, as much as 546 mg. per litre has been found; similar results are obtained with sweet sauternes (Journ. Soc. Chem. Ind. 1923, 285 A.). According to Dubaqué, the clouding of white wines after keeping in glass bottles may be due to the action of sulphur dioxide in the wine upon iron silicates of the glass (Ann. Falsif. 1925, 18, 418; J. Soc. Chem. Ind. 1925, 44, B. 821).

The essential oil of black mustard seed (b.p. 150-7°C.) is soluble in alcohol and ether, but in water only to the extent of 1.16 grms. per litre at 15°C. Its antiseptic power, when used in wines, is such that 1 c.c. of a 1 p.c. solution added to 1 litre of wine is efficient, but the amount required varies with certain factors, such as the amounts of sugar and sulphurous acid in the wine, the quantity and vitality of any yeasts present, and the temperature. The souring of red wines, which generally contain no sugar, can be stopped by the addition of 0.8 c.c. of the 1 p.c. solution above mentioned. Essential oil of mustard is about 200 times as active as sulphurous acid and does not affect the odour or flavour of the treated wines. It does not volatilise from the wine, and therefore does not require to be renewed. It has no action on the colouring matters of red wines, fruit juices, caramel, etc. It is estimated by heating 5 c.c. of the preservative on a water bath for 1 hour, with 10 c.c. of ammonia solution and 55 c.c. 0.1N silver nitrate solution in a graduated 100 c.c. flask connected with a reflux condenser. The solution is cooled, diluted to the mark, filtered from the precipitate, and the silver estimated volumetrically in 50 c.c. of the filtrate (P. Malvezin and G. Bidart, Ann. Falsif. 1923, 181, 534; Analyst, 1924, 49, 140; cf. Moreau and Vinet, Ann. Falsif. 1924, 17, 477; J. Soc. Chem. Ind. 1925, 44, B. 49).

Manufacture of 'sparkling' wines.—The effervescence of a sparkling wine is due to the presence of carbonic acid, produced by the fermentation of added sugar. The chief wines of this class (champagne) are produced in the departments of Marne and Haute-Marne, and in

the vicinity of the Moselle and the Rhine. Both white and red grapes are used, and the wine is amber in colour, the depth of tint depending on the vintage and the proportion of dark grapes employed. The vintage is in the early part of October, and in the pressing the must is separated into two portions, that first produced being of the higher quality. The young wine is allowed to ferment until the winter, when it is racked and after the expiration of a month the operation is repeated, when the wine is fined. It is then mixed with a certain proportion of old wine, and the amount of sugar present determined. If necessary, a quantity of cane sugar is added, and the wine is bottled, the bottles being placed horizontally in piles and left at rest throughout the summer. Carbonic acid is formed, together with a quantity of sediment. The pressure of the gas in the bottles can readily be ascertained when desired, by means of a manometer (such as Salleron's modification of Maumené's 'Aphrometre'), and ranges from 5 atmospheres in *grand mousseux* to less than $4\frac{1}{2}$ in *crémant* wine; in ordinary mousseux wine the pressure varies between 4 and $4\frac{1}{2}$ atmospheres. When required for the market, the bottles are first carefully brought into an inclined position, so as to cause the sedimentary matter to fall gradually on to the cork; on removing the clip which holds the cork within the neck the pressure of the dissolved gas forces out the cork, together with the sediment. A certain amount (from 1 to 4 p.c. depending upon the sweetness desired) of liqueur made of fine wine, sugar, and cognac or a stiff spirit, is quickly added, and the bottles are again filled up, corked, and wired.

Dry champagnes—i.e. containing relatively little sugar—are mainly exported to this country; the sweeter varieties being usually consumed in America and on the Continent.

Wines of France. The pre-eminence of France as a wine-producing country is due mainly to its favourable conditions in regard to both climate and soil, and, no doubt, also to the system of small holdings worked by the thrifty and industrious French peasantry. The chief wine-growing district in France is the Gironde, which is practically divided into five portions, viz., the Médoc, the Graves, the Côtes, the Palus, and the Entre-deux-Mers. To these must now be added the wines from the Alsace-Lorraine territory restored to France by the Treaty of Versailles. Although formerly retained almost exclusively for home consumption, they are now (1926) obtainable on the British market. In the Médoc some six or seven different varieties of vine are cultivated.

Most of the red wine is obtained from the Carbenet Sauvignon, Franc Carbenet, Malbec, and Merlot grapes. The vintage usually begins towards the end of September, and lasts about a fortnight. The wines (usually known as 'clarets') are divided into *payan*, *artisan*, *bourgeois*, and *fine growths*, the last group being further sub-divided into what are known as 'crus' or 'classified growths,' named after the place (Château or Commune) where they are produced; e.g. *Château Latour*, *Pauillac*; *Château Lagrange*, *St. Julien*; *Château Margaux*; *Château Cantenac*, &c. The official classification into 'crus' or 'growths' was made so long ago as 1855 by the *Chambre Syndicale des Courtiers*

since when it has not been found necessary to make any alteration. (*Vide 'Bordeaux et ses Vins,' by Feret, Bordeaux, and Encyclopædia Britannica; art. 'WINE.'*)

The chief white wine producing district is to the south of Bordeaux. The principal vines are the Semillon, Sauvignon, and Muscatelle. The vintage is much later than in the Médoc—viz. in the last weeks of October or early part of November, when the grapes have entirely ripened. Three qualities of must are produced: the first and ripest juice yields a sweet luscious wine (*vin de tôle*), mainly consumed in Russia; the second forms *vin de milieu*, the wine usually known as *Sauterne*; the third quality, or *queue*, yields a dry white wine. The principal varieties are *Barsac*, *Sauterne*, *Graves*, and *Bommes*, *Château Latour-blanc*, and *Château Yquem*, which is generally considered to be the premier white wine of France, if not of the world, and in the classification of Sauternes it takes precedence of the 'First Growths,' being placed in a class by itself.

The department of the Pyrénées Orientales produces a considerable quantity of wine, mostly from the Grenache noir and Carignane grapes. The generic name of the wine of the district is *Roussillon*, of which the most esteemed varieties are muscat of *Rivesaltes*, *Maccabeo*, *Malvoisie*, and *Grenache*, which are liqueur wines (the last-mentioned being simply unfermented must preserved by means of added spirit and sulphurous acid, with frequent racking from deposits); and *Randoc*, dry *Malvoisie*, and *Picfoule*. Languedoc also produces a large quantity of wine (*vins du Midi*), much of which is mixed with the wines of the Gironde and of Burgundy; whilst a considerable amount of the rest is distilled to make 'trois-six' and *eau de vie*. Cognac is produced from the wines of the Charente district (*v. BRANDY*).

The Rhône and Saône valleys produce the chief wines of the east of France, which, with the exception of *Hermitage* and the wines of the *Beaujolais*, seldom occur in trade under their own names.

The best qualities of champagne (*v. supra Sparkling wines*) are produced in the department of Marne and Haute-Marne, the chief centres of the trade being at Rheims, Épernay, Ay, Avize, Châlons, and Dizy. The most famous brands are *Ayala*, *Bollinger*, *Cluquet*, *Heidsieck*, *Irroy*, *Mott*, *Mumm*, *Perrier Jouët*, *Pommery-Gros*, and *Roederer*. Large quantities of sparkling wine are produced in the Saumur, in the department of Maine-et-Loire. Sparkling *Saumur* is made from both black and white grapes—the black being the product of the Breton vine, the white that of the Pineau blanc. The wine is made much in the same way as champagne except that, as a rule, the finished product is a mixture of two successive vintages.

The wines of Burgundy (both red and white) are produced in the departments of Côte-d'Or, Yonne, and Saône-et-Loire. The principal red wines are *Mâcon*, *Beaune*, *Le Corton*, *Romanée Conti*, *Chambertin* and *Clos Vougeot*. *Hermitage* when it can be obtained genuine, is a rich wine with purple colour, produced in the department of Drôme. The white wine of Yonne is known as *Chablis*, and is frequently, though incorrectly, described as 'White Burgundy.'

Spain. *Sherry*, the best known of Spanish white wines, is mainly produced in Andalusia, and derives its name from Jerez or Xeres de la Frontera, the chief centre of the trade, and where most of the wine is produced from must or fruit purchased from the growers. Sherries are essentially 'blended' wines, and are divided as regards type or quality into three classes: *Finos*, *Rayas*, and *Cortados*. The *Finos* are 'clean' and 'dry' in character, the *Rayas* being fuller in 'body,' whilst the *Cortados* partake of the characteristics of the other two types. These wines are exported, however, under various other names, as *Amontillado*, *Manzilla*, *Montilla Solero*, &c. Sherries are almost invariably fortified and plastered, and the commoner kinds sulphured in addition, for the British market.

The sweet red wine known as '*tent*,' which is used for ecclesiastical purposes, is mainly obtained from the Rota district. This and the somewhat similar wines from the Tarragona, Valencia, and Alicante districts were formerly sold under the name of 'Tarragona Port,' or 'Spanish Port.' As the result of recent legislation, such descriptions are now illegal, the use of the term 'port' being applicable only to wines the produce of Portugal (*vide infra*).

Portugal. Port is mainly the produce of the rugged and mountainous district of the Alto Douro in the north-east of Portugal. The vintage usually begins at the end of September. The grapes, from which the stalks are removed, are emptied into stone tanks holding from seven to thirty pipes, and are pressed, first by treading and then by means of a beam or screw press. After from 48 to 60 hours' treading the must is left to ferment, drawn off into vats, and mixed with a sufficient quantity of alcohol to prevent acetous fermentation. After the lees are deposited the wine is again racked and mixed with more alcohol, which is usually obtained by distilling wine. If necessary, the wine is sweetened with 'jeropica,' or sweet must preserved with brandy. In the spring it is sent down to Oporto, where it is stored previous to shipment. 'Vintage wines' are those of the same origin, year, and quality, and are kept separately. The other principal types of port are 'Ruby' and 'Tawny.' These are usually blends, the former being intermediate in character between 'Vintage' and 'Tawny' ports. The latter is matured in wood, thus losing much of its deep red colour. Nearly half the wine exported from Oporto is sent to the United Kingdom.

Port first appeared in England at about the end of the seventeenth century, and its consumption in this country gradually increased up to the middle of the eighteenth century, since when it has gradually declined. The disfavour into which port has fallen may be partly due to the manufacture of numerous brands of inferior wines of port character, which may or may not be distinguished by qualifying names, as 'Hamburg Port,' &c.

As the result of representations by the Portuguese Government, definitions of 'Port' and 'Madeira' have been embodied in recent Acts of Parliament. Thus, in Sect. 1 of the Anglo-Portuguese Commercial Treaty Act, 1914, it is laid down: 'The description "Port" or "Madeira" applied to any wine or other liquor, other than

wine the produce of Portugal and the Island of Madeira respectively, shall be deemed to be a false trade description within the meaning of the M. M. Act, 1887.' Still later, in the Anglo-Portuguese Commercial Treaty Act, 1916 (Sect. 1) it is provided that, 'The description "Port" applied to wine the produce of Portugal imported into the United Kingdom after the passing of this Act shall be deemed a false trade description within the meaning of the M. M. Act, 1887, if the wine on importation into the United Kingdom was not accompanied by a certificate issued by the competent Portuguese authorities to the effect that it was a wine to which by the law of Portugal the term "Port" may be applied.' These enactments apply also to British 'made' wines.

The South of Portugal (Torres Vedras and Collares) produces a considerable quantity of a rough kind of claret, and also a white wine known in England as Bucellas Hoek, which is obtained from the Riesling grape.

Italy. It is only within recent years that Italian wines have found much favour in this country, as they were formerly too sweet for the British market and deficient in keeping qualities. These defects have been largely removed by the adoption of more scientific methods of manufacture resulting in an increased popularity. Northern Italy produces *Barolo*, a red, and *Asti*, a white wine, together with a certain amount of sparkling wine. *Montepulciano* and *Chianti* are made in Central Italy; whilst the Neapolitan district yields *Lacryma Christi* and a variety of Malvoisie and good class Muscat wines. The island of Capri produces a good wine of *chablis* character.

Sicily. The chief Sicilian wine is *Marsala* (a white wine of light amber or brown colour, somewhat resembling sherry), obtained from a mixture of selected and thoroughly ripe grapes of the Madeira variety. It is carefully manufactured and is very uniform in quality, although, as a rule, somewhat heavily fortified, but not plastered.

Austro-Hungary. Both white and red wines are made, but those of German Austria are consumed for the most part locally. The best known are from Vöslau and Gumpolds-Kirchen, and the Tyrol. The most famous of Hungarian wines is the Sweet Tokay or Essentia, which is made from the first runnings of the ripe grapes obtained without pressure. Only a small portion is so obtained, and it rarely, if ever, appears in the market. Other varieties of Tokay are known as *Ausbruch* and *Mastos*. *Carlowitz* resembles port in character, and is produced on the banks of the Danube, about 40 miles to the north-west of Belgrade.

The greater portion of the wine produced in Bohemia (now incorporated in Czechoslovakia) is obtained from the province of Melnik, chiefly from the blue Burgundy grape, originally procured from France.

Excellent red wines, resembling Burgundy, are now made in Dalmatia. The most esteemed varieties are *Moscato Rosa*, *Maraschino*, and *Malvasia*.

Germany. The chief wine-producing districts of Germany are Baden, Bavaria, Hesse, the Rheingau, and Württemberg. The celebrated *Steinberg*, *Johannisberg*, *Radesheim*,

Gräfenberg, and *Rauenthal* wines are produced in the neighbourhood of the Rhine, not far from Mainz, which is the centre of the hock trade. The vineyards of Hesse yield *Liebfraumilch*, *Nierstein*, and *Scharlachberg*; *Hochheimer* is obtained from the Maingau. The chief Rhine wine is the Riesling, which is said to be indigenous, and which has been transplanted and successfully cultivated in many other parts of the world as South Africa, Australia, and the United States

of America. The *Moselle* district also produces excellent wines of characteristic but rather weak flavour, which is often artificially enhanced by the addition of tincture of elder flowers.

The chief product is a white wine. A certain amount of red wine is obtained, notably Assmannshausen, from Riesling and mixed grapes. The results of analyses by König of wines from the principal European countries are shown in the following table.

ANALYSES OF EUROPEAN WINES (König).

	Number of analyses	Specific gravity	Grammes per 100 c.c.									
			Alcohol by weight	Extract	Total acid as tartaric	Free tar- taric acid	Cream of tartar	Volatile acid as acetic	Sugar	Glycerol	Nitrogen	Ash
<i>Germany :</i>												
Moselle	14	0.9964	7.99	2.24	0.79	—	—	—	0.03	0.72	—	0.175
Rhine	23	1.0005	8.00	2.60	0.81	—	0.200	—	—	0.85	—	0.230
Baden	46	—	6.65	2.16	0.91	0.018	0.358	—	0.09	0.49	—	0.207
Württemberg, white wine	15	0.9995	6.10	2.27	0.95	0.095	0.262	—	—	0.57	—	0.250
red wine	6	—	4.73	2.64	1.14	0.091	0.026	—	—	0.46	—	0.250
<i>France :</i>												
Alsace	15	—	6.59	2.07	0.70	0.018	0.168	0.052	—	0.55	0.028	0.229
Lorraine, red wine . . .	10	0.9967	8.08	2.27	0.56	0.032	—	0.155	0.09	0.50	0.019	0.185
Red wine	29	0.9982	7.80	2.56	0.57	—	—	—	0.30	0.73	0.043	0.248
White wine	5	0.9963	8.30	3.03	0.66	—	—	—	—	0.97	—	0.250
<i>Austria :</i>												
Tyrol, red wine	60	0.9940	9.08	2.34	0.62	—	—	—	—	0.65	0.021	0.222
white wine	17	0.9927	8.84	1.87	0.59	—	—	—	—	0.65	0.020	0.175
<i>Russia :</i>												
Red wine	10	0.9939	10.78	2.76	0.56	—	—	0.142	—	0.64	0.036	0.267
White wine	12	0.9931	11.96	2.57	0.49	—	—	0.100	0.46	0.59	0.026	0.204
<i>Italy :</i>												
Spain :	20	—	10.61	3.44	0.52	—	—	—	1.44	0.45	—	0.200
<i>Spain :</i>												
Ordinary red wine	7	—	12.30	3.53	0.49	—	—	—	0.38	1.09	—	0.610
Sweet wine	4	1.0233	12.78	9.69	0.59	—	—	—	6.55	0.63	—	0.740

The Atlantic Isles. Grand Canary and Tenerife produce a small quantity of wine, but since the production of cochineal has fallen off on account of the preference for coal-tar colouring matters, vine culture is increasing, and wines of the Madeira type are being made in larger quantity.

Madeira. The best-known varieties of Madeira wine are *Malmsey*, and *Sercial*, the former being a sweet, and the latter a dry wine. It is a white wine, and its characteristic flavour is probably due to the practice of exposing the young grapes to a prolonged process of partial drying by artificial heat, and of heating the wine shortly after its manufacture to a temperature varying from 25° to 45°. Formerly the same condition was obtained by sending the wine a voyage to the East or West Indies and back. Very little red wine is made in Madeira (*vide supra*, under 'Port').

A small quantity of wine is made in the Azores, particularly on Pico, but it is of very indifferent quality, and is mainly exported as low-class sherry.

Cape of Good Hope. Comparatively little wine is now sent to this country from South Africa, although a century ago the importation of Cape wine into the United Kingdom exceeded that from France. The decline was due to vine diseases and insect pests, to faulty manufacture, and to fiscal changes. The best-known wines are *Veldt Burgundy* and *Claret*, *Wynterger Chablis*, *Schoonewicht Hermitage*, *Tafelberg Hock*, and the sweet pale-red *Constantia* produced

near Cape Town. A great increase in the importation of South African wines has occurred since the war, the quantity imported during the last five years immediately preceding the war being only 15,000 gallons, as compared with over 200,000 gallons imported during the corresponding period since the war (1919-23).

Australia. Of late years the amount of wine from Victoria, New South Wales, and South Australia imported into this country has increased enormously. The industry may be said to be still in its infancy, but the most scientific methods and appliances are adopted, and the produce of such vineyards as Albury, Great Western, Highercombe, and Tintara bids fair to rival the best European wines of similar type.

In Australia (as in the case also of South Africa and California) the practice obtains of naming the wines after the well-known European types they more or less resemble in character, as 'Burgundy,' 'Chablis,' 'Hock,' &c., or after the variety of vine originally imported from Europe, as *Riesling*, *Hermitage*, and *Carbenet*.

United States. The manufacture of wine has been firmly established in California. The produce was originally derived from the 'Mission' grape, supposed to have been imported from Mexico by Franciscan monks, but German, French, and Spanish varieties were introduced, and wines in some degree resembling those of these countries (and named after their original types) were made on a considerable scale. The vine has been also cultivated on a large scale in Ohio and Canada and champagne has been

made in the vicinity of Cleveland and Sandusky. Other wine-producing States were New York, Missouri, Illinois, and Pennsylvania. Whilst the finer wines consumed in the United States were obtained from France and Germany, the importation of foreign wines steadily decreased in favour of the home product.

It is understood that at the present time (1926) the national prohibition law prevents the manufacture and sale of wines in the United States.

The following are analyses, by Bigelow (U.S. Dept. of Agric. Bur. of Chem. Bull. 59), of 525 samples of wines manufactured in California:—

Description	Grams per 100 c.c.											
	Alcohol by volume p.c.	Alcohol	Total acids	Extract	Reduc- ing sugar	ids	K ₂ SO ₄					
<i>Red wines (204 samples):</i>												
Bordeaux, Rhine, Burgundy, and South French types	Min.	0.9900	8.00	6.35	0.330	0.201	1.91	0.030	0.1864	0.0455	0.188	
	Max.	1.0050	19.28	15.30	0.852	0.888	6.88	0.628	0.5544	0.2515	0.430	
<i>White wines (321 samples):</i>												
Rhine, Sauterne, South French, Sherry, and Madeira types	Min.	0.9866	5.00	3.98	0.163	0.181	1.00	0.060	0.0859	0.0453	0.050	
	Max.	1.0560	22.19	17.61	0.971	0.798	19.66	17.219	0.9379	0.1861	0.447	

ANALYSIS OF WINE.

The chemical examination of wine is usually restricted to the determination of those constituents which enable an opinion to be formed concerning its purity or freedom from adulteration, but expert tasting is of great importance and microscopical examination of the deposits obtained from wine may afford useful information. For methods based on the latest chemico-physical principles, the work of Baragiola may be consulted (Zeitsch. anal. Chem. 1914, 53, 100; Analyst, 1914, 127).

For the estimation of the *specific gravity* a determination should be made by the bottle or other form of pycnometer and given accurately to four decimal places. Carbonic acid should first be removed by vigorous agitation.

The *results* are usually given in grms. per 100 c.c. or per litre. Koenig (Zeitsch. anal. Chem. 28, 202), however, deprecates this practice, on the ground that for sweet wines, which are liable to differ widely in sp.gr., the results are no longer directly comparable.

The *alcohol* is best determined by the distillation method, the sp.gr. of the weighed distillate being taken and the proportion of alcohol found from tables. For more exact determinations, the volatile acids should be neutralised before distillation.

Detection of cider in wine.—F. Schaffer (Mitt. Lebensm. Unters. Hyg. 1923, 15; Ann Chim. anal. 1924, 6, 88) has devised a method for detecting cider in wine, based on the diminished reducing power of the wine. The following modified procedure is recommended: Forty c.c. of the wine are decolorised by boiling with 3 grms. of pure animal charcoal and filtered, and the filtrate is heated to boiling with excess of precipitated calcium carbonate. After further filtration the cooled liquid is treated, slowly and with shaking, with 8 c.c. of 10 p.c. barium acetate solution, and again filtered. Five c.c. of the neutral filtrate are mixed with 2 drops of 0.2N silver nitrate solution, and, after being made alkaline by addition of 1 c.c. of 0.1N sodium hydroxide solution, are placed in the dark, and the time elapsing before distinct reduction is apparent is noted; the test should be made in duplicate or even triplicate.

With cider the reduction becomes evident in a few minutes, and with wines containing a marked proportion of cider in 10 to 20 minutes; in some cases comparison of the suspected wine with the natural wine of known purity is advisable (Analyst, 1924, 49, 235). If 1 c.c. of concentrated sulphuric acid be mixed (keeping cool) with 5 c.c. of wine and set aside till next day, genuine wine should remain clear (von Fellenberg, Mitt. Lebensm. Hyg. 1925, 16, 55; J. Soc Chem. Ind. 1925, 44, B. 936).

Determination of extract.—The various methods in use for determining extractive matter in wine differ considerably both in principle and in the details of manipulation. The direct method (by evaporation) does not give comparable results unless the sugar of sweet wines and the potassium sulphate in plastered wines are deducted, and not then unless the estimation is conducted under exactly similar conditions.

The French official method of prolonged heating on a water-bath gives low results, owing chiefly to loss of glycerol. The sugar and potassium sulphate are deducted, an allowance of 1 gm. of each per litre being made to cover the amount of these substances assumed to be naturally present in fully fermented wine. The result is known as the 'reduced extract.'

The most exact determination of extract is made by evaporation (at the ordinary temperature) over sulphuric acid *in vacuo*, but as this requires from 3 to 6 days (according to the temperature) it is unsuitable for ordinary commercial use.

By Njegovius' modification of this method, however, the time may be reduced to within the limits of a working day. The wine (5 c.c.) is absorbed by anhydrous sodium sulphate (5 grams) in a tared bottle and dried in a desiccator under diminished pressure, not exceeding 15 m.m.

The German official method is as follows:—

(a) For wines with an extract amounting to not more than 3 grms. per 100 c.c. (ascertained by the indirect method (c) given below): 50 c.c., measured at 15°, are evaporated to a syrupy consistency on the water-bath in a platinum basin of 85 mm. diameter, 20 mm. height, and 75 c.c. capacity, and the residue is dried for 2½ hours in the water oven.

(b) For wines containing from 3 to 4 grms. of extract per 100 c.c. an amount yielding from 1 to 1.5 grms. of residue is taken. For the necessity of using dishes of similar area and surface in order to obtain comparable results, v. Bouillon (Compt. rend. 103, 498).

(c) For sweet wines, or those containing over 4 grms. of extract per 100 c.c., the indirect method of determining the extract from the sp.gr. of the wine after removal of the alcohol is to be preferred (v. Tables in Windisch, Die chemische Untersuchung und Beurtheilung des Weines, 338; abstracted, J. Soc. Chem. Ind. 1898, 280).

The amount both of extract and of alcohol may be determined by Riegler's refractometer method (Zeitsch. anal. Chem. 1896, 27). One grm. of alcohol and of extract in 100 c.c. of wine are found to raise the refraction by 0.00068 and 0.00145 respectively above that of water. Then if a = the refraction of pure distilled water; $(a+b)$ = the refraction of the wine from which the alcohol has been removed made up to the original volume taken; and N = the refraction of the original wine; then the formula
$$\frac{N-(a+b)}{0.00068}$$

gives the weight of alcohol, and $\frac{b}{0.00145}$ that of the extract as grams per 100 c.c. of the wine.

In completely fermented wines the amount of extract is seldom less than 14 grms. per litre. Wines containing less than this amount after removal of the sugar may be suspected of dilution.

After separation of the non-volatile acids, the remaining extract in natural wine is seldom less than 11 grms. per litre, and after separation of the free acids, as a rule, not less than 10 grms. per litre. The mineral constituents are usually about 10 p.c. of the extract.

The free acid is determined by titration with standard potash or soda-solution, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_4O_6$). Carbonic acid should first be expelled, either by heating just below boiling-point (but rapidly so as to avoid loss of acetic acid), or by agitation and subsequent titration in the cold. Volatile acids are determined by distillation in steam, or, since this partially volatilises lactic acid (Windisch, Zeitsch. Nahr. Genussm. 1905, 9, 70), by the difference in the acidity of the wine before and after evaporation to a small bulk, and are expressed as acetic acid ($C_2H_4O_2$). The fixed acids are estimated by difference between the total and volatile acids, or by direct titration of the extract obtained by evaporation *in vacuo*, and are expressed as tartaric acid. In France the acidity is usually given in terms of sulphuric acid (H_2SO_4).

Old wines have an acid reaction, in consequence of the presence of a certain amount of free acid and potassium hydrogen tartrate. A wine not exhibiting this acid reaction tastes flat. For a long time it was believed that the free acid of wine is tartaric acid alone. Nessler's researches have, however, shown that this is not the case. Tartaric and malic acids often occur together, and more frequently the free acid consists of malic acid entirely. Wines containing malic acid alone taste more tart than

those with only malic acid, or a mixture of malic and tartaric acids.

The presence of free tartaric acid in wine does not necessarily show an improper admixture of tartaric acid with the wine. According to Mach and Rolandi, the amount of free tartaric acid in the grape increases in proportion to the degree of unripeness, so that its absence from wine can only occur under certain conditions of ripeness of the grapes employed. Although unripe grapes are frequently used in considerable quantity in wine-making, yet if the ripe grapes are in excess, the potash salts in them are more than sufficient to separate the free tartaric acid in the form of tartar, and this explains the fact that wine so made generally contains no free tartaric acid. A wine may be suspected of having been sophisticated if, with a small amount of free acid, an undue proportion of it is tartaric (J. Nessler and H. Wachter, Bied. Zentr. 1880; Chem. Soc. Abstr. 1880, 775).

The estimation of total tartaric acid, free tartaric acid, potassium bi-tartrate, and tartrates of the alkaline earths (lime and magnesia) is best made by the methods of Halenke and Möslinger, and of Barth (Zeitsch. anal. Chem. 1895, 279-290). These methods were officially adopted by a German Imperial Decree of 1896, an abstract of which is given in the J. Soc. Chem. Ind. 1898, 277. Certain modifications were introduced by Kulisch in 1901. Full details of these, as well as the French official methods, will be found in Post and Neumann's *Traité complet d'analyse chimique appliquée aux essais industriels*, 1910, tome ii. 661. The last three estimations are necessarily empirical, being founded on the assumption that all the bases present in the organic salts of the wine, or as carbonates in the ash, were originally combined with tartaric acid to form bi-tartrates.

A rapid and fairly accurate method of estimating tartaric acid and potassium in wine is that of Kling and Lassieur (Ann. Falsif. 1914, 7, 410; Analyst, 1915, 155). Mathieu (Ann. Falsif. 1919, 11, 80) recommends a method originally described by Pasteur in 1873. For details, see Analyst, 1919, 238. In a later communication he describes the process as follows: about 20 c.c. of the wine are shaken with 20 c.c. of amylic alcohol; the alcoholic layer is separated and shaken with an equal volume of water; the aqueous layer is drawn off, evaporated to dryness, the residue dissolved in 5 c.c. of water and the solution treated with 1 drop of calcium chloride solution (150 grams of crystallised $CaCl_2$ and 40 grams of NH_4Cl per litre) and 2 c.c. of 1-ammonium tartrate solution (20 grms. of the salt per 1 litre of dilute alcohol). A precipitate of calcium racemate forms immediately if the wine contains not less than 0.5 grm. of free tartaric acid per litre (Mathieu, Bull. Assoc. Chim. Sucr. 1921, 38, 352).

Numerous methods have been suggested for the estimation of malic and succinic acids, but they are too uncertain and inexact to be of much value for analytical purposes. The methods for estimating lactic and citric acids are more trustworthy, and the estimation of these is more important, since the former is a constant constituent of wines, and is often the cause of excessive acidity, whilst the latter is never present in genuine wines, except in small amounts.

but is sometimes added to sophisticated wines.

The best methods for estimating *lactic acid* are those of Kunz (Zeitsch. Nahr. Genussm. 1901, 4, 673) and Möslinger (*ibid.* 1901, 4, 1123). *Citric acid* may be estimated by Möslinger's method, weighing as lead citrate, as officially adopted by the U.S. Dept. of Agriculture (Bur. of Chem. Bull. 107, 81).

The determination of *glycerol* in wine has given rise to numerous processes, the best known of which are based upon either extraction by means of alcohol and ether or ethyl acetate or acetone and weighing, or oxidation to and estimation as oxalic acid.

Various methods have been proposed, as steam-distillation under reduced pressure (Bordas and Raczkowski, Compt. rend. 1897, 124, 240); or by conversion into triacetin (Böttger, Chem. Zeit. 1897, 659); or into isopropyl iodide and weighing as silver iodide (Zeisel and Fanto, Zeitsch. anal. Chem. 1903, 549).

The Zeisel-Fanto method always gives low results. Correct values, however, can be obtained when organic acids, such as acetic, propionic, succinic, or tartaric acid, which have a decomposing action on the polyglycerol formed, are added to the reaction mixture. Lowering the concentration of hydriodic acid has no influence on the result: 200 c.c. of wine after treatment with tannin and barium acetate in the usual way are concentrated to about 30 c.c., and diluted with water to 40 c.c. 10 c.c. of the filtrate are then diluted to 50 c.c. with acetic acid, and 5 c.c. of this solution employed for the determination (C. Marchi, Staz. sperim. agrar. ital. 1923, 56, 231; Chem. Zentr. 1923, 94, [iv.] 1011; J. Soc. Chem. Ind. 1924, 43, B. 110).

A method by Rothenfusser, claimed to be more rapid and less laborious and expensive than the official method described below, is given in Zeitsch. Nahr. Genussm. 1913, 26, 535.

The older methods, especially extraction with alcohol and ether, are generally preferred, since, although somewhat empirical, they yield results which are comparable with the enormous amount of similar data acquired by previous observers. It is essential, however, that the exact details of the given methods should be rigidly followed.

The method officially adopted in Germany is as follows, (a) being adopted in the case of dry wines or those containing less than 2 grms. of sugar per 100 c.c.; and (b) for sweet wines containing more than this proportion of sugar.

(a) 100 c.c. of wine are evaporated down to 10 c.c. in a porcelain capsule on a water-bath. 1 gm. of quartz sand is added and milk of lime (40 p.c.) equivalent to 1½–2 grms. CaH_2O , for each gram of extract present, and evaporation continued almost to dryness. The residue is then repeatedly boiled with small quantities of 96 p.c. alcohol, the various extracts being decanted into a 100 c.c. flask, made up to bulk at 15°, filtered, and 90 c.c. of the filtrate evaporated in a porcelain capsule on the water-bath (without boiling). The residue is washed into a stoppered graduated cylinder with small quantities of absolute alcohol until 15 c.c. are collected, then shaken up with three successive

portions of ether (7.5 c.c. each time), and, when clear, the whole (including the rinsings of the cylinder with alcohol-ether, 2:3) evaporated on the water-bath to a syrup, but without boiling. The residue is dried for 1 hour at 100°, cooled, and weighed. The weight in grams, multiplied by 1.111, gives the number of grams of glycerol in 100 c.c. of the wine.

(b) 50 c.c. of wine are heated on the water-bath in a large flask, 1 gm. of quartz sand added, also milk of lime until the dark colour at first produced disappears, and an alkaline odour becomes evident. After cooling, 100 c.c. of 96 p.c. alcohol are added, the precipitate filtered off and washed with alcohol. The filtrate is evaporated and treated as in (a). The factor 2.222 is necessary in this case to obtain the number of grams of glycerol in 100 c.c. of the wine.

A method of estimating glycerol in wine based upon its conversion into acetaldehyde by means of boric acid, the distilled aldehyde being determined by standard silver nitrate solution (Heiduschka and Englert, Zeitsch. anal. Chem. 1921, 60, 161).

For a process involving the use of acetone as solvent, see Beis, Bull. Soc. Chem. 1912, 11, [iv.] 618; Analyst, 1912, 37, 351; Bertainchand, *ibid.* 1913, 38, 368.

The sugar in wine is a variable mixture of dextrose and levulose, and occasionally sucrose. The usual method of examination consists in estimating the total quantity of sugar by titration with copper solution, then ascertaining by the optical method the proportions of the two glucoses and estimating the sucrose after inversion with hydrochloric acid.

Valuable information as to the nature and proportions of the sugars (both natural and added), as well as of other optically active substances introduced for the purpose of sophistication, may be obtained by the use of the polarimeter. Pure wine which still contains unfermented sugars turns the plane of polarisation to the left, whilst perfectly fermented wine either does not polarise at all, or only very slightly to the right. Wines sweetened with commercial glucose may contain considerable proportions of dextrorotatory non-fermentable substances.

It is essential to remove alcohol and colouring matters, and Nessler and Barth show that it is a matter of considerable importance also to remove the tartaric acid present in the wine, and they add, before precipitating with alcohol, a few drops of a strong solution of potassium acetate, thus separating the tartaric acid as potassium hydrogen tartrate.

The wine is carefully neutralised, and the alcohol eliminated by evaporation, the residue filtered, if necessary, and made up to original bulk, decolorized with lead acetate, the excess of lead removed with sodium carbonate or sulphate, and the polarimeter reading corrected for the increased volume due to these additions. The use of bone black should be avoided if possible, and complete decolorization is not necessary if the liquid is clear. Turbidity can be removed by the addition of alumina cream.

A complete scheme, based upon the German official methods (Veröffentl. d. Kaiserl. Gesundheitsamts, 1896, 20, 557) is given in Allen's

Commercial Organic Analysis, 1924, vol. i. 229. The results are obtained from observations in a 900 mm. tube, and expressed in terms of the sugar scale of the Schmidt and Haensch half-shadow saccharimeter.

For the estimation of sugar by Barreswill's (Fehling's) solution, the tannin must first be removed by lead acetate, the excess of lead being precipitated by sodium carbonate or sulphate. Ordinary fully fermented wine usually contains under 0.1 p.c. sugar, and may be decolorised by a small quantity of animal charcoal. Either the gravimetric method (weighing the precipitated copper as CuO) or the volumetric (using as indicator either potassium ferrocyanide or ferrous thiocyanate as recommended by Ling (Analyst, 1905, 182; 1908, 160)) may be used.

Sucrose may be determined by difference between the directly reducing sugars formed as just described, and the total reducing sugar after inversion with hydrochloric acid on the water-bath, deducting one-twentieth of the difference (invert sugar) thus found to obtain its equivalent as sucrose; or the Clerget polariscopic method may be employed, using Herzfeld's modification of the Clerget formula (*v. art. SUGAR*).

The shoots and leaves of the vine, as well as unripe grapes, contain both sucrose and dextrose. The quantity of sucrose in the grapes gradually diminishes to zero as the grapes ripen, whilst the quantity of dextrose reaches a maximum at the period of ripeness. Sucrose, when added to wine, is gradually converted into dextrose, an addition of 5 p.c. being no longer traceable after five months, and 8.5 p.c. being completely transformed in six months. Boiled grape juice contains a substance which, after hydrolysis with acids, reduces Fehling's solution, and might thus be taken for sucrose. No rotation of polarised light can, however, be detected, and the substance is probably glucosan. In the case of wines, therefore, which have been sweetened with boiled grape juice or coloured with caramel, it is unsafe to conclude, from the reduction of Fehling's solution, that sucrose is present unless its presence is also indicated by examination in the polarimeter (O. Klein, *Zeitsch. angew. Chem.* 1924, 37, 111; *J. Soc. Chem. Ind.* 1924, 43, B. 486).

Gum arabic and dextrin, which are sometimes used for sophisticating wines, may be detected by adding to a little of the wine about twice its bulk of the strongest alcohol. If a decided flocculent and viscous precipitate be formed the gum is obtained by evaporating 100 c.c. of the wine to about 5 c.c., and precipitating by the gradual addition of 90 p.c. alcohol. The precipitate is filtered off, dissolved in about 30 c.c. of water, 1 c.c. of strong hydrochloric acid added, and the liquid heated in a flask provided with a long glass tube as a reflux condenser for 3 hours on a bath of boiling water. The sugar thus produced is then estimated in the usual manner by Fehling's solution.

Tannin.—There is no very exact method for the estimation of tannin in wine. That of Neubauer-Löwenthal is recommended, and is described, with modifications, by Fresenius and Borgmann in 'Analyse des Weines,' 1922, p. 74.

Mineral matter is found by cautious incineration of the residue from the evaporation of 50 c.c. of the wine, taking the usual precautions for

separation of carbon from the alkaline salts. Rapid weighing is essential owing to the hygroscopic nature of potassium carbonate.

The determination of the ash (and of several other constituents) of wine containing much sugar is often facilitated and made more exact by eliminating the alcohol and removing the sugar by fermentation.

Wine containing less than 1.3 mineral matter per litre may be suspected unless it can be shown that natural wine from the same district and of the same vintage actually contains so small an amount of inorganic matter. The ratio of mineral matter to extract is, as a rule, about 1 to 10.

Estimation of chlorine in wine.—It is well known to wine falsifiers that chemists lay much stress on the proportion of mineral matters contained in wine, and therefore they frequently add sodium chloride to artificial or adulterated wines in order to increase the extract and to bring the total amount of ash up to the normal quantity. It is also said to hasten clarification and to have a preservative effect. Owing to the volatility of sodium and calcium chlorides on incineration, chlorine is best determined in the wine itself and not in the ash, but the ordinary method of titration is inapplicable owing to the solubility of silver chromate in the free acid of the wine. The chlorine is either precipitated and weighed as silver chloride, or the method of Nessler and Barth may be employed as follows:—50 c.c. of the decolorised wine are acidified with nitric acid, an excess of standard silver solution is added, and then standard thiocyanate solution is run in until a drop of the liquid when mixed on a plate with ferric sulphate solution just shows a pink coloration.

Wines containing more than 0.05 p.c. sodium chloride may as a rule be suspected. Exceptions may occur in the case of wines which have been produced in the neighbourhood of the sea-shore.

Alkaline earths in wine.—The ash of wine always contains calcium and magnesium salts. The amount of calcium (3–11.4 mg. in 100 c.c. of wine) is greatest in young wines and gradually diminishes with age, probably in consequence of the separation of neutral calcium tartrate. The amount of magnesium, on the other hand, remains almost constant and is always in excess of the calcium. The largest amount of magnesium found by Kayser was 24 mg. in 100 c.c. of Malaga wine. The phosphoric acid and magnesia show a constant proportion of 10 : 6, corresponding with the formula $MgHPO_4$ (Kayser, *Chem. Zentr.* 1881; 394; *Chem. Soc. Abstr.* 1882, 121).

Barium and strontium salts are sometimes added, to remove sulphuric acid, in the process of 'deplastering' wines, and are best detected in the ash, which should be taken up with dilute hydrochloric acid, filtered, and the filtrate evaporated to dryness. The dry residue is then examined by the spectroscope. If barium or strontium is present they are determined quantitatively in the usual manner.

Sulphuric acid is precipitated directly with barium chloride in wine acidified with hydrochloric acid, and determined in the ordinary manner.

A normal wine contains not more than 1.4 gm. K_2SO_4 per litre, and when the amount

exceeds 2 grms., the wine may be regarded as plastered or sulphured.

The determination of phosphoric acid is to be effected in the ash by the molybdc method. (For details, see J. Soc. Chem. Ind. 1898, 280.)

The total phosphoric acid may be determined directly (without incinerating the residue) by Grete's volumetric method (Ber. 1909, 42, 3106).

The addition of dicalcium phosphate is sometimes made instead of 'plaster,' and is said to have certain advantages over the use of gypsum.

Nitric acid is sought for by carefully adding a few c.c. of the wine to a solution of diphenylamine in (pure) concentrated sulphuric acid, without mixing, and avoiding rise in temperature. An intense blue colour at the junction of the liquids indicates the presence of nitric acid.

Fresenius (Zeitsch. anal. Chem. 28, 67) finds that in wines containing much sugar a loss of phosphoric acid takes place during the incineration of the residue. A higher result is obtained when the residue is deslagged with alkaline carbonate and nitrate. Destruction of the sugar by fermentation by addition of a very small quantity of yeast leads to the same result.

The assumption that the better kinds of wine always contain more phosphoric acid than the poorer ones is unfounded. At the same time the amount of the phosphoric acid can, in many cases, serve as a valuable means of ascertaining the character of a wine, especially of wines used for medical purposes, or of those of a particular district in which the amount of phosphoric acid varies between definite limits.

Examination for colouring matters.—The principal substances used in red wines are vegetable colouring matters, coal-tar colours (especially fuchsines), and cochineal. White wines are frequently coloured with caramel or coal-tar colours used as substitutes.

According to Jean and Frabot (Ann. Chim. anal. 1907, 12, 52), wines artificially coloured may be distinguished from natural wines by the following test. The wine (50 c.c.) is heated on a water-bath with a little formalin (1 c.c.) and hydrochloric acid (4 c.c.), and when a precipitate is formed the liquid is made alkaline with ammonia and the excess expelled by further heating. The liquid, on cooling and filtration, yields a colourless filtrate in the case of genuine wines, whilst artificially coloured wines yield a coloured filtrate.

(a) *Vegetable colours.*—These are derived chiefly from bilberries, black cherries, elderberries, hollyhock or rose-mallow, poke-berries (*Phytolacca*), indigo and lichens (archil, &c.), alkanet root, Campeachy, Pernambuco, and other dye-woods.

The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring matter of bilberries gives a blue precipitate; mallow and elderberries a green. The colour of *Phytolacca berries* differs from that of red wine by giving a red-violet lead precipitate (see also Lens, Zeitsch. anal. Chem. 1895, 635).

Alkanet-red, which, with Dupré's test (v.

infra), behaves very like the natural colouring matter of wine, is very easily taken up from its solutions by amyl alcohol. On adding to the amyl alcohol a solution of a few drops of olive oil or oil of almonds and evaporating off the alcohol, the oily residue (after washing with water) has a fine red colour, which, on saponification becomes a rich blue, or if the alkanna used was old, a green (Herz, Zeitsch. anal. Chem. 23, 637; Chem. Soc. Abstr. 1890, 311).

Beetroot juice is used in colouring wines for the purpose of concealing the presence of magenta. The absorption-bands of magenta are hidden by those of beetroot, but if a few drops of copper sulphate solution are added to the wine, the beetroot bands gradually vanish and the magenta spectrum becomes visible.

The fresh colouring matters of bilberries and wines are similar but not identical, and, according to H. W. Vogel (Ber. 21, 1746), they are readily distinguished by their absorption spectra after careful neutralisation with ammonia, or, better still, when they are treated with a trace of alum before addition of ammonia. (Care must be taken that the wine is not too concentrated or the ammonia in too great excess.)

Detection of logwood in wine.—When a solution of logwood is treated with manganese dioxide it becomes brown, and this brown liquid, by the action of zinc and hydrochloric acid, gives a colourless solution of hæmatoxylin. This may be detected by the ordinary reagents for that substance, alkalis and their carbonates giving a blue-violet coloration, calcium hydroxide a red-violet, stannous chloride or ammonium molybdate, in a solution slightly acid with nitric acid, a violet coloration. Advantage has been taken of this reaction for the detection of logwood in wines. 20 c.c. of the wine is agitated with 2 grms. finely powdered manganese dioxide, filtered, and the brown liquid treated with zinc and hydrochloric acid, which reduces the oxidised logwood colouring matter to hæmatoxylin. The solution is then divided into several portions, and tested with the reagents given above. Pizzi has examined wines to which other red colouring matters have been added, and although these yield brown solutions with manganese dioxide, the reduced solution does not give the hæmatoxylin reactions. Brazilwood is the only one which has any analogy to logwood, but here also there are differences (Chem. Soc. Abstr. 1881, 761).

Spaeth (Zeitsch. Nahr. Genussm. 1899, ii. 635; Analyst, 1900, 11) gives a table of reactions which may be found useful for the detection of the most commonly used vegetable colours.

(b) *Coal-tar colours.*—In most cases the presence of a coal-tar colour in wine may be recognised by the following methods:—

a. By shaking the filtrate, after with basic lead acetate, with amyl alcohol, or (i.) the wine itself, also (ii.) a portion of the wine acidified with sulphuric acid, and (iii.) a portion made alkaline with ammonia. In the latter case, excess of ammonia should be avoided, as, if more than 3 p.c., the amyl alcohol may remain colourless, although the wine contains a coal-tar colour. The amyl alcohol extract in (i.) and (ii.) may contain natural colouring matter of the wine, but if the colour remain unchanged by ammonia, the presence of a coal-tar colour may

be inferred. The amyl alcohol extract from (iii.) should be shaken up with water and the aqueous solution tested with ammonia or by the wool test.

b. By the wool test, using alum and sodium acetate as a mordant, and adding about 1 p.c. of potassium sulphate in solution.

c. By Cazeneuve's oxide test (Vierteljahrsschrift für Chemie der Nahrungsmittel, 1886, 90; Compt. rend. 102, 52).

The oxides employed are yellow mercuric oxide in the proportion of 0.2 grm. per 10 c.c. of wine; lead hydroxide, containing 50 p.c. of water, in the proportion of 2 grms. per 10 c.c.; and gelatinous ferric hydroxide, containing 90 p.c. of water, in the proportion of 10 grms. per 10 c.c.

Mercuric oxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, erythrosin, eosin J, methylene blue, Coupler's blue, and diphenylamine blue. It partially absorbs orange I., safranin, chrysoidine, chrysone, methyleosin, yellow II., red NN, red I., and Ponceau RR. It does not absorb the sulpho-conjugated derivative of rosaniline, Bordeaux red B, Ponceau R, Ponceau B, orange R, orange RRR, orange II., orange RR, tropæoline M, tropæoline II., yellow I., solid yellow, dinitronaphthol yellow, U. S. yellow.

Lead hydroxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, methylene blue, Coupler's blue, diphenylamine blue, and erythrosin. It differs from mercuric oxide in not absorbing the rosanilines, and also in absorbing the sulpho-conjugated derivative of rosaniline, Bordeaux red B, the purple red, and soluble red of rocelline.

Ferric hydroxide does not absorb erythrosin, the sulpho-conjugated derivative of rosaniline, Bordeaux red B, purple red, soluble red, and solid yellow. It absorbs the natural colouring matter and foreign vegetable colours, cochineal, and all the derivatives of rosaniline, except the sulpho-conjugated derivative.

Zinc hydroxides and stannous hydroxide behave similarly. The latter retains the natural colouring matter, but does not absorb cochineal or orchi. After the wine has been treated with the hydroxides, the colouring matters must be distinguished by special tests. If the wine is treated with magnesia and hot amyl alcohol, a number of blues which are precipitated by the above-mentioned hydroxides can be isolated and distinguished.

d. Shaking the wine with ether before and after supersaturation with ammonia.

Five to 6 c.c. of the wine to be tested are poured into a glass test-tube of about 20 c.c. capacity, and then three-quarters of its bulk of ether is added. After a few minutes the ether rises to the surface of the wine. If the ether be coloured yellow, and assumes, on addition of some drops of ammonia, a deep-red tint, Campeachy-wood has been used to colour the wine. If the ether becomes red and violet, and remains so even on addition of a large quantity of ammonia, the wine contains colouring matter derived from some of the lichens.

If the red-coloured ether loses its tint on mixing with ammonia, without passing into violet, then only the natural colouring matter of the wine is present. If the red-coloured

ether loses its red tint with ammonia, without imparting any colour to the latter, then fuchsin has been added to the wine. When the ether rises uncoloured, a fresh sample of the wine to be tested is taken, twice its volume of water is poured into it, and half its volume of ammonia added. If the wine now assumes a brownish-red colour, it contains cochineal; if, however, it turns green, then it can be assumed that none of the substances mentioned is present.

e. The formation of isonitriles when aniline derivatives are warmed with potash and chloroform serves for the direct determination in wine of even minute traces of many of the aniline colours. The evolution of the isonitrile is accelerated by adding excess of strong sulphuric acid.

According to A. Dupré, fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about $\frac{1}{2}$ -inch side. These cubes are made by dissolving 10 grms. of gelatin in 100 c.c. of warm water, and pouring the solution into a flat dish or mould; from the plate thus obtained the cubes are cut. After 24-48 hours the cube, on examination by transmitted light, will be found to be coloured more or less deeply by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of $\frac{1}{8}$ -inch at the most. The colouring matter of alkanet root also penetrates but slowly, whereas rosaniline, cochineal, logwood, brazilwood, indigo, litmus, red cabbage, beet-root, *Malva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly (Chem. Soc. Trans. 1880, 572).

The nature of the colouring matter may be determined either by the colour of the jelly or spectroscopically, or by the action of dilute ammonia, which turns cochineal purple, logwood brown, red cabbage dark green, and decolorises rosaniline (v. SPECTRUM ANALYSIS).

Bordeaux verdissant or 'colorant introuvable' is a mixture of acid fuchsin with methylene blue and diphenylamine orange, the two latter colours being used to produce a green which becomes visible on decolorising the Bordeaux red with ammonia, thus simulating the effect of ammonia on natural red wine. The diphenylamine orange can be extracted with amyl alcohol, the acid fuchsin detected by Girard's mercuric acetate test, and the methylene blue by dyeing cotton fibre.

A substance known as *Tintura por los vinos* is said to have been largely used for colouring certain Spanish wines. It is alleged to contain Biebrich red, sodium sulphate, and arsenious oxide. The presence of arsenic, if a fact, is of special importance.

The methods employed in the Paris Municipal Laboratory for the investigation of the colouring matters in wine will be found in Girard and Dupré's 'Analyse des matières alimentaires.'

Removal of added colouring matter from wine.—So much artificially-coloured wine is confiscated in certain districts in Italy that the authorities are considering the advisability, in the interests of economy, of merely removing the added colouring matter from the wine instead of denaturing the latter before returning it to the owners. For effecting this removal the following methods may be employed: (1) Addition

to the wine of must, thus causing a fresh alcoholic fermentation; (2) addition of young wine, the proteins of which may form insoluble compounds with the colouring matter; (3) clarification by means of egg albumin, fish glue gelatin, &c.; (4) keeping the wine for some time, with repeated transference. The colouring matter most commonly used is 'vinolin,' a mixture of Bordeaux B, Bordeaux R, and Poncau RRR, which may be eliminated by re-fermentation of the wine in presence of vinasse (F. Sourti, *Annali Chim. Appl.* 1923, 13, 194-200; *J. Soc. Chem. Ind.* 1923, 42, 993 A).

Detection and estimation of *preservatives* most commonly used in wine. *Abrastol* or *asaprol* (calcium α -monosulphonate of β -naphthol) is a white or slightly reddish scaly powder readily soluble in water and alcohol, and decomposing at 50°. It is extracted from alkaline solution by amyl alcohol, the extract evaporated to dryness, and the residue tested by Sinibaldi's method (*Mon. Sci.* 1893, [iv.] 7, 842; U.S. Dept. of Agric. Bur. of Chem. Bul. 59, 91).

Boric acid (according to Baumert, *Ber.* 21, 3290) is naturally present in many wines as well as in the leaves and tendrils of the grape-vine. It is detected in the ash by extracting with a large excess of strong hydrochloric acid, and testing with turmeric paper. For its quantitative estimation, see Windisch, *Die Chemische Untersuchung und Beurtheilung des Weines*, 235.

Fluorides are strongly antiseptic and are usually employed in very small quantity in the form of the ammonium or sodium salts which are soluble in water. The fluorine is precipitated as calcium fluoride from alkaline solution by means of calcium chloride, and the precipitate, after filtering, washing, drying, and heating in a platinum crucible, is tested by means of the 'etching' test. A blank experiment should be made with the reagents employed. For *fluoborates* and *fluosilicates* the ash containing the calcium salts is extracted with dilute acetic acid and filtered. The filtrate contains the boric acid which, if present, is detected as above. The calcium fluoride and silicate remain in the insoluble portion, and can be detected by the usual methods (*v. Bull.* 59, 63, U.S. Dept. of Agric. Bur. of Chem.).

For detecting *saccharin* (which is used as a preservative as well as a sweetening agent), the wine (about 100 c.c.) is shaken up with a mixture in equal parts of ether and light petroleum, and the extract, after evaporating off the solvent, is fused with sodium hydroxide and tested by means of ferric chloride for salicylic acid. It is assumed, of course, that the absence of salicylic acid in the original wine has been proved and the presence of saccharin indicated by the sweet taste of the residue from the ether extraction.

The estimation of the saccharin may be made by acidifying (if necessary) with phosphoric acid, extracting with ether as above, and fusing the evaporated residue with a mixture of sodium carbonate and nitre, precipitating the resulting sulphate with barium chloride and calculating the saccharin from the weight of barium sulphate obtained ($\text{BaSO}_4 \times 0.785 = \text{saccharin}$).

Saccharin may also be estimated by hydrolysing the residue from the ether extract with hydrochloric acid, and estimating the ammonia

thus formed by distillation into standard acid (Proctor, *Chem. Soc. Trans.* 1905, 242).

Salicylic acid is best sought for by agitating the wine with carbon disulphide or a mixture of equal volumes of ether and light petroleum (taking care to avoid an emulsion), evaporating down and testing the residue with ferric chloride. If much more than 100 c.c. are used, a faint colour may be occasioned by other substances giving a similar reaction and present as normal constituents of the wine.

An approximate estimation of the quantity of salicylic acid may be made colorimetrically, by comparing the colour given by an alcoholic solution of the residue after ether extraction with that yielded by standard alcoholic solution of salicylic acid of known strength, using, if possible, a liquid similar to that under investigation.

Sulphurous acid and sulphites.—Wine will absorb as much as 0.36 grm. of sulphurous per litre when it is shaken in a barrel in which sulphur has been burnt, and if the treatment is repeated the sulphurous acid may reach 0.5 grm. per litre. Sulphur is burnt in the barrels to prevent the formation of mildew, and sulphites are sometimes used as a preservative. Much of the sulphurous acid is combined with aldehyde when it is considered to be much less objectionable than in the free state.

Sulphurous acid is determined by distilling a portion of the wine, to which phosphoric acid has been added, in a stream of carbon dioxide, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed. The details of the method are as follows (*B. Haas, Ber.* 15, 154): the wine, to which 5 grms. of syrupy phosphoric acid have been added, is distilled in a current of carbon dioxide, and the distillate is collected in a suitable apparatus (a bulbous U-tube) containing 50 c.c. of iodine solution (containing 5 grms. pure iodine and 7.5 grms. potassium iodide per litre), thus oxidising the sulphurous acid. As soon as the distillate amounts to about half the original volume of the wine used, the contents of the U-tube are washed out, acidified with hydrochloric acid, precipitated with barium chloride, and the barium sulphate washed, dried, heated to redness, and weighed. This method gives very good results. The sulphurous acid may also be oxidised by means of hydrogen peroxide, using barium peroxide, and weighing as barium sulphate (Levi, *Ann. Falsif.* 1913, 6, 5; *Analyst*, 1914, 87).

Opinions vary as to how much sulphurous acid a wine may contain. According to the medical faculty of the University of Vienna, not more than 8 mg. per litre should be allowed, whereas other authorities regard 80 mg. as not an excessive amount. In France and Switzerland the maximum limit is fixed at 200 mg. of SO_2 per litre, of which, in France, not more than 30 mg., and in Switzerland, not more than 20 mg. should be 'free' or uncombined.

Poisonous metallic substances in wine.—Traces of arsenic may be present owing to the use of impure coal-tar colours (acid fuchsine, &c.), and commercial glucose. Copper and mercury may be due to the compounds used as insecticides and fungicides, but are, no doubt, largely removed in an insoluble form during the process of fermentation.

mentation. Lead has been traced to the use of litharge to mask acidity and to lead shot used for cleaning bottles. Zinc is often present in appreciable quantities when the wine has been stored in vessels of unalloyed zinc. These metals may be detected and estimated by the usual methods.

Hydrocyanic acid may be present in wine to which potassium ferrocyanide has been added to remove the iron. For its detection and estimation, see Mach and Fischler (Zeitsch. Unters. Nahr. Genussm. 1924, 47, 329; Reichard, *ibid.* 1924, 47, 339; Zeitsch. angew. Chem. 1924, 37, 957).

Alum is occasionally present in the coal-tar colours employed, and is sometimes added to wine as a clarifying agent, and to impart astringency, particularly to wines which have been diluted. The alumina may be estimated as follows (Louvet, Chem. Zentr. 1881, 252): 200 c.c. of wine are evaporated to dryness, the residue incinerated, and the ash fused in a platinum crucible with 3 grms. sodium carbonate, whereby the lime, magnesia, and ferric oxide are converted into insoluble carbonates. The mass is dissolved in water, and the solution filtered. As the solution may contain sodium aluminate, it is acidified with hydrochloric acid, treated with a large excess of sodium carbonate, and the alumina collected on a tared filter. The insoluble portion of the fused mass, containing the chief portion of the alumina, is fused with a few grams of pure soda, and the fused product digested with water and the solution treated for alumina as above described. The precipitates are collected, thoroughly washed, dried, ignited, and weighed. If any considerable proportion of phosphate is present, the phosphoric acid should be estimated and deducted from the total weight, the difference being Al_2O_3 .

Adulteration of wine.—Of the various processes already described which, strictly speaking, might be considered as 'adulteration,' some, as fortifying with spirit, sweetening with sugar, glucose, or glycerol and 'plastering,' are defended as legitimate trade practices of long standing or are officially tolerated within certain limits. Others, as dilution with water, the addition of antiseptics, astringents, colouring matters, and mineral acids, and of potassium hydrogen tartrate and cinnathic ether to give the fictitious character of age, have, as a rule, no other object than that of fraud.

In addition, wine is mixed with the juice of fruit other than the grape, and spurious wines containing no grape-juice whatever are made to simulate well-known types, as port, sherry, claret, and burgundy. The fruit basis of these is usually apple juice (v. p. 480), the other principal ingredients employed being crushed raisins, alcohol, sugar, tartar, flavouring essences, and colouring matters derived generally from the juice of such fruits as bilberry, elderberry, black currant, etc.

For the detection of dilution with water, fortifying with spirit, the addition of acids, tartar, glycerol, sugar, and other forms of sophistication of wines, reliance is placed in France and Germany upon the ratios which the respective principal constituents of the genuine wines of those countries bear to each other (e.g. in France, alcohol : extract (reduced) :

maxima and minima are adopted for the constants of genuine wines; but it does not necessarily follow that these can be accepted as standards applicable to the wines made in other countries and by different methods of manufacture. Whenever possible the suspected wine should be compared with a similar wine from the same district and vintage and known to be genuine. A concise and clear *résumé* of these constants and ratios will be found in Allen's Commercial Organic Analysis, 1924, vol. i. 242-7; see also Thudichum and Dupré's Treatise on the Origin, Nature, and Varieties of Wine; Windisch's Die chemische Untersuchung und Beurtheilung des Weines; Villiers et Collin, Traité des alterations et falsifications des substances alimentaires; Leach's Food Inspection and Analysis; and Post and Neumann's Traité complet d'analyse chimique appliquée aux essais industriels. J. C.

WINE GUM v. GUMS.

WINTER GREEN, OIL OF, v. OILS, ESSENTIAL, and SALICYLIC ACID

WITGATBOOM. The dried root of *Boschia Transvaalensis*, Pest., *B. rehmanni*; *Marrua pedunculata*, Sim.; and *Capparis albitrunca*, Burch. Used as a substitute for chicory in certain parts of South Africa. For the microscopic and analytical characters of the roots and their aqueous extracts, see McCrae and Klooh, Analyst, 1918, 373.

WITHANIA SOMNIFERA, a plant found in South Africa, on the west coast of India, and along the shores of the Mediterranean. The root contains an essential oil, a quantity of sugar yielding *d* phenyl-glucosazone (m.p. 210°); a black resin from which the following substances have been isolated: hentriacontane $C_{31}H_{64}$; a phytosterol $C_{27}H_{46}O$ (m.p. 135°-136°); palmitic, stearic, cerotic, oleic, and linolic acids; ipuranol $C_{22}H_{42}O_2(OH)_2$; a monohydric alcohol, *withanol*, $C_{22}H_{42}O_4.OH$, decomposing at 305°, and having $[\alpha]_D + 91.2^\circ$, and an amorphous alkaloidal principle, which, on treatment with alkalis, yielded a crystalline base, $C_{17}H_{19}N_3$ (m.p. 116°).

The leaves and stems contain, in addition, a monohydric alcohol, *somnirol*, $C_{22}H_{42}O_4.OH$, decomposing at 205°, and having $[\alpha]_D + 34.8^\circ$; a dihydric alcohol, *somnitol*, $C_{22}H_{44}O_4(OH)_2$, decomposing at about 250°, and having $[\alpha]_D + 21.2^\circ$; and an acidic hydrolytic product, *withanic acid*, $C_{22}H_{42}O_5.CO_2H$ (m.p. 226°), the methyl ester of which decomposed at 255° (Power and Salway, Chem. Soc. Trans. 1911, 99, 490). These authors were unable to confirm the sedative and hypnotic properties attributed to this plant.

WITHERITE. Native barium carbonate ($BaCO_3$) crystallising in the orthorhombic system and isomorphous with aragonite and cerussite. The crystals are, however, invariably twinned, giving rise to pseudo-hexagonal forms; these may be either lenticular or pyramidal in habit, and in the latter case the six-sided pyramids present a certain degree of resemblance to crystals of quartz. Globular aggregates and compact fibrous masses also occur. The colour is white or grey; sp. gr. 4.3; H. 3½. The mineral occurs in some abundance in the lead-bearing veins traversing limestones, &c., at several places in the north of England and

on the borders of Shropshire and Montgomeryshire. It has been formed, in some instances at least, by the action of carbonated waters on barytes (L. J. Spencer, *Min. Mag.* 1910, 15, 310); and it is itself sometimes altered to barytes, as shown by the pseudomorphs of barytes after witherite. The best known locality, which has yielded many finely crystallised specimens, is the Fallowfield mine near Hexham; whilst the largest quantity (about 8000 tons per annum) is produced by the Settling-stones mine also in Northumberland. The mineral is also known from a few foreign localities, but only in small amounts.

Witherite is used in the manufacture of plate glass and porcelain, and for the preparation of barium dioxide (used in the manufacture of hydrogen peroxide), barium hydroxide (for refining beet-sugar), and barium salts (used, e.g. for giving the green light of fireworks). The mineral is also used for the preparation of the finer quality of barium sulphate ('blanc-fixé') used for facing glazed papers. The addition of a small proportion of witherite to clay (1 oz. per cwt.) in brick making prevents any efflorescence and discoloration due to soluble sulphates. Although insoluble in water, it is poisonous, since it is readily acted upon by the gastric juice; and the powdered mineral, mixed with meal, is used as rat poison.

References.—Special Reports on the Mineral Resources of Great Britain, *Mem. Geol. Survey*, 2nd ed. 1916, vol. ii; Barium Minerals (1913-1919), Imperial Mineral Resources Bureau, London, 1921. L. J. S.

WITT'S RULE *v.* COLOUR AND CHEMICAL CONSTITUTION.

WOAD (*Vouède*, *Pastel*, Fr.; *Waid*, Ger.). This commercial product is a dark clay-like preparation made from the leaves of the woad-plant, *Isatis tinctoria* (Linn.), an erect, herbaceous, biennial plant, belonging to the *Cruciferae*, bearing yellow flowers, small flat elliptical pods, and large smooth lanceolate or spatulate leaves.

The term 'woad' is derived from the Saxon 'wad,' which it has been suggested is derived from Woden, the Saxon God of War. It is synonymous with the Gallic *glastum*, with which, according to Pliny, the ancient Britons dyed their skin blue, in time of war and in connection with certain religious observances.

The plant is a native of Southern Europe, and from very early times has been employed in dyeing blue, for which purpose, previous to the introduction of indigo from India, it was largely cultivated in various parts of Europe—e.g. Thuringia, Languedoc, Piedmont, &c. Its cultivation has now declined almost to the vanishing-point.

In this country woad is now only grown, to a very small extent, in the fen lands of Lincolnshire and Huntingdon. The seed is sown in the early spring, March or April, and the young plants having been duly thinned and weeded, the leaves are ready for the first plucking in June, which, at intervals of five or six weeks, is repeated once or twice, or as often as fresh leaves shoot up.

The newly-gathered leaves are at once crushed or ground in edge-runner mills to a pulp, which is then placed in small heaps, to

drain, till sufficiently dry to cohere and be submitted to the 'balling' process. This consists in working the pasty mass by hand into balls, 4-6 ins. in diameter. These are at once spread out on wicker-work trays or 'fleaks,' and thoroughly dried in well-ventilated sheds. The balls are stored in a dry airy place till the whole crop has been gathered, and are then submitted to the so-called 'couching'—i.e. a fermentation—process. For this purpose the balls are ground to a coarse powder, which is spread on the floor of the couching-house to a depth of 2 or 3 feet, and there reduced again to the consistency of a paste by frequent sprinkling with water and turning over with shovels. During this process, which lasts from twenty to forty days, the mass becomes heated, and abundant offensive odours are given off. The operation needs to be conducted with some care and skill, so that the fermentation is neither so slow that a 'heavy' product is obtained, nor so rapid as to give one which is 'foxy.' When the fermentation has subsided, and the stiff, pasty mass is sufficiently cooled, it is packed in casks ready for the market.

It has been calculated that 9 parts by weight of woad leaves yield one part of the prepared product.

Although woad was formerly used for the indigo contained in it, it is at present only employed for the purpose of exciting fermentation in the indigo-vat ordinarily used by the woollen dyer, which is therefore termed the 'woad-vat.'

According to Wendelstadt and Binz (*Ber.* 1906, 39, 1627) woad contains two distinct micro-organisms, one of which under suitable conditions appears to be able to reduce indigo.

Spurious woad was sometimes prepared from the leaves of the rhubarb, cabbage, &c., but these products were very inferior to the true woad.

The colouring principle of woad leaves, considered by Schunck to be identical with that present in the *Indigofera*, is now known to be a distinct substance. This has not been isolated in a pure condition, but in its general reactions resembles indoxyllic acid (*see* INDIGO, NATURAL).

Other Literature.—Chevreul, *J. Pharm. Chim.* 1808, 66, 369; 1817, 350; *Ann. Chim.* 68, 284; Gilbert, *Annalen*, 41, 245; 42, 315; Trommsdorff, *J. Pharm. Chim.* 19, 93; Paris, *Mus. Hist. Nat.* Ann. 18, 251. A. G. P.

WÖHLERITE. Silicate, zirconate, columbate, and fluoride of calcium and sodium with the approximate formula $\text{Ca}_{10}\text{Na}_2\text{Si}_{10}\text{Zr}_2\text{Cb}_2\text{F}_{10}\text{O}_{11}$, and containing ZrO_2 15-23 p.c. The monoclinic crystals have the form of rectangular plates of a honey-yellow colour; sp.gr. 3.4; H. 6; decomposed by hot strong hydrochloric acid with separation of silica and columbic oxide. The mineral is usually regarded as a member of the pyroxene group. It occurs in nepheline-syenites in the Langesund-fjord in the south of Norway, in the Los Islands off the coast of French Guinea, and at Red Hill in New Hampshire; and in nepheline-phonolite in Haute-Loire, Auvergne. L. J. S.

WOLFRAM *v.* TUNGSTEN.

WOLFRAMINE *v.* TUNGSTITE.

WOLFRAMITE or **WOLFRAM.** A mineral.

consisting of iron and manganese tungstate ($(\text{Fe}, \text{Mn})\text{WO}_4$), crystallising in the monoclinic system. The name *ferberite* is applied to the members at the iron end of the series (FeWO_4), and *hübnerite* to those richest in manganese (MnWO_4). With this wide difference in composition the percentage of tungsten varies only slightly (WO_3 , 76.3–76.6 p.c.; analyses of the pure mineral show 74–77 p.c.). The mineral fuses readily before the blowpipe to a black, magnetic bead; and it is decomposed by *aqua regia*, with the separation of yellow tungstic oxide. Distinctly formed crystals are rare, but cleavage masses are of common occurrence. There is a perfect cleavage in one direction, parallel to the plane of symmetry. The mineral is opaque with a bright, sub-metallic lustre and a dark brown to black colour; the streak is dark reddish-brown to black; H. 5½. The high sp.gr. (7.2–7.5) and the lath-shaped cleavages are characters which assist in the identification of the mineral; while the latter character helps to distinguish it from other heavy black minerals. The name wolfram originated with the old German miners, and means, apparently, 'wolf froth,' since Agricola (1546) refers to the mineral as *lupi spuma*.

Wolframite usually occurs in veins traversing granitic rocks, and is often associated with tin ore. It is, in fact, obtained commercially mainly from tin mining districts; and formerly, before the mineral was of value, it was a source of trouble to the tin miner, since having about the same density as cassiterite it could not be separated from the ore by the ordinary mechanical methods. At one time it was eliminated in a soluble form by fusing the ore with soda (Oxland's process); but now it is extracted by the electromagnet (wolframite being weakly magnetic), and it forms a product as valuable as the tin ore itself. The principal wolfram-producing countries, arranged approximately in the order of their outputs, are: Lower Burma (at Tavoy), United States (Black Hills in South Dakota, Boulder and Gilpin counties in Colorado, Arizona, Nevada, &c.), Portugal, North Queensland (at Wolfram Camp, &c.), Bolivia, Peru, Argentina, Spain, England (Redruth, Bodmin Moor, and Gunnislake in Cornwall; Carrock Fell in Cumberland), France, Rhodesia, Siam, and New Zealand.

The mineral is used mainly for the manufacture of ferro-tungsten and the hard and tough tungsten-steel for tools and magnets of magnetos, and of some other alloys (e.g. 'partinum,' an alloy of tungsten and aluminium). Metallic tungsten is used as the filament of the so-called 'osram' electric lamps; as contacts for magnetos in place of platinum; and as a catalyser in the synthesis of ammonia. Wolframite is also used for the preparation of sodium tungstates and other salts.

References.—R. D. George, 1st Rep. Colorado Geol. Survey (1908), 1909 (with bibliography); G. P. Merrill, *The Non-Metallic Minerals*, 2nd ed. New York, 1910; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 1911; Special Reports on Mineral Resources of Great Britain, Mem. Geol. Survey, 2nd ed. 1916, vol. i.; F. L. Hess, *Tungsten Minerals and Deposits*, Bull. U.S. Geol. Survey, 1917, No. 662; T. L. Walker, Report on the Tungsten Ores of Canada, Dept. Mines,

Ottawa, 1909, No. 25; L. Hills and L. L. Waterhouse, *Tasmania Geol. Survey, Min. Res.* 1916, No. 1; L. C. Ball, *Geol. Survey, Queensland*, 1916, Nos. 248, 251; R. H. Rastall, *The Genesis of Tungsten Ores*, *Geol. Mag.* 1918, 194, 367; Occurrence and Utilisation of Tungsten Ores, Bull. Imp. Inst. London, 1909, 7, 170, 285; J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy, and Uses of Tungsten*, with special reference to the Black Hills of South Dakota, Bull. South Dakota School of Mines, 1918, No. 12, 264 pp.; R. H. Rastall and W. H. Wilcockson, *Tungsten Ores*, Imp. Inst. Monographs, London, 1920; *Tungsten (1913–1919)*, Imp. Mineral Resources Bureau, London, 1921. L. J. S.

WOLLASTONITE. Calcium metasilicate CaSiO_3 , crystallised in the monoclinic system, and belonging to the pyroxene group (*q.v.*) of rock-forming minerals. It differs, however, from the other members of this group in the directions of its cleavages, which are here along two planes perpendicular to the plane of symmetry and inclined to one another at $84^\circ 37'$. The mineral is white and opaque, sometimes with a pearly or silky lustre; sp.gr. 2.88–2.92; H. 5; decomposed by hydrochloric acid with separation of silica. It is a mineral of metamorphic origin, occurring in siliceous limestones that have been baked by intruded masses of igneous rocks. Bladed crystals are found in the limestone blocks ejected by Vesuvius, and large crystals, up to 10 inches in length and partly or wholly altered to quartz and opal, at the Santa Fé mine, in Chiapas, Mexico. Here, as is often the case elsewhere, the mineral is associated with bodies of metalliferous ores (H. F. Collins, *Min. Mag.*, 1903, 13, 356). The name wollastonite is after William Hyde Wollaston (1766–1828).

When heated, wollastonite changes at 1190° into the β -modification called pseudo-wollastonite (m.p. 1540°), which has been long known in slags and devitrified glasses under the name hexagonal calcium metasilicate. The latter has not been observed in nature, and the presumption is that wollastonite has been formed in contact-metamorphic limestones at a temperature below 1190° (E. T. Allen and W. P. White, *Amer. J. Sci.* 1906, 21, 89; 1909, 27, 1; A. L. Day and R. B. Sosman, *ibid.* 1911, 31, 341).

L. J. S.

WONGSKY, WONGSHY, WONGSCHY, HOANG TCHY. A Chinese yellow dyestuff. It consists of the fruit of the *Gardenia grandiflora*. According to Rochleder (J. 1858, 475), it contains *rubichloric acid* (see **MADDER**) and *crocin*, the glucoside of *Crocinin*, which is also present in saffron (*Crocus sativus* (Linn.)). Wongsky dyes aluminium and tin mordanted fabrics a yellow, whereas with iron mordant an olive colour is produced.

WOOD APPLE GUM v. GUMS.

WOODBURYTYPE v. PHOTOGRAPHY.

WOOD, DESTRUCTIVE DISTILLATION OF.¹ Wood completely freed from water has the following composition:—

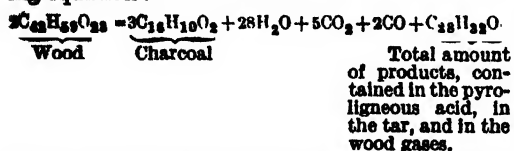
Carbon, 50 p.c.
Hydrogen, 6 p.c.
Oxygen, 42.75 p.c.
Ash, 1.25 p.c.

¹ *W. Klar Technologie der Holzverkohlung*, 1912

The chemical nature of wood may be said to consist principally of cellulose, lignin, water, and of ash-forming materials.

The lignin in wood may be oxidised and removed by treatment with chlorine dioxide (Schmidt and Graumann, *J. Chem. Soc. Abstr.* 1921, [I.] 912; A. C. von Euler, *Cellulosechem.* 1923, 4, 109; *Chem. Soc. Abstr.* 1924, 126, [ii.] 129).

If wood is heated in a closed vessel with the air partly or entirely excluded and the vapours and gases are allowed to escape, the cellulose and lignin molecules are broken up by processes, the nature of which is little understood, but which are characterised by the formation of charcoal, which is left as a residue, and by the formation of gases and vapours, the latter of which, when condensed, is known as pyro-ligneous acid. P. Klason, Heidenstam and Norlin¹ concluded that the destructive distillation of wood may be represented by the following equation:—



They proved further that the destructive distillation of cellulose forms the most important products, viz. charcoal, acetic acid and tar; whilst lignin forms principally charcoal, acetic acid, wood alcohol and tar.

The destructive distillation of wood is occasionally carried out for the purpose of producing charcoal only, but at present it is more frequently the case that the by-products, acetic acid and the wood alcohol, are the most important substances yielded.

As regards the value of various kinds of wood for the process of destructive distillation, it has been shown that hard woods give the best yields of charcoal, acetic acid, and wood alcohol, whilst soft woods give smaller amounts of these products. Soft woods, however, show a larger yield than pine wood, which yields, besides the above-named products, a certain amount of turpentine, pine oils and pine tar oils. Local market conditions must decide in each case what is the most desirable wood for the purpose.

All wood for destructive distillation is split into cord-wood averaging 6 ins. in diameter and 4 ft. long. This initial preparation is usually carried out in the forest, but at manufactories recently erected in the United States large logs are brought to the saw mill where all the timber is utilised, and only those logs unfit for other purposes are used for cord wood. The cord wood is stacked in an exposed situation if possible, where it is allowed to dry and season for about 18 months, after which the moisture content will be found to be quite constant. The length of time required for this seasoning varies with the climate, and although it is thought that the moisture content of 20 p.c. is the most desirable, it is frequently found necessary to use wood containing 30 p.c. or more. A high percentage of moisture in the wood is undesirable owing to the fact that it delays the distilling process, decreases the

yields of acetic acid, wood alcohol and charcoal, whilst at the same time it increases the amount of noncondensable gases and also the amount of fuel used for the purpose of supplying heat for the distillation.

The process of destructive distillation is carried out in closed vessels built of brick or iron, and heated either by allowing the products of combustion to come directly in contact with the wood, excluding any excess of air; or by transmitting the heat through the walls of the vessel. In either case the distilling apparatus is connected with a condenser, the purpose of which is to condense the vapours formed during the reaction.

The apparatus for the destructive distillation of wood may be said to consist of three principal parts:—

- 1st. The container for the wood.
- 2nd. The arrangement for generating and supplying the heat to the container.
- 3rd. A condenser connected with the container by an intermediate vapour pipe.

After the wood has been placed in the distilling apparatus and the heating started, the water contained in the wood is first driven off; when this is accomplished the destructive distillation of the cellulose and lignin begins and will be indicated by the formation of non-condensable gases and by the appearance of the so-called pyro-ligneous acid, a brown liquor of characteristic odour, in which considerable tar is found. When the temperature reaches 270° an exothermic reaction sets in which supplies most of the heat necessary for the distillation process. The end of the process will be indicated by the cooling of the pipe which connects the distilling apparatus with the condenser.

In carrying out this distilling process on a commercial scale, the three phases of the distillation, namely: the expulsion of the water, the heating of the wood to the point at which the exothermic reaction sets in, and the completion of the process by means of the above-named reaction, will not necessarily take place consecutively, owing to the fact that the large-sized apparatus used will not allow the heat to be transmitted uniformly to all the wood in the vessel. Hence part of the wood situated near the heating surface may be in the third phase of the process, whilst that not so near the source of heat may be still in the first phase.

In general, yields of various products from air-dried hard wood in percentage by weight will be as follows:—

Charcoal, 25 to 27 p.c.

Crude pyro-ligneous acid, 45 to 50 p.c.

Gases, 25 to 28 p.c.

The composition of the charcoal will be variable, depending upon the process used and particularly upon the temperature at which the distillation has been finished. The following table gives the composition of charcoal produced by several processes:—

Process	P.c. O	P.c. H	P.c. O+N	P.c. ash	Tempe- rature
Old 'Meller' process	90.36	8.74	5.72	1.1	above 300°
Kilm process	84.18	5.22	11.72	0.78	400°
Retort process	81.15	4.24	13.64	0.78	500°

¹ Ark. Kenn. Min. u. Geol., 1908, Bd. 3, 2.

The *crude pyroligneous acid* will be found to be composed chiefly as follows:—

Water, 81 p.c.

Wood alcohol, 3 to 4 p.c.

Acetic acid, 6 to 8 p.c.

Dissolved and suspended tar, 7 p.c.

Other compounds contained, such as aldehydes, ketones, allyl alcohol, amines, phenols, and hydrocarbons are not of commercial importance and are of interest only in the refining of wood alcohol. The wood tar obtained from hard wood has little commercial value and is generally used as fuel. Small amounts, however, are used for the manufacture of creosote and wood tar pitch.

The *non-condensable gas* obtained by the destructive distillation of wood, amounting to 25–28 p.c. of the weight of the wood, varies in composition during the different phases of the process, and is composed on an average of carbon dioxide, 60 p.c.; carbon monoxide, 30 p.c.; hydrogen and hydrocarbons, 10 p.c. This gas is generally used for heating the retorts or boilers, and its heating value is equivalent to about 4–5 p.c. of the heating value of the wood decomposed in the process of distillation.

DESTRUCTIVE DISTILLATION OF PINE WOOD

The destructive distillation of pine wood containing rosin and turpentine, besides the cellulose and lignin, will produce products

different from those obtained from hard wood. The turpentine being volatile with water vapour is almost completely distilled over during the first phase of the distillation. In this phase, also, the rosin melting and flowing from the wood cells, covers the surface of the wood and the bottom of the distillation retort. During the second phase, this rosin will be decomposed, yielding such products as pinoline, rosin oils, and a residue of rosin coke. The pinoline will be mixed, more or less, with the turpentine originally contained in the wood, the rosin oils will combine with the tar formed in the usual course of wood distillation, and the rosin coke will be mixed with the charcoal. The mixture of turpentine and pinoline is known as crude wood turpentine. The presence of the rosin oils in the pine wood tar gives it a peculiar orange colour when painted on wood, which property makes it of considerable value. The amounts of acetic acid, wood alcohol and charcoal obtained from pine wood are considerably less than in the case of hard wood distillation.

An active demand for wood turpentine, for pine wood tar and pine wood tar oils, with good prices for these products and cheap prices for the wood, may cause, under certain circumstances, pine wood to be preferred to hard wood. But these conditions will not be frequent, and since the yields of acetic acid and wood alcohol and also of charcoal are considerably less, as the container can be filled with a larger weight

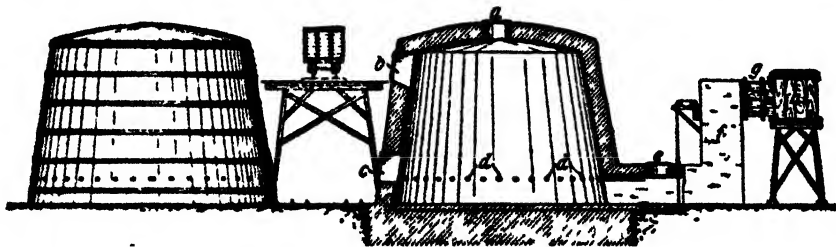


FIG. 1.

Brick wood-distilling apparatus for an 80-cord charge heated by burning a portion of the charge.

of hard wood than of pine wood (on account of the lower specific gravity of the latter), the efficiency of a distilling plant using hard wood is higher than one of the same size employing pine wood.

VARIOUS FORMS OF DISTILLING APPARATUS FOR CORD WOOD.

The number of forms of apparatus actually used for this purpose is large, and still larger is the number of designs which have been described in the literature or by patents taken out in different countries.

Only the most important types in practical use are given in what follows.

I. Distilling Apparatus made of Brick.

a. *Charring of the wood in brick kilns by fire gases which come directly in contact with the wood.*

1. *Fire gases generated inside the distilling apparatus by burning a part of the charge.*—To this type belongs the so-called 'American kiln,' seen in Fig. 1. This apparatus consists of a brick chamber, of about 15,000 cub. ft. capacity,

holding 80 cords of wood filled in by a top iron door *a*. There is a bottom iron door provided for discharging the charcoal. 4 ins. \times 4 ins. air inlet holes *d, d* are provided in the lower parts of the wall, and a couple of these kilns are connected by a brick goose neck *e* with the main smoke pipe, mostly built of wood. This main smoke pipe connects the kilns with the condenser plant *f g h*, and a fan is used for transporting the vapours and the gases from the kilns to the condensers and also for supplying the kilns with a certain amount of air, sufficient to generate the heat required for the destructive distillation of the wood by burning a certain amount of the wood, but avoiding any excess of air.

In the large plants at work in Michigan, often as many as 80 kilns are connected with condensers, using as much as 250 cords of wood per day, and condensing up to 50,000 gallons of crude pyroligneous acid. Unfortunately these kilns do not afford the proper amount of volatile by-products (acetic acid and wood alcohol) and about 50 p.c. of the possible yield is lost by being burnt to carbon dioxide and water. These kilns should only be used when wood is very

fuel and labour prices high and when there is not much demand for calcium acetate and wood alcohol. As these conditions seldom coexist, the kiln system must be considered wasteful and should be no longer used.

2. *Fire gases are generated outside of the distilling apparatus by fuel (mostly wood) in a special fireplace and conducted from there to the wood*—

2 represents such a type, originally known

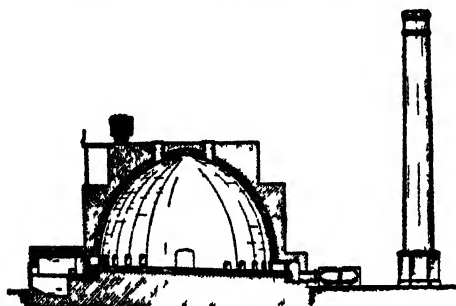


FIG. 2

Brick wood-distilling apparatus according to Schwartz heated by a special open fire

as the 'Schwartz kiln'. The Swedish kilns of Ljungberg and of Ottelumska are of a similar type.

b. *Heating the wood in brick kilns by fire gas which, passed through radiators, transmits the heat by radiation to the wood*

Inside a brick chamber, cast iron or steel radiators are provided, through which fire gases are passed, which transmit the heat by radiation to the wood surrounding these radiators.

The oldest type of this kind of a wood distilling apparatus is represented by the 'Reichenbach kiln.'

Sweden developed a new form of this type called the 'Tube Oven,' seen in Fig. 3

These brick kilns do not permit the charcoal to be discharged immediately after the distillation is finished. In fact, every hok of the oven

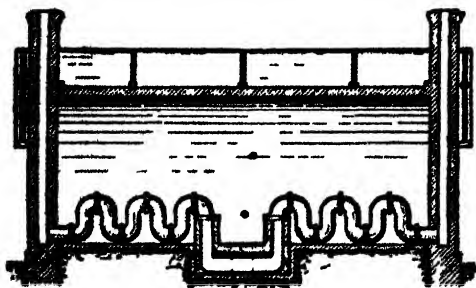


FIG. 3

Brick wood-distilling apparatus heated by steel coil radiators

has to be closed by bricks so as to allow the charcoal to cool with absolute exclusion of air. This cooling process requires, in the case of large sized kilns (50 cords or more), as much as eight days, and the efficiency is decreased correspondingly. In order to discharge the charcoal from kilns heated by radiators, immediately after the close of the distillation, the wood must

be loaded on iron cars capable of being pulled or pushed into the brick container. After the distillation is finished the cars, loaded with hot charcoal, are pulled out quickly and transferred to a steel chamber of the shape of the brick container, when cooling will not require more than 24 to 48 hours. After the cars are withdrawn, other cars, already loaded with new wood and ready for charging, will be put into the brick chamber, still hot by the previous operation.

These brick kilns, heated by radiators, charged and discharged by iron cars, are the newest form of brick distilling apparatus.

A distilling apparatus built of brick is cheaper to build and possibly cheaper to maintain, but gives lower yields than steel apparatus as regards acetic acid and wood alcohol

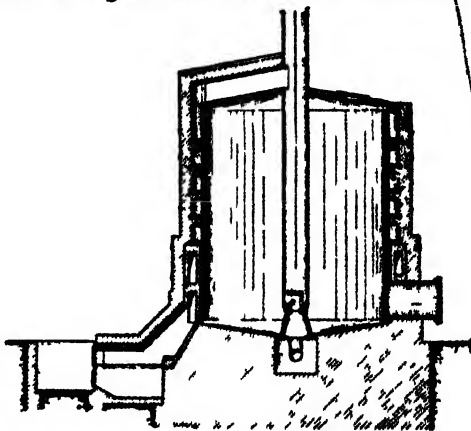


FIG. 4

Vertical steel wood distilling apparatus for large charges, heated by fire gases circulating around the steel container, called 'Carboven', used in Sweden

on account of the difficulty of preventing the brick walls from leaking

II. Steel Distilling Apparatus.

A. Intermittently operated apparatus.

The most important representative of this type is the Swedish 'Carboven,' shown in Fig. 4. This apparatus can be loaded with 100 cords of wood, and will require about three weeks for filling, distilling, cooling and discharging.

A couple of inner vertical heating tubes, instead of one large one, is the characteristic feature of the homie steel distilling apparatus,

B. *Apparatus for discharging the charcoal immediately after the close of the distillation without cooling the charcoal before discharging.*

1. *Horizontal types*—a. *Apparatus for small charges.*—To these belong the distilling apparatus, generally called 'rotorts,' largely used in the past and still employed in Germany, Austria, Russia, Pennsylvania, and other countries or states. These rotorts are about 30 ins. in diameter by 10 ft. in length, are round in section, and contain $\frac{1}{2}$ cord wood. But they are also built for one cord capacity. Usually, one pair

WOOD, DESTRUCTIVE DISTILLATION OF.

These retorts is heated by the same fireplace, the products of combustion being conducted around the horizontally placed steel cylinders. One side of the retort is provided with a cast-iron door, the other tight end with a nozzle which serves to connect the retort with a condenser (see Fig. 5).

The wood is loaded by hand into these retorts. Inside the retort there is a semi-circular scraper, which is pushed to the rear before the retort is loaded and is provided with a rod with a handle ending near the door. After

the distillation is finished, a steel container is placed underneath the front of the door. The door is opened, and by means of the scraper the hot and burning charcoal is quickly emptied into the steel container, the cover of which is then closed air tight. A new charge is loaded immediately after discharging. While the new charge is distilling, the charcoal cools inside the container, which is built of thin sheet steel.

As one of these 39 ins. \times 10 ft. retorts can handle only $\frac{1}{2}$ cord of wood in 24 hours, this type of distilling apparatus is not well adapted for

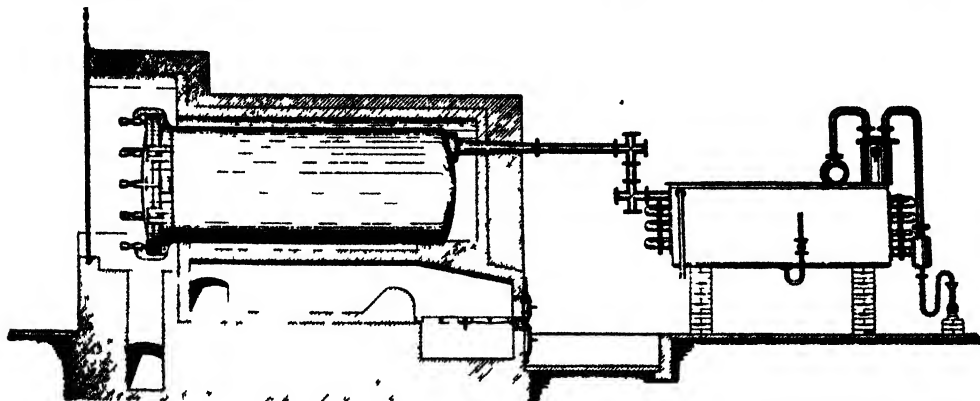


FIG. 5

Horizontal steel retort for small charges; type, F. H. Meyer, Hanover-Hainholz.

the destructive distillation of wood on a large scale.

These small, horizontal retorts have the further disadvantage that the scraper used in discharging them causes much of the charcoal to be broken into small pieces. The charging of the retort by hand also requires many workmen, causing loss of time and decreasing the efficiency of the plant.

B. Wood distilling apparatus for large charges arranged for mechanically charging and discharging —The disadvantages above mentioned may

be avoided by employing retorts of large capacity, provided with mechanical contrivances for filling them with wood and also for discharging the charcoal. The distilling apparatus which meets these conditions best is the so called 'car retort.' A distilling apparatus of this kind consists of a horizontal steel retort, capable of working off a charge of 6 to 10 cords of wood (see Fig. 6). The wood is loaded on cars which are pulled or pushed into the retort; this has rails on the bottom and, according to its capacity, one or two doors for filling and

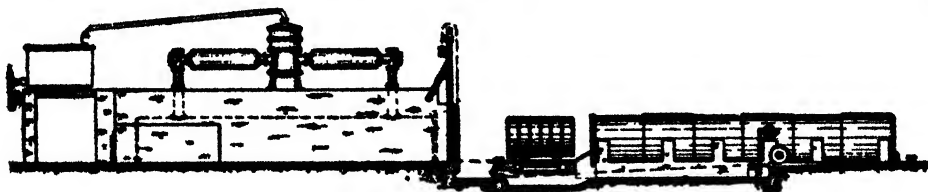


FIG. 6.

Horizontal steel retort, filled and discharged by cars; for charges up to 10 cords; type, F. H. Meyer, Hanover-Hainholz

discharging. Each car, made of steel, contains usually two cords of wood. The retort is connected by necks with one or two condensers of the usual tube type. The heating of these retorts is mainly effected by an open wood or coal fire and, to some extent, also by burning the tar and the gases obtained in the destructive distillation of the wood. The combustion gases travel by flues round the retort and escape in a smoke stack. The heating by an open fire has lately been replaced by producer-gas, obtained either in the usual way, that is generated by gas producers, or as a by-product in

the destructive distillation of the wood. A gas-heated retort will last longer, will use less fuel, and will yield higher results. The question of the best kind of gas producer for this purpose is dealt with later. After the distillation is finished the doors of the retort are opened and the cars, containing the hot charcoal, withdrawn and transferred as soon as possible to a horizontal steel cylinder, exactly corresponding in shape with the retort and also provided with doors for filling and discharging. The withdrawal of the cars is mostly done by means of a locomotive or by means of transportable electric

or steam hoists, and has to be done quickly in order to avoid the combustion of the charcoal. After the cars containing the hot charcoal are transferred to the horizontal steel cylinder, placed opposite the retort, the doors of the cylinder are closed air tight and the charcoal allowed to cool with exclusion of air. The cooling requires, according to the weather and character of the wood, from 24 to 40 hours.

This kind of wood-distilling apparatus further allows of the preliminary heating of the wood before filling it into the retort, by means of the waste combustion gases, which escape from the last retort flue into the smoke stack. In order to utilise this waste heat, the cars loaded with the wood are placed in a brick channel located opposite the charging door of the retort. The waste combustion gases are driven over the wood by means of a fan.

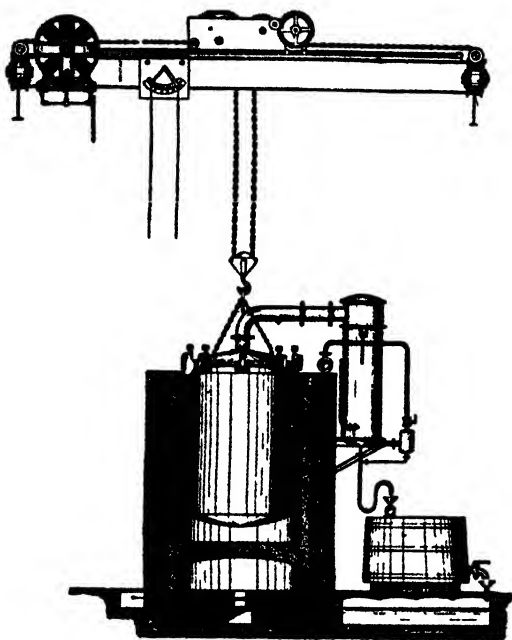


FIG. 7.

Vertical transportable retort; type, F. H. Meyer, Hanover-Hainholz.

Fig. 6 shows a modern distilling apparatus, having a higher efficiency than any other wood-distilling apparatus in practical operation.

A charge of 10 cords of wood is worked off in 24 hours, including filling, distilling and discharging, and it requires also very few workmen to attend to the firing, charging and discharging. By discharging the charcoal in a cold state and without the use of scrapers, a better class charcoal is obtained with the production of only a very small amount of powder or small pieces.

A revolving retort of a capacity corresponding to a charge of 6 to 10 cords of wood has been tried but discarded on account of the difficulty of contriving proper outlets and of keeping these outlets tight. Moreover, revolving retorts gave, of course, large amounts of charcoal powder and small charcoal.

2. *Vertical steel retorts.*—Vertical steel retorts, either built stationary or transportable, are in use in Germany, Belgium, France, Italy,

and also in Russia. France, in particular, is the country of vertical retorts, which are almost always constructed as transportable ones. These retorts contain a charge of 1 to 1½ cords of wood and are heated by an open fire or by a gas fire from underneath (see Fig. 7). They are filled outside of the settings, after being placed in a horizontal position. After the retort is loaded and closed it is lifted, by means of a travelling crane, above the open space in the settings to which the retort belongs. Then the retort is lowered into its place and its cover connected, by means of a copper goose-neck, with the condenser. After the distillation is finished, this copper goose-neck is taken off, the goose-neck hole in the cover closed, and then the whole retort is lifted out of the settings by means of the crane and transported outside of the building, placed in a horizontal position and then allowed to cool down, which will require from 12 to 24 hours, according to the charge and the weather. These retorts give good yields and afford good charcoal, but their efficiency is so good as that of the car retorts already described.

Sometimes these vertical retorts are constructed stationary and provided with a charcoal discharging door on the bottom. They are not as convenient as the transportable ones and do not give the same quality of charcoal, because the discharging is done by dumping, which causes breakages of the charcoal.

C. Continuously-working wood-distilling apparatus.

The distilling apparatus above described is either operated intermittently or only partly continuously.

But there are some types of distilling apparatus which are designed for continuous working as, for instance, the Swedish Groendal retort, which belongs to the type of the car retorts described on p. 493.

The Groendal retort consists of three main parts, namely:

1st. The drying chamber, built either of brick or of steel.

2nd. The distilling apparatus consisting of a horizontal steel retort.

3rd. The cooling apparatus for the charcoal, consisting of a steel cylinder of the shape of the retort.

These three parts are connected together but can be separated one from the other by means of vertical sliding doors of iron. The wood, loaded on cars, is filled in the drying chamber through which the exhaust combustion gases, escaping from the retort flues, are passed. After the drying is complete, the sliding doors between this drying chamber and the retort are lifted and the load transferred into the distilling zone of the system. This distilling apparatus is heated by any kind of heat generated by open fire or gas producers. The combustion gases travel around the steel shells, thus transmitting the heat to the wood inside the shell.

After the wood cars have passed the distilling part of the system, another slide door is opened and the cars with the finished charcoal are transferred into the charcoal cooling chamber, through which the cold non-condensable gases

escaping from the condensers of the wood-distilling apparatus, are passed in order to do the cooling work and preheat the gases. A double sliding door at the other end of the system allows the cooled cars with the cooled charcoal to be continuously passed out.

Another continuously working wood-distilling apparatus which may be mentioned here is the wood-gas producer, which, however, does not yield any charcoal. This wood-gas producer is used for the generating of heating gas from second-class cord wood or wood refuse in order to heat boilers and retorts, but also to recover, at the same time, the by-products of the destructive distillation of wood, viz. acetic acid and wood alcohol. These gas producers (Fig. 8) consist of a vertical brick or brick-lined steel furnace provided on the top with a funnel with double doors for filling the gas producer with wood while in work. The bottom of this

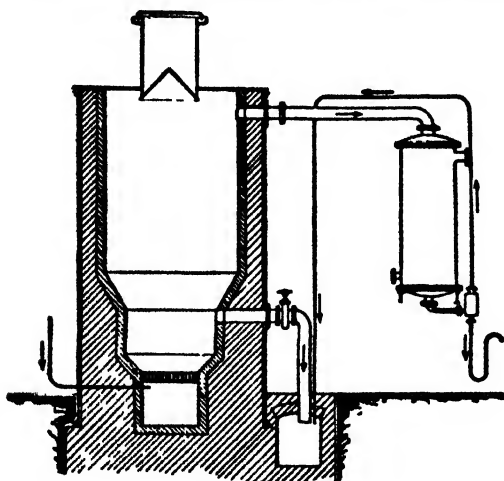


FIG. 8.

Wood-gas producers; type, F H Meyer, Hanover-Hainholz.

gas producer is provided with an iron grate through which a certain amount of air is allowed to enter. The upper part is connected with a condenser. In order to start the gas producers, charcoal has to be put upon the grate and allowed to become red hot. Then the filling in of the wood is started by means of the double-door funnel above-mentioned. The condenser, connected with this gas producer, communicates by means of a gas flue with the smoke stack of the boilers or the retorts, and by the natural draught of this smoke stack a certain amount of air enters through the grate into the gas producer, generating producer gas when coming in contact with the hot charcoal. This hot producer gas carbonises the wood on the top of the charcoal zone on its way up to the outlet, and forms, at the same time, the products of the destructive distillation. These escape, together with the producer gas obtained by passing air through the hot charcoal layer, into the condenser, and while the non-condensable gases escape by the main gas flue, the vapours of pyroigneous acid and of tar are condensed and discharged by means of a siphon. In such a gas producer, there will be a hot charcoal zone on

the bottom, above this there will be wood in the distilling state, and above this zone there will be another zone of wood in the drying period, and on the top of this drying zone there will be the zone of the green wood, filled through the funnel.

These gas producers are not very efficient; they yield no charcoal and only 50 p.c. of the amount of acetic acid and wood alcohol obtainable from the same amount of wood when distilled in retorts. But considering that they produce heating gas and at the same time allow 50 p.c. of the acetic acid and the wood alcohol to be recovered, they are important and economical in working under favourable conditions.

Apparatus for the destructive distillation of pine wood, rich in turpentine and rosin.—As already mentioned, some varieties of pine wood contain, besides cellulose and lignin, large quantities of rosin and turpentine.

As it is the purpose of the pine wood distillation to separate the turpentine in its original state as much as possible before the destructive distillation of the cellulose, lignin and rosin sets in, the apparatus for the destructive distillation of pine wood of this kind must be provided by a heating system which allows a uniform transmission of heat to any and every part of the wood contained in the retort, or which at least allows the temperature to be under control.

It has been proposed to heat the retorts for this purpose by electricity instead of by an open fire or by superheated air or gases circulating around the retort; by oil or metal bath contained in a double jacket; or by superheated steam brought directly in contact with the wood.

These proposals are still in the experimental stage, but it would seem that these methods of heating are too expensive, inasmuch as a carefully designed gas-heating system, using gas, producer gas, or natural gas, will do the same work more economically.

Any one of the apparatus already described may in general be employed for pine wood distillation. But for recovering the turpentine in its original state, or at least not very much contaminated with the products of the destructive distillation of the wood and rosin, the smaller units (6 cords capacity) of car retorts, heated by means of uniformly distributed gas burners, are most to be recommended.

DESTRUCTIVE DISTILLATION OF WASTE WOOD OR SPENT WOOD.

The splitting of the logs and cutting these into cord wood furnishes a large amount of small-sized wood waste. Also cutting the log into timber and working up the timber furnishes another class of waste wood known as slabs, edgings, shavings, sawdust, and so on.

As long as this wood waste consists of pieces large enough to furnish charcoal of the usual size, it can be handled just as cord wood in the standard retorts, and it will yield almost the same amount of charcoal, wood alcohol and calcium acetate as cord wood obtained from the same log, when these figures are referred to the weight and not to the volume of the wood, as a cord of slabs or edgings will weigh very much less than a cord of real cord wood.

With regard to the destructive distillation of

sawdust or shavings, this raw material is not capable of being distilled in any one of the standard apparatus previously described, on account of its voluminous character or by reason of the fact that there is not enough air space between the small, single wood pieces whereby the escape of the vapours and gases, formed on distillation, is rendered impossible. Back

pressure, and under unfavourable circumstances even an explosion, will be the consequence of trying to distil sawdust or other wood of this form in the standard wood distilling apparatus.

There have been numerous proposals to distil sawdust or other fine wood, and almost every one of these proposals is based either on the use of thin layers of sawdust or the use of stirring

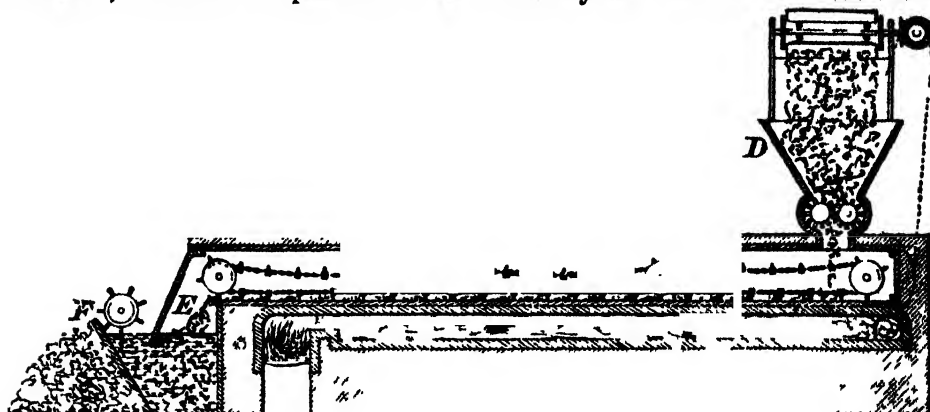


FIG. 9.

Retort for distilling small wood waste

contrivances, or of a combined system of thin sawdust layers and stirring contrivances or scrapers, or finally on the briquetting of the sawdust before it is distilled.

None of these apparatus has taken a practical form, at least on a large scale up to the

price, for the large quantities of charcoal powder produced.

Figs 9 and 10 show types of apparatus which are used for this purpose. The apparatus (Fig 9) transfers the sawdust continuously by means of scrapers over fire heated steel plates, while in the apparatus in Fig. 10 the sawdust continuously drops down in thin layers by its own gravity between the space of the fire-heated shell of the vertical retort and the cast iron rings, which serve as outlets for the vapours and gases.

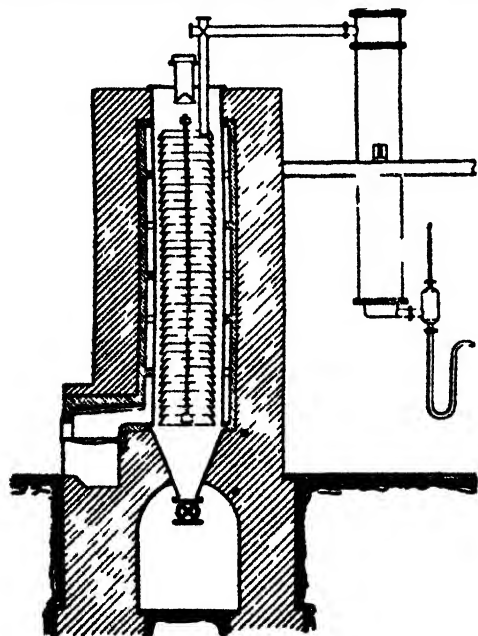


FIG. 10.

Vertical retort for the continuous distillation of small wood waste, type, F. H. Meyer

present time, neither small nor large plants which handle sawdust or a similar class of wood, are operated economically on account of the large initial outlay, which is out of proportion to the value of the output and on account of the fact that there is no market, at a sufficient

TREATING THE CRUDE PYROLIGNEOUS ACID.

Crude pyroligneous acid consists of a watery solution containing acetic acid, wood alcohol and its companions (aldehydes, ethers, ketones, allyl alcohol, phenols) and tarry matters in solution. This brown liquid is further mixed with tar in suspension.

Crude pyroligneous acid cannot be sold in large quantities, but acetate of lime and crude wood alcohol are in large demand.

The object of treating the crude pyroligneous acid is to separate the acetic acid and the wood alcohol from the water and the tarry materials.

First the tar, suspended in the liquid, is separated by allowing the liquor to stand. The tar will settle either on the top or on the bottom of the pyroligneous acid and is then drawn off.

But the remaining liquid still holds tar in solution and this dissolved tar must be separated in order to make marketable acetate of lime, which must contain at least 80 to 82 p.c. $(CH_3COO)_2Ca$.

There are several methods employed in order to separate the tarry matters in solution or suspension from the crude pyroligneous acid. The oldest process, still in use in some plants, consists in a simple redistillation of the crude pyroligneous acid in copper stills, connected

with a condenser and heated either by an open fire or better by a steam coil (Fig. 11). The tar remains as a residue. The distillate is a more or less water-white liquid, which is now practically free from tar and contains principally water, acetic acid, wood alcohol and its associated products above mentioned.

This method of removing the dissolved tar by simple distillation requires about 50 p.c.

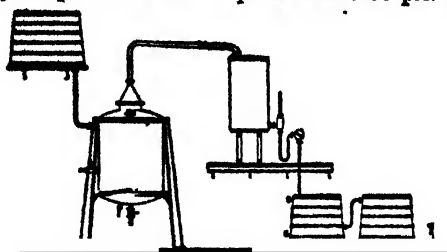


FIG. 11.

Apparatus for distilling crude pyroligneous acid; type, F. H. Meyer.

the total amount of fuel or steam generated in a wood-distilling plant.

The author of this article introduced new methods of distillation of the crude pyroligneous acid, and up to date the crude pyroligneous acid of about 1000 cords of wood is so treated.

This process is based on the principle of the multiple effect evaporators, originally used in the manufacture of sugar (Fig. 12). Two or

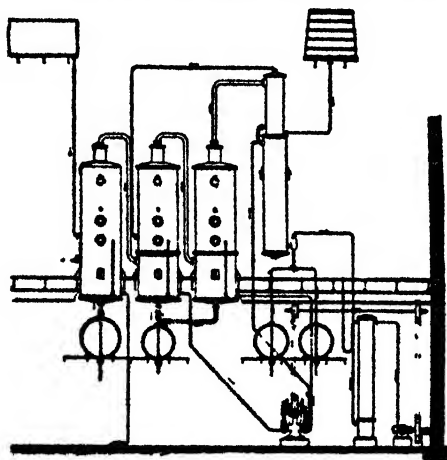


FIG. 12.

Apparatus for continuous distillation of crude pyroligneous acid in multiple effect distillers; type, F. H. Meyer.

more distilling stills are used, one connected with the other and provided with contrivances to maintain a different but gradually lowered boiling-point or a different but gradually lowered working pressure in each one of the stills. For instance, still 1 will be heated by steam of 15 lbs. pressure, using a steam coil or any other heating contrivance.

The liquor, surrounding this steam-heated contrivance, is kept under atmospheric pressure. The pyroligneous acid vapours, generated in still 1 by means of the heating effect of the steam, enter the heating contrivance of the second still, kept under a lower pressure by means of vacuum and therefore a lower

boiling-point of the liquid than in still 1. Therefore the pyroligneous acid vapours, escaping from the first still, heat and distil the crude pyroligneous acid in the second still. This system can be continued indefinitely theoretically, but a system of four combined stills is all that can be reached practically.

A distilling apparatus of this type requires only one-third of the amount of steam or fuel hitherto used for distilling the crude pyroligneous acid in simple distilling apparatus; or the saving may amount to 100 p.c. when sufficient exhaust steam is available. Fig. 12 shows such an installation, based on the multiple effect distilling system.

Besides these two processes, used for redistilling the crude pyroligneous acid, there is another, employed more particularly in German plants.

This process combines the distillation of the crude pyroligneous acid with the neutralisation of the tar-free distillate by means of milk of lime or soda ash and the separation of the wood alcohol from the acetate solution.

The pyroligneous acid is distilled in a copper still, heated by a steam coil. Instead of passing the vapours of pyroligneous acid into a condenser, they are forced through milk of lime or soda ash solution, contained in closed copper or iron tanks, which are connected with a condenser (Fig. 13). The acetic acid thus combines with the lime or the soda, forming acetate solutions, whilst the wood alcohol and water vapours escape to the condenser from which an aqueous solution of the alcohol is discharged containing 5 to 12 p.c. wood spirit.

All the processes described above for removing tarry matters before treating the pyroligneous acid with milk of lime or soda ash solution, are based on the *distillation principle* and handle the gross distillate discharged from the condensers connected with the wood distilling apparatus.

The writer has introduced another patented process which is not based on the redistillation of crude pyroligneous acid, but depends on separating the total amount of tarry matters from the vapours escaping from the wood-distilling apparatus *before* these vapours are condensed. This is effected by washing the vapours and gases by means of crude wood tar or a mixture of crude wood tar and pyroligneous acid in two or more gas washing apparatus, which are combined together, and maintaining in each one a gradually decreasing temperature.

For instance, in the tar washer 1, a temperature of about 300°F. may be maintained and in the last tar washer, or the washer next the condenser, a temperature of 212°F. may be maintained.

By the combined effect of the fractional condensation of the tar and of the absorbing affinity of the large amounts of tar used as a washing liquid, for the small amounts of tar contained in the form of vapours in the products, the pyroligneous acid discharged from the condenser will be practically free from tar and ready to be neutralised by milk of lime or soda ash.

This process is successfully used in many wood-distilling plants and saves entirely the expenses of the redistillation of the crude liquor.

WOOD, DESTRUCTIVE DISTILLATION OF.

MANUFACTURE OF ACETATE OF LIME FROM CRUDE PYROLIGNEOUS ACID.

As already mentioned, grey acetate of lime, 80 to 82 p.c., is the product into which the acetic acid, contained in the pyroligneous acid, has to be transformed for the purposes of shipment.

The manufacture of grey acetate of lime starts with the tar-free distillate, obtained from the crude tar containing pyroligneous acid by one of the processes already described. This distillate is neutralised either by mixing it with milk of lime in a wooden tank, provided with a stirrer and cover, or by passing the vapours through layers of milk of lime.

The milk of lime combines with the acetic acid; it partly saponifies any methyl acetate; it transforms some of the aldehydes into insoluble resins; and it combines with phenols, forming insoluble lime compounds. After adding the milk of lime, the neutralised liquor is allowed to stand in order that the precipitates, formed by the neutralising processes, shall settle.

The next operation on the settled liquid, containing principally wood alcohol and its associates, acetate of lime and water, consists in separating the wood alcohol from the aqueous solution of the acetate of lime, either in form of a weak alcohol solution by means of a simple intermittently operated still, or in form of

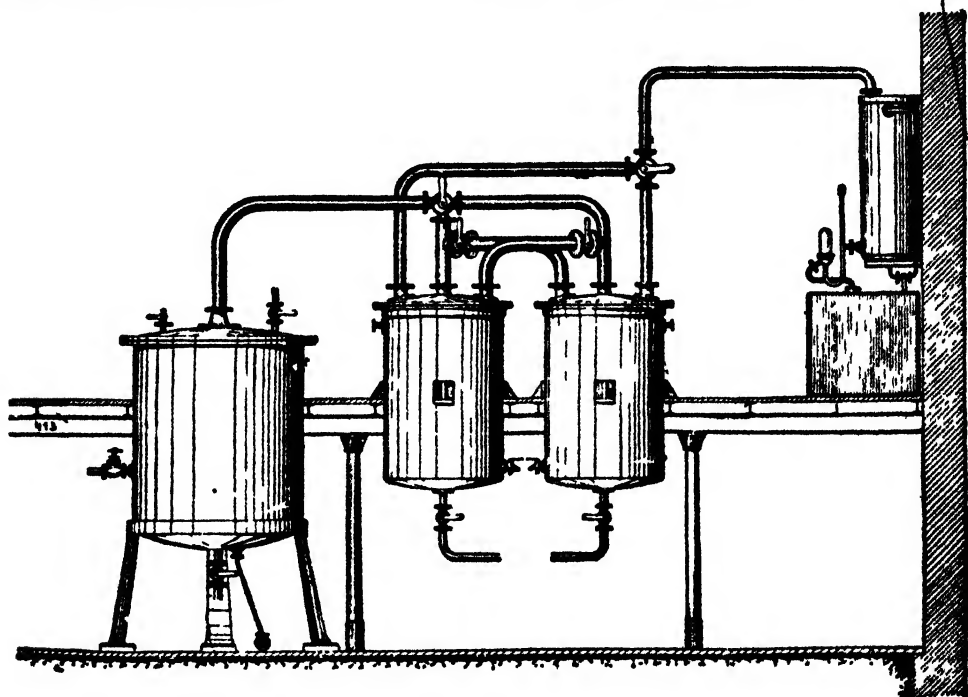


FIG. 13.

Apparatus for distilling crude pyroligneous acid by passing acid vapours through layers of milk of lime; type, F. H. Meyer.

concentrated wood alcohol by means of an intermittently or continuously operated rectifier.

The simple distilling still furnishes a weak wood alcohol solution, containing from 8 to 10 p.c. of wood alcohol, whilst the rectifier turns out a single operation crude wood alcohol from 30 to 95 p.c., depending upon the design of the rectifier.

The simple still consists of a steel or copper still, provided with a copper heating coil and connected with a condenser.

The intermittently operated rectifier, shown in Fig. 14, is built of a steel or copper still with a copper heating coil, a copper column with rectifying sieve or bell plates, a separator and condenser. The working principle of these rectifiers is based on fractional distillation, and the 'columns' used for this purpose are very similar to those employed in manufacturing grain alcohol and known as the 'Savalle apparatus' from the name of the inventor. The

continuously working rectifiers, for separating the crude wood alcohol in a concentrated state from the neutralised liquor, are the most modern and most economically working apparatus for this purpose (Fig. 15). They have been introduced in the wood-distilling industry by the author of this article, and they furnish by a single operation the so-called 'crude wood alcohol' of 95 p.c. and separate at the same time the oils, originally contained in the neutralised liquor and also the acetone, if desired.

The continuously working apparatus are principally built of two columns; at the top of one column the neutralised liquor enters and the second column takes the wood-alcohol vapours escaping from the first column. The neutralised liquor travels in the first column downwards from plate to plate and meets on its way down the steam, entering into the bottom section. The wood alcohol, containing about 30 p.c. of wood alcohol and 70 p.c. of water,

WOOD, DESTRUCTIVE DISTILLATION OF.

escapes from the top section of the first column, while the acetate of lime solution freed from wood alcohol, is continuously discharged from the bottom section of this column. The 30 p.c. wood alcohol vapours enter the bottom part of second column, and on their way *upwards* from plate to plate they are concentrated by means of fractional distillation and discharged from

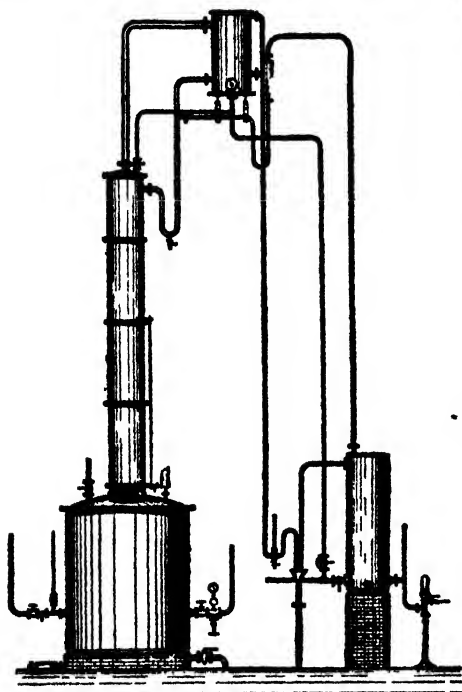


FIG. 14.

Intermittent-working rectifier for wood alcohol; type, F. H. Meyer.

the top section to a separator and from there to a final condenser, leaving the latter as a product containing up to 95 p.c. wood alcohol.

This product corresponds in chemical composition and physical characters with the so-called 'American Crude Wood Alcohol,' shipped in immense quantities from the United States to Europe. It still contains the total amount of acetone, aldehydes, ketones, esters, ammonia, amines, and allyl alcohol, originally contained in the neutralised liquor, and also some of the 'wood oils,' which always accompany the wood alcohol.

The average composition of this product may be given as follows:—

- 16 p.c. acetone and other ketones.
- 6 p.c. aldehydes, methyl acetate, and allyl alcohol and oils.
- 70 p.c. methyl alcohol.
- 8 p.c. water.

The following substances have also been found in 'wood spirit oil,' the residue left after the isolation of methyl alcohol from wood spirit: methyl ethyl ketone, methyl isopropyl ketone, dipropionyl-ethane, mesityl oxide, trimethyl acetic aldehyde, isovaleric aldehyde, Δ^4 -hexene-3-one, cyclopentanone (Fringsheim and Leibowitz, Ber. 1923, 56, [2] 2034; Chem. Soc. Abstr. 1923, 124, 1, 1062).

In order to manufacture 'pure' methyl alcohol from the crude wood alcohol, all these contaminating products have to be separated.

This is done by fractional distillation, carried out systematically by means of intermittently or continuously operated rectifiers, similar to those above described. The separation is usually assisted by adding chemicals—for instance, caustic soda and sulphuric acid—which destroy, polymerise, or saponify the products to be separated—for instance, aldehydes, esters, ketones, phenols, amines, and so on.

The separation of the acetone and the allyl alcohol, which are always associated with the methyl alcohol, is *entirely done* by a carefully repeated fractional distillation, which yields the concentrated acetone in form of 'head ends' and the allyl alcohol in form of 'tail ends.'

A mixture containing in specified proportion these head ends and tail ends represents the 'denaturing wood alcohol,' used practically everywhere for denaturing alcohol. This material must conform to certain specifications and tests prescribed by the different Governments.

The final product of such a repeated fractional

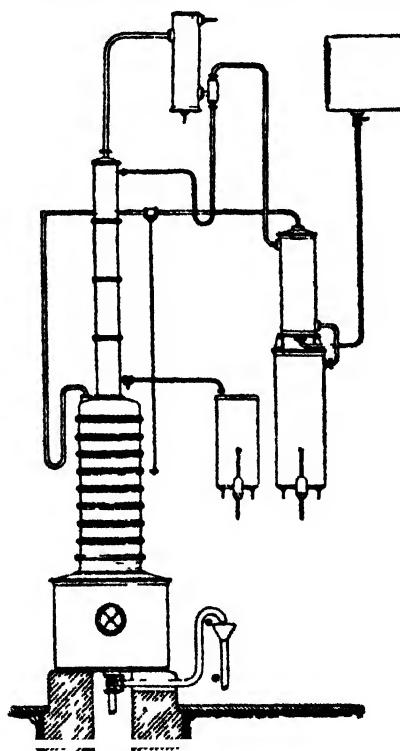


FIG. 15.

Continuous-working rectifier for wood alcohol; type, F. H. Meyer.

distillation, carried out either by intermittently working or continuously working rectifiers, represents the 'pure' methyl alcohol, which is free from acetone or contains only traces of it, and contains up to 99 p.c. real CH_3OH .

Besides this final product, free from acetone, and the 'denaturing wood alcohol' containing acetone, allyl alcohol, and other impurities, a

number of other wood alcohol grades are on the market; for instance, 'pure' methyl alcohol of 99½ p.c. with 0.1 to 1 p.c. of acetone and many other grades demanded by customers.

The pure grades are used for the manufacturing of aniline colours, of formaldehyde, of perfumes; the other grades for varnishes, as solvents, and the poorest grades for denaturing or burning.

The distillation of the neutralised liquor yields, as above shown, two products:

Wood alcohol, as a volatile product;

Acetate of lime solution as a non-volatile residue.

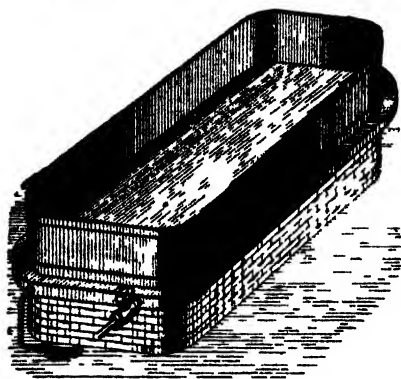


Fig. 16.

Open pan for evaporating acetate of lime solution.

This latter solution holds in suspension insoluble polymerised products, formed by a reaction between phenols and aldehydes with acetate of lime or traces of lime in excess, which must be settled by allowing the liquor to stand.

The settled solution contains varying quantities of acetate of lime, according to the nature of the original liquor and to the process used for distilling off the crude wood alcohol.

These quantities differ from 7 to 25 p.c.; this means, 100 lbs. acetate of lime solution may contain from 7 to 25 lbs. dry acetate of lime, 80–82 p.c. As it is impossible to recover the acetate of lime by a crystallising process on account of its equal solubility in cold and hot water, the solution must be boiled down until the salt is left in the solid state.

Up to the present this boiling was done in two steps. By the first step, the acetate of lime solution is evaporated in open, steam-heated, double-jacket pans (Fig. 16) just to the point at which the concentrated solution becomes solidified by crystallising. This point is reached when the acetate of lime solution contains about 35 to 40 p.c. of the dry salt. The crystallised magma is then spread out in thin layers upon an open drying floor, built of cast-iron plates or steel plates, heated by an open fire or by waste fire gases.

The operation of boiling down the acetate of lime solution to a magma of crystal requires very large amounts of steam on account of the coating of the heating surface by crystals and scales and by the immense reduction of the heat transmitting capacity.

Furthermore, the drying upon an open drying floor necessitates much hand work, as the material must be turned over and

usually transferred from one end of the drying floor to the opposite one, whereby it travels with the current of the fire gases. This ensures that the wet acetate of lime, which can stand a high temperature, comes in contact with the hot fire gases, while the dried salt or partly dried salt comes only in contact with the fire gases of a lower temperature, in order to protect it against decomposition into acetone.

The author has introduced a drying process, in which the solution of acetate of lime will be continuously and mechanically evaporated and dried, doing away entirely with the steam-heated open pans and the high wages required by opening drying floors.

By this new process, already in successful operation in plants of all sizes from 30 cords up to 250 cords, the acetate of lime solution is continuously evaporated in specially designed multiple effect evaporating apparatus, on the same principle as above described for the multiple green liquor distillers.

The weak solution enters the first evaporator, travels from there to the second, and from second to the third, leaving the same or the last one as a concentrated liquor, which contains up to 30 to 35 p.c. dry salt. This liquor will not crystallise when kept hot.

The liquor flows to a pan into which a rotary drum is dipping, heated inside by steam. This drum becomes coated with a thin layer of the concentrated solution.

While rotating, the thin layer dries quickly, and before the drum dips again into the concentrated solution the magma of crystals, which now coats the surface of the drum, is scraped off by means of knives, working on the surface of the drum (Fig. 17).

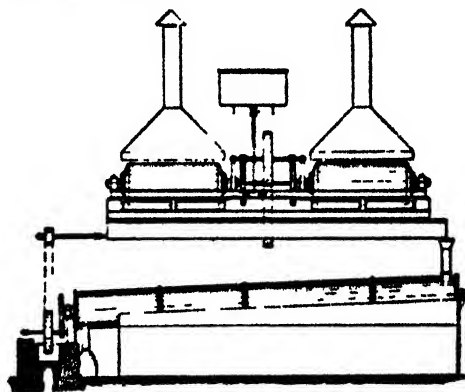


Fig. 17.

Continuous-working rotary evaporator for evaporating and drying acetate of lime; type, F. H. Meyer.

The magma of crystals then travels by means of a conveyor to a belt dryer, built of endless canvas belts or wire cloth belts, upon which the wet salt is transferred against a current of hot air or over pipe coils, heated by exhaust steam. This new type of apparatus for evaporating and drying acetate of lime does away with any kind of hand work; it obviates the disagreeable and unhealthy work of drying upon an open floor; and it saves almost all the wages hitherto spent for drying, and it saves, too, large amounts of fuel. Moreover, the acetate of lime obtained by this process, is of an even

form like peas; it does not contain much dust; it is of a brighter colour and is soft and voluminous, yielding on this account more acetic acid and acetone, when worked up into these products.

MANUFACTURE OF ACETATE OF SODA.

Next to acetate of lime, acetate of soda is the most important salt of acetic acid manufactured in wood-distilling factories.

In order to produce sodium acetate in a crystallised state, the distillate of pyroligneous acid, obtained by one of the processes already described, is neutralised by soda ash. The acetate of soda solution is then freed from wood alcohol by the methods before mentioned, and boiled down by open double-jacket pans, or by

modern multiple effect evaporating apparatus, until the crystallising point is reached. By the next step the condensed solution is completely dried in cast-iron, fire-heated pans, provided with scrapers, and the heating is continued until the whole of the water is driven off and the anhydrous sodium acetate is completely melted, when the liquid mass will have a temperature of about 320°. At this temperature, sodium acetate is not decomposed, but sodium propionate and butyrate, as well as tarry or resinous matters present in the original product, will be destroyed and converted into insoluble matters.

After melting, the mass is dissolved in water to form a concentrated solution and the charred matter separated by filtering the solution,

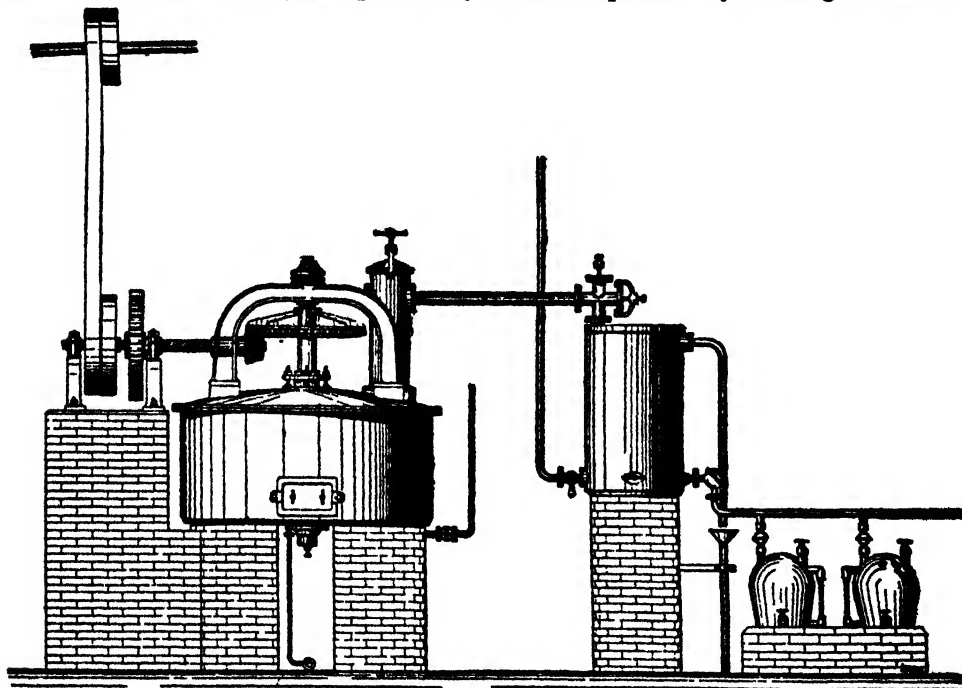


FIG. 18.

Cast-iron still for decomposing acetate of lime by sulphuric acid; type, F. H. Meyer, Hanover-Hainholz.

usually by a filter press. The filtrate is transferred to crystallising vessels and the crystals and mother liquor separated by a centrifugal machine. The crystals are recrystallised and the mother lees returned to the evaporating pans.

TREATING OF THE PRIMARY MARKETABLE PRODUCTS RESULTING FROM THE DESTRUCTIVE DISTILLATION OF WOOD.

The first products resulting from the destructive distillation of wood are: charcoal, crude pyroligneous acid, tar, when hard wood is distilled; or charcoal, crude pyroligneous acid, crude turpentine, crude pine oil and crude pine tar, when pine wood, containing turpentine and rosin, is employed. Of these, the charcoal only is ready for sale. The other products must be further treated in order to convert them into marketable commodities.

From the crude pyroligneous acid acetate of lime, acetate of soda and crude wood alcohol

are obtained, and from the latter the 'pure' methyl alcohol, the refined wood alcohol, and the denaturing alcohol as above described.

Many of the wood distilling factories work up the acetate of lime into acetic acid or acetone and the methyl alcohol into formaldehyde.

Manufacture of acetic acid.—In order to manufacture acetic acid, only acetate of lime, 80–82 p.c., is used nowadays as raw material. This is mixed with sulphuric acid of 92 to 98 p.c. in a closed cast-iron still, provided with stirrer and scrapers and heated by high-pressure steam (Fig. 18). After the mixing process is finished the acetic acid is distilled off, a vacuum being maintained in the still during the process of distilling. The crude acetic acid, resulting from the process, contains about 80 p.c. acetic acid (propionic and butyric acid included), traces of sulphur dioxide, and is of a yellow colour. This acid can be used for many purposes in the arts, as, for instance, manufacturing white lead, amyl acetate, &c.

In order to produce 'pure' glacial acetic acid of 96 to 99½ p.c., the crude 80 p.c. acetic acid, obtained by the action of sulphuric acid on acetate of lime, must be rectified in a copper rectifier (Fig. 19).

First a weak acetic acid is obtained containing propionic and butyric acid; then the distillate becomes gradually stronger and after distilling over 40 to 50 p.c. of the original charge, glacial acetic acid distills over: this has a melting-point of 14°-16° and contains 99 to 99½ p.c. CH_3COOH . At the end of the process the melting-point again falls, and with it the content of acetic acid owing to the presence of propionic and butyric acids.

In order to manufacture 'pure' acetic acid, 99½ p.c., corresponding to the requirements of the pharmacopoeas of different countries, the glacial acetic acid, obtained from the first rectification of the crude 80 p.c. acetic acid, will be oxidised and then redistilled by use of a simple still connected with a silver condenser.

Manufacture of acetone.—Acetone is manufactured by the dry or destructive distillation of

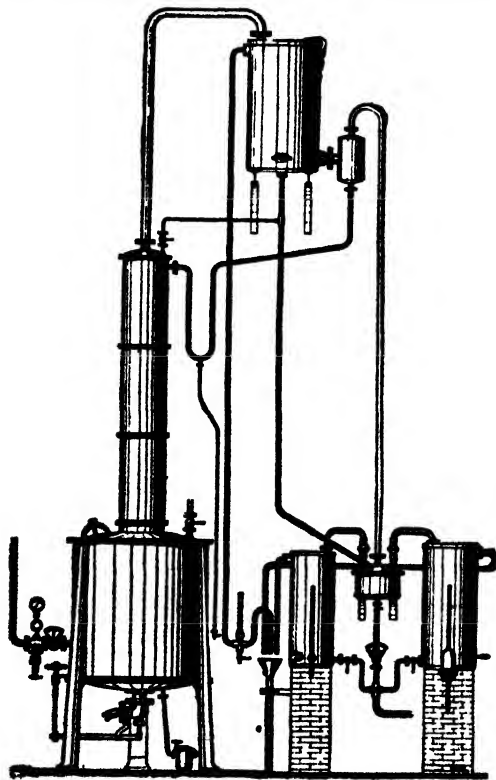
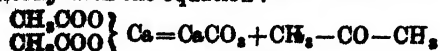


FIG. 19.

Apparatus for rectifying crude acetic acid in order to manufacture glacial acetic acid; type, F. H. Meyer.

calcium acetate. The process corresponds theoretically with the equation:



According to the author's patented process, used in most of the existing acetone factories, acetate of lime is spread out in thin layers on steel plates, to be placed one above the other upon platforms on steel cars, allowing sufficient

clearance from platform to platform (Fig. 20). These cars are pushed into horizontal steel retorts, heated by fire gases. The retorts are capable of treating from 3000 to 15,000 lbs. of

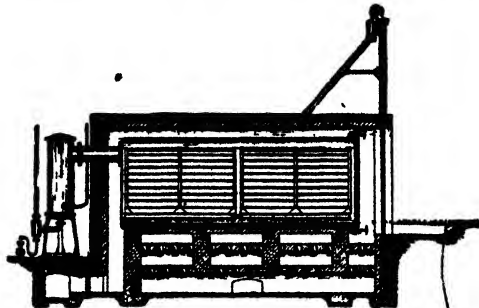


FIG. 20.

Retort for decomposing calcium acetate; type, F. H. Meyer.

calcium acetate in 24 hours and are conned with a condenser. The destructive distillation sets in at about 300°. After the charge is charred, the cars are withdrawn and other cars, already loaded, charged into the retort.

By the older acetone process, calcium acetate was distilled in charges not exceeding 1000 lbs. by means of fire-heated, closed, cast-iron pans, provided with a stirrer and scrapers. But these forms of apparatus yielded only 17 lbs. 'pure' acetone from 100 lbs. of calcium acetate instead of from 20 to 21 lbs. as obtained by the process above described.

There is a third process used, based on the distillation of calcium acetate by means of a stream of superheated steam which is brought directly in contact with the acetate.

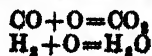
The crude acetone obtained by one or other processes contains, besides the acetone, tarry matters, formic and acetic acids, aldehydes, ketones formed by the propionic acid and butyric acid originally contained in the crude material, hydrocarbons, and other products.

By means of repeated fractional distillation, assisted by the use of small amounts of caustic soda and sulphuric acid, acetone of 99½ p.c. is obtained, whilst the tarry matters remain in the residue. The acids are fixed by the alkalis, which destroy the aldehydes, and the foreign ketones and hydrocarbons are obtained as 'tail ends' from the rectifier, from the fact that their boiling-point is considerably higher than that of acetone.

FORMALDEHYDE.

This important disinfectant is obtained from the 'pure' methyl alcohol by oxidising it by the oxygen of the air under the influence of catalytic agents: $2\text{CH}_3\text{OH} + \text{O} = 2\text{CH}_2\text{O} + 2\text{H}_2\text{O}$. The manufacturing process differs in some respects from the theoretical equation, as side reactions set in whereby a part of this formaldehyde is broken up into carbon monoxide and hydrogen, according to the equation $\text{CH}_2\text{O} = \text{CO} + 2\text{H}$.

The excess of oxygen under the influence of the red hot catalytic material combines with the carbon monoxide as well as the hydrogen:



Carbon dioxide and water are products formed by another side reaction.

Theory indicates that 93.75 lbs. of formaldehyde of 100 p.c. should be obtained from 100 lbs. methyl alcohol of 100 p.c., but by the best practical process only 80 lbs. formaldehyde, as a maximum, can be obtained, which means only about 85 p.c. of the theoretical yield.

The product on the market is an aqueous solution of formaldehyde, containing from 35 to 40 p.c. CH_2O by weight. This solution is liable to polymerise, forming paraformaldehyde by the condensation of 3 mols. of CH_2O , a product which is not soluble in water and therefore causes the solution to become more or less turbid.

In order to avoid this polymerisation and to meet commercial demands, various substances are added to the formaldehyde solution. As methyl alcohol has the peculiar property of preventing polymerisation, a certain amount is added to the formaldehyde solution of the market, which averages

35-40 p.c. (by weight) CH_2O	
12-15 p.c. $\text{CH}_3\cdot\text{OH}$	
53-45 p.c. H_2O	

This solution is manufactured by mixing vapours of methyl alcohol with a corresponding amount of air.

The processes adopted for manufacturing formaldehyde differ in regard to the apparatus or contrivances used for furnishing this vapour mixture of a constant composition.

About half the factories existing at present are using the author's process, which is a continuous one, whereby liquid methyl alcohol is introduced in the form of a spray into the top section of a so-called 'carburator' (constructed on the same principle as that used for carbureting coal gas with benzene) and at the same time blowing a stream of hot air which enters the bottom of the 'carburator' against the methyl alcohol spray, whereby the methyl alcohol will be evaporated and mixed with the air in the right proportion. The mixture of methyl alcohol vapour and air is passed over the catalytic material, consisting of rolls of copper wire-net heated to about 400° , before allowing the mixture of methyl alcohol and air to enter.

To avoid explosions and to prevent the methyl alcohol burning into carbon dioxide and water, an excess of methyl alcohol must be used.

The products of the reaction, that is the vapours escaping from the apparatus, contain this excess of methyl alcohol, which is recovered by a fractional condensation of the escaping vapours, whereby the formaldehyde solution will be condensed first and the methyl alcohol last.

As already mentioned, the whole process is a continuous one, as methyl alcohol and air enter at one end of the apparatus, and the formaldehyde solution, the excess of the methyl alcohol used, and the nitrogen with the gases formed by the reactions will be discharged, of course each one separately, on the other end of the apparatus (v. FORMALDEHYDE).

CRUDE HARD-WOOD TAR.

The hard-wood distilling process yields two kinds of tar, namely: the settled tar, deposited

from the crude pyroligneous acid; the residue tar, obtained as a residue by distilling the crude pyroligneous acid.

The composition of these two varieties of tar is quite different, as the 'residue tar' contains principally pitch and pyroligneous acid, whilst the 'settled tar' contains, besides pitch and pyroligneous acid, the total amount of phenols and hydrocarbons, usually called 'tar oils.'

There are no two samples, taken from different plants, which are alike, and therefore exact figures concerning the composition of tar, obtained by the destructive distillation of wood, cannot be given.

Wood-tar is a burden on the hands of the wood distillers, on account of the difficulties it causes in the treatment of the pyroligneous acid, and on account of its small value as a commercial article.

The coal tar industry furnishes pitch and tar oils much cheaper and in much greater quantities than can be obtained from wood tar. The treatment of tar has therefore no great importance for the wood distiller, and usually it is limited to the recovery of the wood alcohol and acetic acid, the remaining tar compounds being, for the most part, used as fuel.

In order to recover methyl alcohol and pyroligneous acid, contained in both varieties of tar, the tar is subjected to distillation in copper stills, provided with a heating coil and also a perforated coil for adding live steam.

The water with the acetic acid, as well as with the wood alcohol, and light wood oils floating on water, is distilled, and when by increased steam supply the amount of distillate diminishes, live steam is added by the perforated coil and the distillation continued until the distillate contains only a small amount of acids. The distillate is allowed to stand, whereby the light oils rise to the top. The clear liquid is drawn off and treated together with the distillate obtained from the bulk of the crude pyroligneous acid.

The residue of this tar distillation, or that obtained by distilling off the pyroligneous acid from the tar, is a liquid similar to thick molasses, and is generally used as fuel which is burned by spraying it by means of steam into the fireplaces of boilers or retorts. Sometimes the settled tar is subjected to distillation in order to recover the heavy tar oils, containing the phenols and creosote and to manufacture pitch. Such distillation must be carried out in cast-iron stills, heated by an open fire. First the light oils, floating on water, and the pyroligneous acid distil over, as in the process described above. This phase of the distillation must be done very carefully on account of the frothing to which the tar is liable. After this period is over and when only small amounts of water flow from the condenser, the fire can be increased, when heavy tar oils, sinking in water, distil over. The distillation will be continued until the pitch, left as a residue in the still, proves to have the melting-point desired.

Sometimes hard pitch with a high melting-point, sometimes soft pitch with a low melting-point is the purpose of this distillation.

The heavy tar oils or the oil which sinks in water are usually sold to chemical works,

which manufacture creosote, and only exceptionally are they sold for the manufacture of dyes. Only a very few factories deal with the recovery of creosote, which contained up to 1 p.c. in the hard wood tar, particularly in beech tar.

The raw material is the 'heavy tar oil' obtained by the distillation of the settled tar in fire-heated stills. These oils still contain considerable amounts of tar and must be redistilled before being subjected to any other treatment. The redistilled oils are then subjected to a systematic extraction by means of caustic soda solution, which separates the total amount of phenols from the bulk of hydrocarbons contained in the tar oils.

The alkaline solution of phenols is then mixed with acid, usually a mineral acid, liberating the phenols, which are drawn off from the salt solution, after allowing the mixture to stand. Repeated fractional distillation is the next operation to which these mixtures of phenols are subjected in order to concentrate the fractions which contain the real creosote. These fractions are again subjected to repeated treatment with caustic soda and mineral acid, and from the last fractions of the distilled creosote, 'pure' creosote is obtained.

Crude turpentine and crude pine tar.—As described above, the destructive distillation of pine wood, rich in turpentine and rosin, yields the turpentine, partly in the state as originally contained in the wood, partly contaminated or mixed with the products of the destructive distillation of cellulose, lignin and rosin, i.e. with tar, tar oils, rosin oils, &c. The more nearly the distilling apparatus allows of a uniform distribution of heat to each piece of wood contained in the retort, the better will be the separation of the real turpentine, uncontaminated with the products above mentioned.

The destructive distillation of pine wood containing turpentine and rosin, yields three fractions, which are usually taken separately:

Fraction 1, containing only small amounts of tar, tar oils and rosin oils.

Fraction 2, containing less than 50 p.c. of the contaminating products.

Fraction 3, containing more than 50 p.c. of the contaminating products.

Fraction 1 represents the material, called 'crude wood turpentine,' which is exported from Sweden and Russia, and which is also manufactured in many factories situated in the Southern States of America, as Georgia, Alabama, Virginia, &c.

The 'crude wood turpentine' obtained by destructive distillation consists principally of terpenes. In addition it contains tar, acids, phenol, aldehydes, furfural, 'silvan,' dimethyl-furfural, benzene, toluene, xylene, diacetyl, acetyl-propionyl, &c.

The first treatment consists in fractionally distilling the crude wood turpentine by means of steam-heated stills, which allows also of the addition of live steam (Fig. 21), whereby the turpentine is separated from the products of lower and higher boiling-point. After the products of lower boiling-point have been got rid of, live steam is turned on and the mixture of vapours of turpentine and water is passed through caustic soda solution or milk of lime

in a container connected with the still and the condenser.

Phenols, rosin oil, aldehydes, acids, &c., are kept back or destroyed by the alkaline bath, whilst the turpentine and water vapours escape to the condenser and are separated after their condensation by their varying specific gravity.

The refined turpentine obtained by this process is of a water-white colour, but its smell is not 'sweet' enough to meet the requirements of the market.

It is therefore subjected to a second alkaline treatment and then to a treatment with sulphuric acid, whereby other contaminating products will be separated or destroyed.

Finally a fractional vacuum distillation by means of steam-heated rectifiers yields a duct, which is now of a water-white colour, of a 'sweet' smell, and has the same boiling point, specific gravity, and optical characteristics as ordinary turpentine.

'Pine wood tar' is obtained as the residue of the first distillation of the crude wood turpentine.

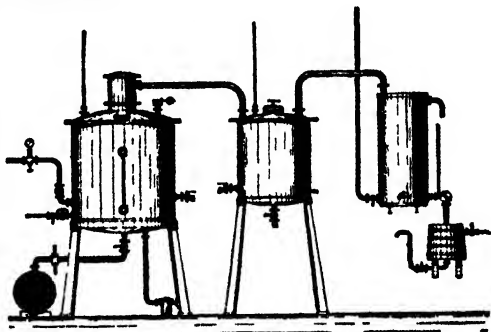


FIG. 21.

Distilling apparatus for separating turpentine from pine-wood tar-oils and pine-wood tar; type, F. H. Meyer.

The second fraction of the destructive distillation of pine wood, containing up to 50 p.c. tar and rosin oils, is also subjected to distillation as above described. The distillate is a mixture of turpentine, other terpenes and hydrocarbons of a higher boiling-point, called 'pine oil,' and the residue consists of pine tar.

The mixture of turpentine and pine oil is then subjected to fractional distillation by means of a vacuum rectifier and the turpentine obtained by this treatment mixed and treated together with the refined turpentine obtained from the first fraction.

The third crude fraction, mainly consisting of tar, is subjected to similar treatment and furnishes pine oils and, as a residue, the bulk of pine tar. M. K.

WOOD GUM v. GUMS.

WOOD OIL v. GURGUM v. OLEO-RESINS.

WOOD-OPAL v. OPAL.

WOOD-PITCH, WOOD-SPIRIT, WOOD-TAR, v. WOOD, DESTRUCTIVE DISTILLATION OF.

WOOD'S ALLOY v. TIN.

WOOD-TAR. According to Marcumson and Picard (Chem. Umschau, 1921, 28, 257), the composition of beech-wood tar and pine-wood tar is respectively as follows: unsaponifiable matter, 10.18 p.c., 53.5 p.c.; hydroxy-acid anhydrides, 9.5 p.c., nil; hydroxy acids,

52.3 p.c., 14 p.c.; resin acids, 7.7 p.c., 17 p.c.; fatty acids, 3.2 p.c., 6 p.c.; phenols, 9.3 p.c., 9.5 p.c. The residues (pitches) obtained after distilling these tars are composed respectively of: neutral tar resins, 14 p.c., 1.5 p.c.; unsaponifiable matter, 6 p.c., 19.7 p.c.; phenols, 1.5 p.c., 8 p.c.; hydroxy-acids and anhydrides, 7.7 p.c., 31.8 p.c.; resin acids, nil, 35.2 p.c.; fatty acids, 1.5 p.c., 2.8 p.c.; mineral matter, nil, 1 p.c.

Wood-tar pitches can be distinguished from other artificial asphalts by the high content of hydroxy-acids and the presence of phenols (J. Soc. Chem. Ind. 1921, 840 A.).

WOOD-TIN v. CASSITERITE.

WOODY NIGHTSHADE v. DULCAMARA.

WOOL. The woolly covering of the sheep is composed of modified hairs which grow in the same manner as the hairs of other animals, but differ from them considerably in physical structure and characteristics, including fineness, softness, waviness, and highly serrated surface. The wool fibre arises in the dermis or middle layer of the skin. Its root or follicle is a gland which produces a lymph-like secretion which nourishes the hair during its development and growth. This gland also secretes an oily substance, the wool-oil, which becomes a constituent part of the fibre and improves its elasticity and flexibility. Contiguous to the follicle are the sebaceous glands which secrete a fatty substance, the wool-grease, which coats the surface of the fibres, thereby protecting them from mechanical injury during growth and preventing them from becoming matted or felted together.

The dried perspiration of the animal also adheres to the fibres and can be removed by means of cold water in which it is soluble. It consists largely of a mixture of potassium salts, and is usually recovered as a by-product of the industry. The residue obtained after treating the wool with cold water and evaporating the solution to dryness is known as 'sudorate of potash.' Raw wool yields about 8 p.c. of this product.

Before the wool can be used for the manufacture of textiles, not only must the dried perspiration be removed, but also the wool-grease; the extraction of the latter is generally effected by the process of scouring with soap and water. In order to avoid the removal of the wool-oil from the interior of the fibre, the temperature at which the scouring is carried out does not usually exceed 50°.

When examined with the microscope, the typical wool fibre presents the appearance of a more or less cylindrical rod covered with irregularly-shaped scales which overlap one another by their free margins and cause the fibre to exhibit numerous serrations. The free edges of the scales always point in the direction of growth of the fibre. It is to this peculiar imbricated nature of the surface that the felting property of wool is due. The shrinking which wool fabrics undergo on washing is also attributable to the serrations; the rubbing of the material causes the projecting edges of the scales to become closely interlocked, and thus reduces the amount of space occupied by the fibres, and this behaviour is facilitated by the lubricating action of the soap. The cortical layer beneath the scales constitutes the bulk of the fibre and is

composed of long, narrow cells with pointed ends. Within this is the medulla which consists of larger and rounded cells and often contains pigment to which certain wools owe their characteristic colour. In the finer wools, the medulla is often so much reduced as to be almost indistinguishable. The wool of carelessly-bred sheep frequently contains defective fibres in which the scales and cellular structure are but slightly developed; these appear as stiff, straight, coarse, opaque hairs which cannot be dyed, and are termed 'kemps.'

The value of wools and their suitability for different purposes depend very largely on their physical properties, such as length, strength, elasticity, fineness, softness, curliness or waviness, lustre, felting property, colour, and freedom from impurities and kemps. The extent to which a wool possesses these characters varies greatly with the particular breed of sheep, the climatic conditions, the nature of the pasturage, and the care exercised in selection and rearing. The quality of the fibre also varies considerably in different parts of the same fleece. The wools of commerce may be roughly divided into three classes: (1) long-stapled, (2) medium-stapled, and (3) short-stapled.

(1) The long-stapled class includes the typical English varieties, such as the Lincoln, Leicester, and Cotswold wools. The fibre is from 6 to 10 ins., or even up to 15 ins. in length, has an average diameter of about 0.001 in., and bears from 600 to 1400 serrations per inch. It is nearly white, lustrous, of good elasticity, and has a smoother surface and less wavy character than the fibres of the other classes. The scales are horny and closely attached to the cortical layer and, in consequence, the felting power is poor. These wools are specially adapted for the manufacture of worsted yarns.

(2) The medium-stapled class is represented by the wools produced by the Southdown sheep and those of the Cheviot Hills, Shropshire, Hampshire, Oxfordshire, and Dorset; it also includes certain cross-bred wools, such as those of Australia, New Zealand, and South America, which are produced in very large quantities. The characters of the fibre are intermediate between those of the long- and short-stapled kinds. The length is from 3 to 8 ins., the average diameter about 0.0008 in., and the average number of serrations is about 2000 per inch.

(3) The short-stapled class comprises the finest grades of wool, including those of the merino type of Australia, South America, and the Cape Province of South Africa. The fibre is from 2 to 5 ins. long, has an average diameter of about 0.0005 in., and bears about 2800 serrations per inch. It is either white or of a greyish tint, has little or no lustre, and is very elastic, very soft, and curly. The scales are small and adhere to the cortical layer by only a small portion of their length, so that the upper part is free and protruding, and for this reason the wool has good felting properties. Wools of this class are particularly suitable for the manufacture of woollen fabrics.

Wool fibre is composed of a protein substance of the group known as the keratins, which also includes those derived from hair, horn, whale-bone, feathers, and egg-membrane. All the

members of this class differ from other proteins in yielding a large proportion of cystine on hydrolysis. The average elementary composition of wool keratin is approximately as follows: C, 51; H, 7; O, 21; N, 17; S, 4 p.c.

Sulphur is the most variable constituent and ranges from 2.5 to 4.5 p.c. Raikow (Chem. Zeit. 1905, 29, 900) found that when wool is kept for some time in contact with syrupy phosphoric acid, sulphur dioxide is evolved. Baudisch (*ibid.* 1908, 32, 620) confirmed this result and also showed that the sulphur of wool is partly oxidised to sulphur trioxide by the action of hydrogen peroxide. The experiments indicate that some of the sulphur is in direct combination with oxygen and is probably present in the form of a sulphite-like complex. This conclusion, however, has been challenged by Strunk and Priess (Zeitsch. physiol. Chem. 1912, 76, 136).

Schützenberger (Compt. rend. 1878, 86, 767) investigated the decomposition of wool keratin by solution of barium hydroxide at 170°, and found that 100 grms. of purified wool yielded nitrogen (evolved as ammonia), 5.25 grms.; carbon dioxide, 4.27 grms.; oxalic acid, 5.72 grms.; acetic acid, 3.2 grms.; pyrrole and volatile products, 1-1.5 grm.; whilst the residue consisted of leucine, tyrosine, and other nitrogenous substances.

The hydrolysis of wool keratin by hydrochloric acid was studied by Abderhalden and Voitnovici (Zeitsch. physiol. Chem. 1907, 52, 348), and it was found that various amino acids were produced in the following quantities p.c.: glycine, 0.6; alanine, 4.4; valine, 2.8; leucine, 11.5; tyrosine, 2.9; serine, 0.1; cystine, 7.3; proline, 4.4; aspartic acid, 2.3; and glutamic acid, 12.9. A comparison of these results with those obtained by the hydrolysis of the keratins of hair, horn, and feathers showed that all these substances are different, and led to the conclusion that keratin is a mixture of proteins.

Purified wool contains 1-2 p.c. of mineral constituents. The following analyses of the ash of a sample of Lincoln wool are due to Bowman. The wool, after being scoured, washed, and dried, yielded 1 p.c. of ash, of which 75 p.c. was soluble in water.

	Whole ash	Soluble ash	Insoluble ash
Potassium oxide K_2O	31.1	42.3	trace
Sodium oxide Na_2O	8.2	17.3	trace
Calcium oxide CaO	16.9	4.5	51.2
Alumina Al_2O_3	13.1	3.6	37.7
Ferric oxide Fe_2O_3	5.8	4.1	11.1
Silica SiO_2	20.5	24.8	trace
Sulphur trioxide SO_3	4.2	3.4	—
Carbon dioxide CO_2	trace	trace	trace
Phosphorus pentoxide P_2O_5	trace	trace	—
Chlorine	trace	trace	—

100.0 100.0 100.0

Scoured wool usually contains about 13-14 p.c. of water. The fibre is hygroscopic and the amount of moisture present therefore varies a good deal with the state of the atmosphere. On this account, it is the custom for the moisture in a consignment of wool to be estimated before sale, and the true selling weight calculated on a certain standard percentage of moisture, the

so-called 'regain.' The standard adopted at Bradford and Manchester for scoured wools is 16 p.c. of the weight of the dried fibre.

Determinations of the moisture-absorbing capacity of different kinds of wool in the various forms met with in industry have been made by Shorter and Hall (J. Text. Inst. 1924, 15, 305; J. Soc. Chem. Ind. 1924, 43, B. 628).

Wool is very susceptible to attack by dilute alkali hydroxide and is easily dissolved by a boiling 5 p.c. solution of sodium hydroxide. This reaction is employed for estimating the amount of wool in a material composed of a mixture of this fibre and cotton. When, however, wool is treated at the ordinary temperature with a strong solution of sodium hydroxide (sp.gr. 1.4-1.5), the fibre is not destroyed, but becomes white and lustrous, acquires a 'scoop' (the grating sound caused by rubbing the fibre) resembling that of silk, shows a greater affinity for dyestuffs, and increases in strength to an extent of about 30 p.c. Wool treated in this manner is said to be 'mercerised.' The process results in the removal of a large proportion of the sulphur; Matthews found that a sample of wool, originally containing 3.42 p.c. of sulphur, retained only 0.53 p.c. after being mercerised.

Strong solutions of potassium and sodium carbonate at high temperatures cause the disintegration of the fibre; but weak solutions at moderate temperatures are not injurious, and are extensively used in the scouring process.

By boiling purified wool with solution of barium hydroxide, removing the excess of the reagent with carbon dioxide, and adding solution of lead nitrate, a precipitate is produced which on treatment with hydrogen sulphide yields a product termed 'lanugine acid' (Champion, Compt. rend. 1871, 72, 330). This substance has been re-examined by Knecht (J. Soc. Dyers, 1889, 71), who describes it as a brownish-yellow solid which dissolves slowly in cold water and easily in hot water. Its aqueous solution precipitates acid and basic colouring matters with formation of coloured lakes. Knecht found the substance to have the following composition: C-41.61; H-7.31; N-10.26; S-3.35; O-31.44.

Wool is completely destroyed by strong mineral acids, but is little affected by dilute acids. When heated with dilute nitric acid, the fibre assumes a permanent yellow colour. If it is warmed with dilute sulphuric or hydrochloric acid, it becomes harsher to the touch and acquires an increased affinity for dyes. The resistance of wool to the action of sulphuric acid enables it to be quantitatively estimated in a fabric composed of a mixture of wool and cotton or other vegetable fibre. The fabric is steeped for some hours in a mixture of equal volumes of concentrated sulphuric acid and water, with the result that the vegetable fibre is destroyed, whilst the wool is not attacked and can be collected, washed, dried, and weighed.

Nitrous acid seems to diazotise the amino groups of wool keratin. Wool which has been treated with this reagent is harsh to the touch, non-hygroscopic, and assumes various colours when brought into contact with alkaline solutions of certain phenols.

Kann (Färber-Zeit. 1914, 25, 73) has found that small quantities of formaldehyde render

wool less sensitive to alkali although this does not affect its behaviour towards nitrous acid. He therefore concludes that the wool molecule does not contain amino- and keto-groups but imino- and carboxy-groups.

Wool is very little affected by dry chlorine, but is decomposed by the gas in presence of moisture. The fibre is capable of absorbing chlorine from weak solutions and becomes harsh, acquires a 'scroop,' loses its felting properties, thus becoming 'unshrinkable,' and also acquires an increased affinity for colouring matters.

For further information, reference should be made to Bowman's Structure of the Wool Fibre, or to Matthews' Textile Fibres. E. G.

WOOL BLACK, v. AZO-COLOURING MATTERS.

WOOL FAT consists of a mixture of the esters of cholesterol and of alcohols of the fatty series, including ceryl alcohol and alcohols with a smaller number of carbon atoms. Isocholesterol and carnaubyl alcohol would appear to be absent. The fatty acids are cerotic, palmitic, stearic acids, and hydroxystearic acid (?), together with resin acids, and lanoceric anhydride (Röbmann, Biochem. Zeitsch. 1916, 77, 298). It melts at about 30° to 40°, and is characterised by the readiness with which it absorbs water.

According to Lifschutz, the fat from the surface wool of the sheep contains a larger proportion of fatty acids and soaps than that near the roots. The latter contains isocholesterol, while the surface fat contains oxycholesterol (Zeitsch. physiol. Chem. 1924, 241, 146).

WOOL OILS. The trade term 'wool oils' or 'cloth oils' comprises all those oils used by woollen manufacturers for lubricating the wool before spinning, or for oiling the rags before 'grinding' and 'pulling.'

The best wool oils consist of pure fatty oils, such as olive oil, lard oil, neat's foot oil. Besides these, oleic acid ('saponification oleine' or 'saponified oleine,' 'distillation oleine' or 'distilled oleine' (see SAPONIFICATION)) is used largely as a cheaper kind of wool oil.

Cheap wool oils, for use with the lowest textile goods, include 'distilled grease oleine,' and even 'waste oils,' such as 'black recovered oil,' 'seck oil,' and 'brown grease oil'; which contain considerable amounts of unsaponifiable matter. Besides these oils there are found in commerce large quantities of 'manufactured oils,' representing blends of the above-named wool oils, as also blends containing mineral oils. For the detection of hexaline in textile oils, see Marcusson (Chem. Zeit. 1924, 49, 656), and for general methods of examination, see Lewkowitsch, Chem. Techn. J. L.

WOOL SCARLET v. AZO-COLOURING MATTERS.

WOOTZ. An Indian name for steel.

WORMSEED v. SANTONICA.

WORMSEED, OIL OF, v. OILS, ESSENTIAL.

WORMWOOD. The leaves and tops of *Artemisia Absinthium* (Linn.) contain a volatile oil, *absinthol* (q.v.), and a bitter principle, *absinthin* (q.v.). Wormwood is a bitter stomachic tonic, and is used in medicine as a remedy for atonic dyspepsia, and as an anthelmintic.

WORT v. BREWING.

WOURALI, WOURARA, WOURARI v. CURARA.

WRIGHTINE v. CONESSINE.

WULFENITE (*Gelbbleierz*, *Molybdänbleispat*, Ger.). A mineral consisting of lead molybdate $PbMoO_4$ crystallising in the tetragonal system (hemimorphic-tetrahedral class) and isomorphous with scheelite (q.v.). Next to molybdenite (q.v.) it is the most abundant of the few minerals containing molybdenum. It has been found in some quantity at Bleiberg in Carinthia, and at several places in Arizona, Nevada, Utah, Mexico, Spain, and Morocco, often as beautifully crystallised specimens of rich yellow or red colours.

L. J. S.

WURTZILITE. A mineral hydrocarbon, found in Utah and elsewhere, and used in the manufacture of varnishes, roofing compositions, &c.

WURTZITE. A native form of zinc sulphide (ZnS) crystallising in the hexagonal system, and thus dimorphous with the more common cubic mineral zinc-blende (q.v.). It was described from Oruro in Bolivia by C. Friedel, and named after the French chemist C. A. Wurtz (1817-1884). Crystals are hemimorphic and very like those of zincite (ZnO , q.v.); but, as a rule, the mineral forms fibrous masses. Much fibrous and shelly blende which is optically birefringent, and known by the names 'spiauterite' and 'Schalenblende,' really belongs to this species; and it sometimes, no doubt, forms an important part of massive zinc sulphide ore. The colour is brownish-black with resinous lustre, and the streak is brown; sp.gr. 3.98 (for artificial crystals 4.087); H. 3½-4. The phosphorescence shown by the mineral when struck has often been observed by miners.

The hexagonal zinc sulphide used for coating phosphorescing screens in Röntgen-ray work is the artificially prepared material. This was first obtained by J. Durocher in 1851, by E. H. Sainte-Claire Deville and L. Troost in 1861, and more successfully by T. Sidot in 1866 (Compt. rend. 62, 999; 63, 186). Sidot obtained long, colourless and transparent, hexagonal prisms by subliming blende in a current of sulphur dioxide. On the artificial production and stability relation of the two modifications of zinc sulphide, v. E. T. Allen and others (Amer. J. Sci. 1912, 34, 341; 1914, 38, 412).

L. J. S.

X

XAMETRIN. Syn. for hexamethylenetetramine.

XANTHALINE v. OPIUM.

XANTHEIN. The name applied by Fremy and Cloez to the soluble yellow colouring matter of flowers.

XANTHENE COLOURING MATTERS.

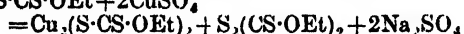
XANTHENE COLOURING MATTERS, a name sometimes applied to the dyestuffs con-

taining the group $\begin{array}{c} \diagup \text{O} \diagdown \\ | \\ \diagdown \text{O} \diagup \end{array}$ and including the *pyro-*

nine colouring matters and triphenylmethane colouring matters (*q.v.*).

XANTHIC ACIDS (*Alkylordithiocarbonic acids*) $\text{RO}\cdot\text{CS}\cdot\text{SH}$, may be prepared by dissolving sodium in the required pure dry alcohol and adding the calculated quantity of dry carbon disulphide, the mixture being stirred and cooled. In this way a sodium xanthate is formed, which, on treatment with dilute sulphuric or hydrochloric acid, yields the free xanthic acid (Ragg. Chem. Zeit. 1908, 32, 630, 654, 677; *ibid.* 1910, 34, 82).

Xanthic acid (*Ethylhydrogen dithiocarbonate*) is a colourless, transparent, heavy oil, insoluble in water and quickly decomposing into alcohol and carbon disulphide, due to autocatalysis, the alcohol, formed as a product of the decomposition, being the catalyst. If the xanthic acid is mixed with phosphoric acid it becomes more stable and can be kept for weeks (*see* von Halban and Kersch, Zeitsch. physikal. Chem. 1913, 82, 325; Zeitsch. Elektrochem. 1918, 24, 65, who have studied the kinetics of its decomposition). It forms a large number of metallic salts. The sodium or potassium salts when treated with a copper salt yield *cuprous xanthate* and *ethylthioxythiocarbonate* (*dixanthogen*) thus:



The cuprous salt is yellow, and it is this reaction which led to the adoption of the name for these salts. When the metallic xanthates are heated to 350° they decompose with evolution of hydrogen sulphide, carbon dioxide, and small quantities of combustible gases containing carbon monoxide. Amongst the liquid products are carbon di- and oxy-sulphide, ethyl hydrogen sulphide, ethyl mono- and disulphide, and ethyl alcohol, but in the case of the silver and nickel salts, the liquid product consists of almost pure ethyl xanthate and the dry distillation of the nickel salt is recommended for the preparation of the ethyl salt (Hébert, Compt. rend. 1911, 152, 869).

Potassium propylxanthate has been proposed as a reagent for cobalt and nickel salts; with the latter it yields a yellow precipitate, whilst with the former a green precipitate is formed. In dilute solutions the nickel is precipitated before the cobalt. *Potassium methyl xanthate* is also a good reagent giving with nickel a soluble, with cobalt an insoluble, salt in ammonia (Ferrer Hernández and Campo y Cedán, Anal. Fis. Quim. 1911, 9, 173). *Cf.* Whitby and Beardwood (J. Chem. Met. Soc. S. Africa, 1921, 21, 199), who employ potassium or sodium xanthate for the separation of nickel and cobalt.

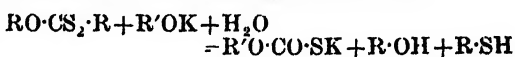
Arsenic xanthate $\text{As}(\text{S}\cdot\text{CS}\cdot\text{OEt})_3$, m.p. 94.8° (corr.), prepared by the action of potassium xanthate (3 mols.) on a solution of any compound of arsenic (1 atom), is absolutely insoluble in hot or cold water, or cold acetic acid, readily soluble in benzene, carbon disulphide, carbon tetrachloride or chloroform. The formation of

this compound may be employed as a quantitative method for the determination of small quantities of carbon disulphide (Tarugi and Sorbini, Chem. Zentr. 1912, ii, 1398).

Molybdenum xanthate $\text{Mo}(\text{S}\cdot\text{CS}\cdot\text{OEt})_3$, m.p. 108° (decomp.), is prepared when CS_2 is treated with alcoholic KOH and then with ammonium molybdate and dilute sulphuric acid. Cadmium xanthate can be prepared in like manner (Cecchetti. Gazz. Chim. Ital. 1925, 55, 104; Chem. Soc. Abstr. 1925, i, 503). Alkyl- and aryl-mercuric hydroxides react with CS_2 and an alcohol forming alkyl- and aryl-mercuric xanthates such as $\text{MeHg}\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ and $\text{C}_6\text{H}_5\text{Hg}\cdot\text{S}\cdot\text{CS}\cdot\text{OMe}$ (Koten and Adams, J. Amer. Chem. Soc. 1924, 46, 2764; Chem. Soc. Abstr. 1925, i, 236).

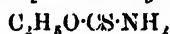
When sodium or potassium alkyl xanthate is treated with chloracetyl carbamides, the following products are obtained: chloracetyl carbamates, arylamines, xanthylacetyl carbamides, ethyl carbamates, and arylamides (Freilichs and Rentschler, Arch. Pharm. 1906, 244, 77).

The esters of xanthic acid and its homologues may be obtained by treating the alkali salts with alkyl halide. They are volatile liquids which react with alkali alkoxides thus:



(Salomon, Ber. 1875, 8, 1507; Wallach, *ibid.* 1880, 13, 530).

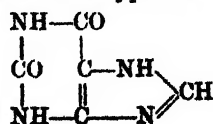
When treated with ammonia they yield mercaptan and *xanthamides* (alkylthiocarbamates) $\text{RO}\cdot\text{CS}\cdot\text{NH}_2$. The *ethyl salt*



which is known as *xanthamide*, has m.p. $40^\circ\text{--}41^\circ$ (Debus, Annalen, 1850, 75, 128; *ibid.* 1852, 82, 262; Salomon, J. pr. Chem. 1874, [ii.] 8, 115; Rosenheim and Stadler, Zeitsch. anorg. Chem. 1906, 49, 1). Mixed xanthic anhydrides have been prepared (Richter, Ber. 1916, 49, 1026).

Xanthic derivatives of certain carbohydrates, such as starch, have been prepared by first saturating the dry powdered carbohydrate with carbon disulphide and then adding the required quantity of caustic soda solution (Fr. Pat. 370505, 1906; J. Soc. Chem. Ind. 1907, 267). For other literature, *see* Tschugaceff, Ber. 1900, 33, 735; Bull. Soc. chim. 1901, [iii.] 26, 184, 298, 502; Leuckart, J. pr. Chem. 1890, [ii.] 41, 179; Holmberg, *ibid.* 1905, [ii.] 71, 264; Billmann, Annalen, 1906, 348, 133; Friedländer and Lenk, Ber. 1912, 45, 2083; Billmann and Madson, 8th Inter. Cong. App. Chem. 1912, 25, 339; Ramberg, Ber. 1913, 46, 1696; Dubsky, J. pr. Chem. 1914, [ii.] 90, 61; Holmberg, Zeitsch. physikal. Chem. 1914, 88, 385; Dubsky, J. pr. Chem. 1916, [iii.] 92, 142; Ferrer, Anal. Fis. Quim. 1918, 16, 724; Delépine and Compin, Bull. Soc. Chim. 1920, [iv.] 27, 469.

XANTHINE. 2:6-dioxypyrimine

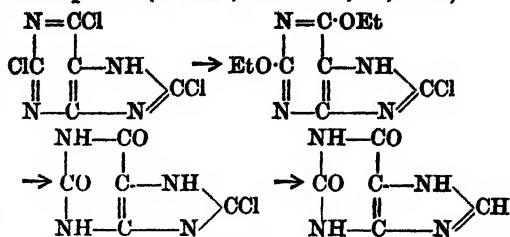


was discovered in 1817 by Marcet in a urinary calculus and called 'xanthic oxide,' because of the yellow residue it left when evaporated to

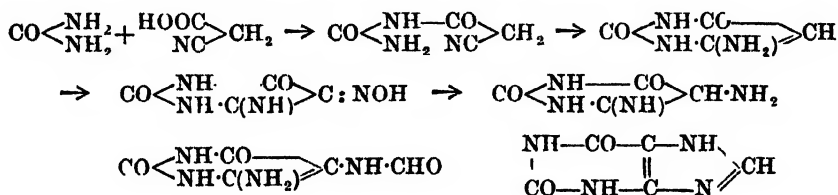
dryness with nitric acid. Wöhler and Liebig analysed the compound, which they isolated from another calculus, and found that it differed from uric acid in containing one atom of oxygen less in the molecule (Annalen, 1838, 26, 340). It occurs in guano (Strecker, *ibid.* 1861, 118, 157), to a small extent in urine, 10,000 litres contain 10.11 grms. (Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 24, 371; 26, 367); in the muscles, liver, spleen, pancreas, thymus and brain (Micko, Zeitsch. Nahr. Genussm. 1903, 6, 781; 1904, 7, 257). It is also found in the actively growing tissues of plants, in yeast, tea, and seedlings of lupins and malt; and has been isolated, together with other purine bases, from the soil (Schreiner and Shorey, J. Biol. Chem. 1910, 8, 385). According to de Waele (Chem. Zentr. 1913, 11, 519, from Zeitsch. Imm. expt. Therapie, 1913, 18, 11, 410) xanthine is an intermediary product in poisoning by nucleoproteins.

Synthesis.—Xanthine can be prepared by heating 2:6:8-trichloropurine with sodium ethoxide, and reducing the 2:6-diethoxy-8-chloropurine either directly by hydrogen iodide,

or after preliminary hydrolysis, to 2:6-dioxy-8-chloropurine (Fischer, Ber. 1897, 30, 2232).



Xanthine is also obtained by heating 2:6-di-iodopurine with hydrochloric acid under pressure (Fischer, *ibid.* 1898, 31, 2550). Traube (*ibid.* 1900, 33, 1371, 3043) has effected the synthesis of xanthine from cyanacetyl-urea; this is converted by the action of alkalis into 4-amino-2:6-dioxypyrimidine which, by the action of nitrous acid and subsequent reduction, yields 4:5-diamino-2:6-dioxypyrimidine: on heating the sodium salt of the formyl derivative of this compound, xanthine is obtained.

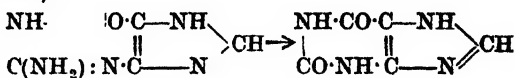


When uric acid is reduced by nascent formic acid, it yields xanthine. This may be effected by heating a mixture of uric acid, formic acid, chloroform, and alkali on the water bath: or by heating a mixture of equal weights of uric acid, calcium formate and calcium hydroxide in a combustion furnace until evolution of gas begins; or, more simply and with a yield of 30–33 p.c., by heating at 200° uric acid mixed with oxalic acid and excess of glycerol (Sundvik, Zeitsch. physiol. Chem. 1897, 23, 476; 1898, 26, 131; 1912, 76, 486; Skan. Arch. Physiol. 1911, 25, 256). Johns and Hogan (J. Biol. Chem. 1913, 14, 299) obtained xanthine by boiling hypoxanthine-2-thiolacetic acid with 20 p.c. hydrochloric acid.

The following technical preparation of xanthine from thioxanthine is described by C. F. Boehringer and Soehne, D.R.P.P. 141974, 142468, 143725. An alkaline solution of isouric acid absorbs sulphuretted hydrogen, forming a salt of γ -thio- ψ -uric acid, which is converted by boiling with mineral acids into thioxanthine (2:6-dioxy-8-thiopurine); or the thioxanthine may be prepared by warming 4:5-diamino-2:6-dihydroxypyrimidine with carbon disulphide and potassium hydroxide. On oxidising thioxanthine by means of nitrous acid, hydrogen dioxide in alkaline solution or manganese dioxide in neutral solution, it is converted into xanthine.

Xanthine is conveniently prepared from guanine by the action of nitrous acid, or, more readily and with a yield of 60–70 p.c. by heating it in a reflux apparatus for 32 hours with

25 p.c. hydrochloric acid (Fischer, Ber. 1910, 43, 805)



Properties.—Xanthine crystallises with one molecule of water which it loses at 125°–130°, forming a colourless micro-crystalline powder that acquires a waxy lustre by friction (Wöhler and Liebig, *l.c.*); it dissolves in 14,151 parts of water at 16° or 1300–1500 parts at 100°, and is insoluble in alcohol or ether. It dissolves readily in solutions of sodium or potassium hydroxides or in ammonia, but is precipitated from the solution by acids, even carbon dioxide. Xanthine sublimates slightly when heated, but decomposes without melting, yielding carbon dioxide, ammonia, hydrocyanic acid and cyanogen.

Xanthine is oxidised by chlorine oxides or chlorine water, yielding alloxan and urea (Fischer, Annalen, 1882, 215, 253).

Milk and certain animal tissues contain a *xanthine oxydase*, which is probably identical with Schardinger's enzyme and with Haas and Hill's 'atite' (Morgan, Stewart and Hopkins, Proc. Roy. Soc. 1922, [B], 94, 109; Haas and Hill, Bio-Chem. J. 1923, 17, 671; Dixon and Thurlow, *ibid.* 1924, 18, 971, 976, 989; 1925, 19, 507, 672; 1926, 20, 703).

Detection and estimation.—Xanthine gives the murexide reaction when evaporated to dryness with chlorine water or hydrochloric acid and potassium chlorate and the residue moistened with ammonia solution; this is commonly

called 'Weidel's test' for xanthine, although this author described it as a test for *hypoxanthine* (Annalen, 1871, 168, 365), and Kossel showed that the reaction was due to the presence of *xanthine*, pure *hypoxanthine* not responding to the test (Zeitsch. physiol. Chem. 1882, 6, 431).

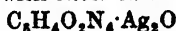
Xanthine dissolves in hot nitric acid without evolution of gas, and the yellow residue obtained on cautious evaporation of the acid solution turns reddish-yellow on addition of sodium or potassium hydroxide and changes to reddish violet on heating. If ammonia be used instead of the alkali hydroxides, no violet colour is produced, and this test distinguishes xanthine from uric acid which gives the murexide reaction when similarly treated.

If dry xanthine be sprinkled on an alkaline solution of bleaching powder, each particle becomes surrounded with a dark green ring or scum which quickly changes to brown and finally disappears. Xanthine develops a red colour when added to an alkaline solution of diazobenzenesulphonic acid.

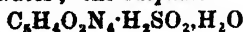
Xanthine can be estimated by precipitating the insoluble silver compound by means of silver nitrate from an ammoniacal solution, and estimating the nitrogen present in the carefully washed precipitate by the Kjeldahl method; or the silver may be estimated gravimetrically or volumetrically.

For the separation of xanthine from the purine bases in urine or extract of tissues, see Abderhalden's Handbuch der Biochemischen Arbeitsmethoden, vol. iii. part 2. p. 894. Also Thiéry (J. Pharm. Chim. 1921, 23, 494).

Salts and derivatives.—Xanthine forms compounds with certain metallic oxides and salts, the compound with *silver oxide*



is a flocculent precipitate obtained by precipitating an ammoniacal solution of xanthine with ammoniacal silver nitrate; with *silver nitrate* $C_5H_4O_2N_4 \cdot AgNO_3$ a flocculent precipitate prepared by mixing a nitric acid solution of xanthine with silver nitrate solution; the compound with *lead* $C_5H_4O_2N_4 \cdot Pb$ is white and crystalline; and the compound with *barium hydroxide* $C_5H_4O_2N_4 \cdot Ba(OH)_2$ is sparingly soluble. Xanthine forms crystalline salts with the mineral acids which are generally readily hydrolysed by solution in water; the *sulphate*

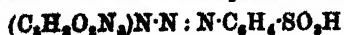


crystallises in pearly rhombic plates from hot strong sulphuric acid, or in microscopic needles from dilute acid; the *hydrochloride*



crystallises in warty masses; the *nitrate* $C_5H_4O_2N_4 \cdot HNO_3$ is precipitated as a heavy crystalline powder, when a warm solution of xanthine in sodium hydroxide is added to a cold solution of nitric acid (2:3); the *periodide* $C_5H_4O_2N_4 \cdot HI \cdot I_2$ forms characteristic green crystals from alcohol (Linarix, J. Pharm. Chim. 1909, [vi.] 30, 241). The phospho-tungstate crystallises in straw coloured cubical plates (Drummond, Bio-chem. J. 1918, 12, 5):

Xanthine-7-diazobenzenesulphonic acid



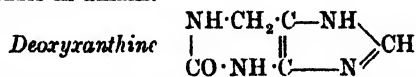
dark red crystalline needles that do not decom-

pose at 265°, soluble in water or alkalis, insoluble in ether, sparingly soluble in alcohol (Burian, Ber. 1904, 37, 703).

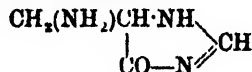
8-Chloroxanthine $C_5H_3ClO_2N_4$, obtained by hydrolysing 2:6-diethoxy-8-chloropurine with hydrochloric acid, forms a sparingly soluble crystalline powder which blackens without melting when heated (Fischer, Ber. 1887, 30, 2236).

8-Bromoxanthine $C_5H_3BrO_2N_4$, obtained by direct bromination at 100°, or by the action of nitrous acid on bromoguanine; is a crystalline powder, insoluble in cold, sparingly soluble in hot water, insoluble in alcohol or ether, and decomposes without melting (Fischer and Reese, Annalen, 1883, 221, 343).

8-Thioxanthine $C_5H_3(SH)O_2N_4$, obtained by heating 8-bromoxanthine with potassium hydrogen sulphide solution in a sealed tube at 120° (Fischer, Ber. 1898, 31, 433), or by methods already referred to in the description of the synthesis of xanthine: is a colourless heavy crystalline powder which blackens without melting on being heated, sparingly soluble in concentrated hydrochloric acid and readily soluble in alkalis.

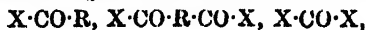


obtained by the electrolytic reduction of xanthine dissolved in sulphuric acid, using lead electrodes; forms colourless crystals that decompose without melting after becoming brown at 250° (Tafel and Ach, Ber. 1901, 34, 1166). It is very readily hydrolysed when gently heated with acids, yielding carbon dioxide, ammonia and 5-aminomethyl-4-iminazolone



Tafel and Mayer, Ber. 1908, 41, 2546).

For *acyl* derivatives of xanthine series, compounds of the general formula



where X is xanthine or a mono- or dialkyl substituted xanthine and R is the radicle of an alcohol, phenol or amine, v. Merck (D. R. P. 290910; J. Soc. Chem. Ind. 1916, 35, 654); they combine the diuretic action of xanthine with the therapeutic properties of the phenol, etc.

For formaldehyde derivatives which are of therapeutic value, v. Bayer & Co., D. R. P. 54488; and for soluble derivatives, v. Bayer & Co., D. R. P. 264389. M. A. W.

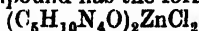
XANTHINE (CHRYSANILINE) v. ACRIDINE YESTUFFS

XANTHOCROITE v. GREENOCRITE.

XANTHOCREATININE, CHRYSOCREATININE and AMPHICREATININE are the chief members of the creatinine leucomaines isolated by Gautier from the muscles of large animals; they are alkaloidal in properties, and when administered to animals act more or less powerfully on the nerve centres inducing sleep, and in some cases vomiting and purging in a manner similar to the alkaloids of snake poison. These bases are formed during life and occur in the urine, saliva, and various glandular secretions (J. Pharm. Chim. [v.] 13, 354, 401; Bull. Soc. chim. 48, 16).

Xanthocreatinine $C_8H_{10}ON_4$ is the most

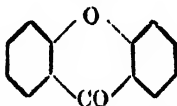
abundant of the creatinine leucomaine group of bases. It was extracted from muscle by Gautier and also by Monari (Gazz. chim. ital. 1887, 16, 538) and from the urine of the lion by Colosanti (*ibid.* 21, ii. 188). In chemical properties it closely resembles creatinine from which it differs in empirical constitution by CH_2N . It crystallises in light sulphur-yellow spangles which have a slightly bitter taste and an odour, similar to that of crude acetamide. The base is soluble in cold water and can be crystallised from boiling alcohol. It is amphoteric in character, turning blue litmus red and red litmus blue. It forms a salt with hydrochloric acid which yields soluble crystalline double salts, with the chlorides of gold, platinum, mercury and zinc. The latter compound has the formula



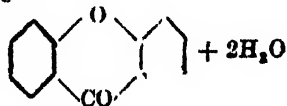
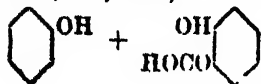
Chrysocreatinine $\text{C}_8\text{H}_9\text{ON}_4$ crystallises in orange-yellow crystals, is feebly alkaline towards litmus paper and has a slightly bitter taste. It forms a crystalline non-deliquescent hydrochloride, which yields crystalline double salts with platinum, auric and zinc chlorides respectively.

Amphicreatinine $\text{C}_8\text{H}_9\text{O}_4\text{N}_7$ crystallises from boiling water in bright, pale yellow prisms and is less readily soluble than either of the two preceding bases. When heated at 110° the crystals become colourless and opaque without, however, changing their form. It forms a crystalline hydrochloride. The *platinochloride* is soluble in water, and insoluble in alcohol and crystallises in lozenge-shaped plates, and the *aurichloride* is very readily soluble and crystallises in microscopic hexahedral and tetrahedral crystals.

XANTHONE. Xanthone or diphenoylpyrone—



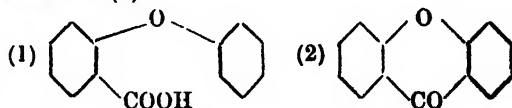
known also as *diphenylene ketone oxide*, *benzophenone oxide*, *carbodiphenylene oxide* $\text{C}_{13}\text{H}_8\text{O}_2$, was first prepared by Kolbe and Lautermann (Annalen, 1860, 115, 197), by the action of phosphorus oxychloride on sodium salicylate and has been subsequently obtained from salicylic acid and its derivatives by the employment of various dehydrating agents. The most convenient method consists in distilling a mixture of acetic anhydride and salicylic acid (W. H. Perkin, Chem. Soc. Trans. 1883, 43, 35; cf. also Graebe, Annalen, 254, 265), when the higher boiling fraction on cooling deposits crystals of xanthone. During the reaction some phenol is produced and is indeed found to some extent in the distillate, and the reaction though probably more complex, may be considered to consist of the condensation of phenol and salicylic acid with formation of the xanthone. See also Dhar (Chem. Soc. Trans. 1920, 117, 1055).



Phenyl salicylate (Siefert, J. f. prakt. Chem. [ii.] 31, 472) by long digestion at the boiling temperature yields xanthone, and it is also produced when salicylic acid phenyl ether

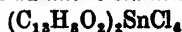


is warmed with sulphuric acid (Graebe, Ber. 21, 503). Other methods of this type have been described by Richter (J. f. prakt. Chem. [ii.] 28, 275), Jeiteles (Monatsh. 17, 66), Staedel (Annalen, 283, 179), Goldschmidt (Monatsh. 4, 123), and Klepl (J. f. prakt. Chem. [ii.] 28, 217). Fosse (Compt. rend. 1903, 136, 1006) has also obtained xanthenes by warming the phosphoric esters of phenols with potassium carbonate. For the theory of xanthone formation the paper of Strohbach (Ber. 1902, 34, 4136) should be consulted. Ullmann and Zlokasoff (*ibid.* 1905, 2111), by the interaction of sodium phenoxide and sodium *o*-chlorobenzoate in the presence of copper powder, obtained *o*-phenoxybenzoic acid (1) which by elimination of water passes into xanthone (2).

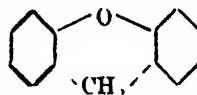


Xanthenes of the anthraquinone series can be prepared by the action of condensing agents on phenyl, naphthyl, or anthraquinonyl esters of 1-hydroxyanthraquinone 2-carboxylic acids (D. R. P. 251696).

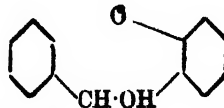
Xanthone crystallises in long colourless needles, m.p. 173° – 174° and dissolves in sulphuric acid to form a blue fluorescent liquid. The oxonium salts *xanthone hydrobromide* $\text{C}_{13}\text{H}_8\text{O}_2\text{Br}$ and *xanthone stannichloride*



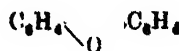
have been obtained by Gomberg and Cone (Annalen, 1910, 376, 183). By distillation with zinc-dust or by the action of fuming hydriodic acid at 160° , it is converted into *xanthene* (methylene diphenylene oxide) or diphenoylpyran—



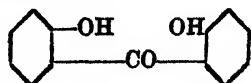
which may also be regarded as the anhydride of 2,2'-dihydroxydiphenylmethane. By oxidation with chromic acid, xanthone can be reproduced (Merz and Weith, Ber. 14, 192). With boiling alcoholic soda and zinc-dust xanthone gives *xanthidrol* (Meyer and Paul, Ber. 1893, 26, 1276)—



and with zinc-dust and acetic acid *dioxo-xanthylene* (Gurgenganz and v. Kostanecki, Ber. 1895, 28, 2310) is produced—

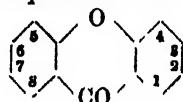


Fusion with alkali gives *xanthonic acid*, dihydroxybenzophenone



and from this by means of dehydrating agents xanthone can again be reproduced. The disruption of the γ -pyrone ring in this manner by the action of hydrolytic agents is characteristic of compounds containing this and the γ -pyran nucleus. In the flavone group this hydrolysis takes place even more readily, and to this to some extent may no doubt be ascribed the lack of permanence of these colouring matters when applied to fabrics as compared with those of the anthraquinone group.

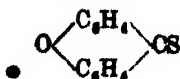
Interesting is the fact that when ketone colouring matters, and indeed all hydroxyketones, are alkylated in the usual manner with alkyl iodide and alcoholic potash, the hydroxyl in the ortho position to the carbonyl group remains unaffected, a fact which may be considered as an example of steric hindrance. This, at first pointed out by Herzig (Monatsh. 12, 161) in connection with the ethylation of euxanthone (dihydroxyxanthone) and quercetin, was observed by v. Kostanecki and Dreher (Ber. 1893, 26, 71) to be the property of all xanthenes containing hydroxyls in the position 1 or 8



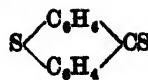
and the non-reactivity of the hydroxyl in this position has served in many cases as an indication of the presence of a carbonyl group. Such partially methylated compounds are as a rule, insoluble in aqueous alkali, but give with alcoholic potash insoluble salts, which are readily hydrolysed with water. It has, however, been shown by Perkin in special instances that the alkylation of this hydroxyl group can be readily effected if a considerable excess of the reagents be employed, and it is probable that this method is of a general application (Chem. Soc. Trans. 1913, 103, 1632).

a-Dinitroxanthone, m.p. 190° (Richter, l.c.; Graebe, l.c.), *b*-dinitroxanthone, m.p. 262° (Perkin, Chem. Soc. Trans. 43, 189), *a*-diaminoxanthone, m.p. 209° (Graebe), *b*-diaminoxanthone (Perkin), xanthone disulphonic acid (Perkin), monobromoxanthone, m.p. 125°-127° (Graebe), dibromoxanthone, m.p. 212° (Perkin), xanthone phenylimine, m.p. 134°-135°, and xanthone oxime (Graebe and Röder, Ber. 32, 1689) have been directly prepared from xanthone.

3-Nitro-xanthone, m.p. 176°, 3-chloroxanthone, m.p. 171° (Ullmann and Wagner, Annalen, 1907, 356, 359), 3-aminoxanthone, m.p. 232°, 3-methoxyxanthone, m.p. 129°, 3-hydroxyxanthone, m.p. 243°, 1-hydroxyxanthone, m.p. 147° (Ullmann and Panchaud, *ibid.* 350, 108), 2,4-dinitroxanthone, m.p. 206° (Ullmann, *ibid.* 1909, 366, 79), 4-chloroxanthone, m.p. 130°, 4-bromoxanthone, m.p. 126° (Gomberg and Cone, *ibid.* 1909, 370, 142), xanthione, m.p. 156° (Graebe and Röder)—

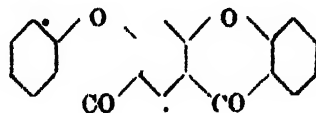


and dithioxanthone—

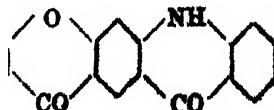


have been obtained indirectly.

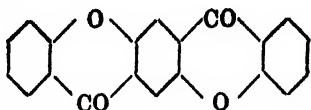
The following derivatives have also been prepared:—Ootochloroxanthone, m.p. 324° (Eckert and Steiner, Monatsh. 1915, 36, 175); 1-chloroxanthone, m.p. 100°; 2-chloroxanthone, m.p. 165°; dichloroxanthone, m.p. 225°; 2-bromoxanthone, m.p. 150°; tetrabromoxanthone, m.p. 298°; hexabromoxanthone, m.p. 308°; 1-nitrobromoxanthone, m.p. 210°; 2-nitroxanthone, m.p. 200°; 4-nitroxanthone, m.p. 127°; 2:3:7-trinitroxanthone, m.p. 205°; six isomeric tetranitroxanthenes, β -nitroaminoxanthone, m.p. 265°, giving an acetyl derivative, m.p. above 300°; α -nitroaminoxanthone, m.p. 204°-206°, giving an acetyl derivative, m.p. above 300°; dinitroaminoxanthone, m.p. with decomposition 205°-210°; α -dinitroxanthhydrol, m.p. 185°; β -dinitroxanthhydrol, m.p. 196°; nitroxanthoquinoline, m.p. 205°-210°; dibromodinitroxanthone, m.p. 235°-237°; tetrabromodinitroxanthone, m.p. 300°; 2-chlorotetranitroxanthone, m.p. 205°; 4-chlorotetranitroxanthone, m.p. 235°; 4-chlorodinitroxanthone, m.p. 195°-200°; dichlorodinitroxanthone, m.p. 240°; 2-bromo- α -tetranitroxanthone, m.p. 210°; 2-bromo- β -tetranitroxanthone, m.p. 212°; 1-anilinoxanthone, m.p. 120°-125°; dibromodinitroxanthone (C₁₂H₈O₂Br₂(NHPh)₂, m.p. 140°-145°; hexaanilinoxanthone, m.p. 180°-183°, phenyliminodinitroxanthone (C₁₂H₈O(NO)₂:NPh, m.p. 170°-175°; β -nitroxanthone-azo- β -naphthol, β -nitroxanthone-azo:1:5-dihydroxynaphthalene, α -nitroxanthone-azo-phenol, dinitroxanthone-azo- β -naphthol, m.p. 270° (Dhar, Chem. Soc. Trans. 1916, 109, 744; *ibid.* 1920, 117, 998, and 1053); 8-hydroxy-2:3-quinoxanthone and its derivatives (Dean and Nierenstein, Chem. Soc. Trans. 1920, 117, 802). Xanthone 4-carboxylic acid, m.p. 289°, its derivatives and salts (Anschütz and Cloasen, Ber. 1922, 55, [B] 680); 5:6:7-trichloro-2-methylxanthone 8-carboxylic acid (Ullmann and Schmidt, Ber. 1919, 52, [B] 2098); 2:3:4-trichloro-6-hydroxyxanthone 1-carboxylic acid, m.p. 279°-280°, and its salts (Orndorff and Adamson, J. Amer. Chem. Soc. 1918, 40, 1235); 3-bromo 2-methylxanthone, m.p. 146°; 3-bromo-xanthone 2-carboxylic acid, m.p. 338°-340°, its methyl ester, m.p. 154°-155°. Dixanthone



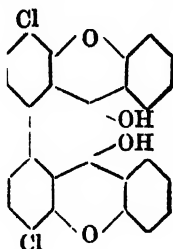
m.p. 353°, by heating 4:6-diphenoxyisophthalic acid with conc. H₂SO₄; 3-anilinoxanthone 2-carboxylic acid, m.p. 310°-313°, the acid chloride of which gives with AlCl₃ the acridone xanthone



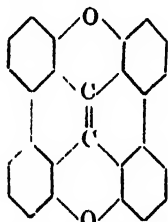
2:5-diphenoxyterephthalic acid gives the dioxanthone



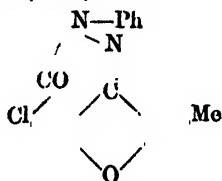
(Eckert and Seidel, J. pr. Chem. 1921, [ii] 102, 338); 1:4-dichloroxanthone, m.p. 159°-161°; 4-chloro-1-methoxyxanthone, m.p. 156-158°; 4-chloro-1-hydroxyxanthone, m.p. 156°; 4:4'-dichloro-1:1'-dixanthonyl, m.p. 290°, which on reduction gives the pinacone, m.p. 276°-278°



from this meso-benzdixanthylene, m.p. 236°-237°, dixanthonyl and mesonaphthidianthylene, m.p. 140°-150°



were obtained (Eckert and Endler, J. pr. Chem. 1922, [ii] 104, 91). 7-Chloro-2-methylxanthone 8-carboxylic acid, m.p. 286° (corr. decomp.); 7-chloro-2-methylxanthone, m.p. 169° (corr.); 7-phenoxy-2-methyl-xanthone 8-carboxylic acid, m.p. 270°-280 (corr.); 2-methyl-dixanthone, m.p. 249°-252° (decomp.); 7-anilino-2-methyl-xanthone, m.p. 255°-259° (corr.); 7-chloro-N-phenyl-2-methyl-pyridazonexanthone, m.p. 264°-268° (corr.)

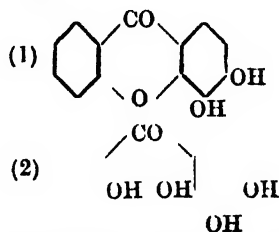


and the 5-chloro compound, m.p. 266°-271° (corr.) (V. dem Knesebeck and Ullmann, Ber. 1922, 55, [B] 306) have also been obtained.

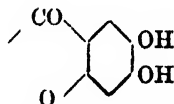
A general method for the preparation of the hydroxyxanthones consists of distilling a mixture of a phenol and an o-hydroxy-carboxylic acid with acetic anhydride, and this has been employed in numerous syntheses. In this manner 1-hydroxyxanthone (Michael, Amer. Chem. Soc. 5, 91; Graebe, Annalen, 54, 590), m.p. 146°-147°, 2-hydroxyxanthone (v. Kostanecki and Rutishauer, Ber. 25, 1648), m.p. 231°, 4-hydroxyxanthone (v. Kostanecki and Rutishauer), m.p. 224°, 3-hydroxyxanthone (v. Kostanecki and Nessler, Ber. 34, 3981), m.p. 243°, 3:6-di-

hydroxyxanthone (isoeuxanthone) (v. Kostanecki, *ibid.* 18, 1986), m.p. 243°, Nishikawa and Robinson (Chem. Soc. Trans. 1922, 121, 841) gave m.p. 259°, 2:5-dihydroxyxanthone (v. Kostanecki, *ibid.* 27, 1991), m.p. 280°, and gentisin and euxanthone, the two natural representatives of this group, have been prepared.

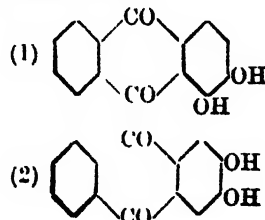
These latter are both feeble dyestuffs, and this is explained by the fact that they do not possess two hydroxyls in the ortho position relatively to one another. Graebe and Eichen-grun (Ber. 1891, 24, 969) obtained such a compound (1), 3,4-dihydroxy-xanthone by heating 2,3,4,2'-tetrahydroxy-benzophenone (2) with water at 180°-220°—



This melts at 240°, is a strong dyestuff giving an aluminium mordant yellow, and on iron mordant greyish-black shades. The position of the ortho-hydroxyl grouping is, however, of importance in that the 2,3-dihydroxy-xanthone of Liebermann and Lindenbaum (Ber. 1904, 37, 2728)—



and which is produced by the interaction of hydroxy-quinol and salicylic anhydride in the presence of sulphuric acid, is practically devoid of dyeing property. As is well known, a similar distinction is to be observed between alizarine (1) and hystazarine (2)—



and it is of interest that similar rules (cf. Liebermann and v. Kostanecki) to those which are applicable to the hydroxy-anthraquinone dyestuffs, also hold good with the xanthone colouring matters. On the other hand, it will be observed, notably in the flavonol group of colouring matters, that ortho hydroxyls are not entirely essential for dyeing property. The statement by Tschirch and Polacco (Arch. Pharm. 1900, 238, 459) that a trihydroxy-xanthone rhamnocitrin occurs in the berries of the *Rhamnus catharticus* has been shown by Oesch and Perkin (Chem. Soc. Trans. 1914, 105, 2350) to be incorrect.

A. G. P.

XANTHORHAMNIN v. GLUCOSIDES; PERSIAN BERRIES.

XANTHORRHOEA RESINS OR BALSAMS v. BALSAM.

XANTHOSTEROL $C_{31}H_{46}O$ is obtained by extracting the bark of *Xanthoxylum Budrunga* with light petroleum. Slender white needles, m.p. 213° – 214° . For colour reactions and derivatives, see Dieterle, Arch. Pharm. 1919, 257, 260; Chem. Soc. Abstr. 1920, i. 42; cf. Dieterle, Arch. Pharm. 1922, 259, 244). According to Ultée, xanthosterol is identical with lupeol, as is also the phytosterol of Oestling from *Fagara xanthoxyloides*, Lam.

XANTHOXYLUM ESSENTIAL OILS (Simonsen and Rau, Indian Forest Rec. 1922, 9, 111) The seeds of *X. alatum*, Roxb., yield an oil containing over 85 p.c. of *l*- α -phellandrene, together with small amounts of linalool and a sesquiterpene. The oil obtained from the seeds of *X. acanthopodium*, DC., has sp.gr. 0.8837 at 30° ; $n_D^{20}=1.4746$; $[\alpha]_D^{20}=+6.54^{\circ}$; sapon. value, 60.79; sapon. value after acetylation, 242.5. The chief constituents are dipentene, methyl cinnamate, and over 50 p.c. of linalool in addition to *l*- α -phellandrene and a small quantity of an aldehyde or ketone and a mixture of fatty acids.

X. Budrunga, Wall., seeds yield an oil apparently identical with that found by Semmlé to occur in *X. alatum*. The terpene present is *l*-sabinene, in addition to small quantities (Lautermann) of terpinene (J. Soc. Chem. Ind. Jan. 12, 1923, 30 A).

XANTHYDROL $C_{13}H_{16}O$, or $O\left\langle\begin{array}{c} C_6H_4 \\ C_6H_4 \end{array}\right\rangle CH\cdot OH$.

Prepared by slowly adding zinc dust to a boiling mixture of xanthone (10 grms.), NaOH (40 grms.), and alcohol (400 c.c.). Precipitated in minute needles on adding water (R. Meyer and Saul, Ber. 1893, 26, 1276). Decomposes on melting. Reproduces xanthone on heating in the air. If a methyl-alcoholic solution of xanthydrol is mixed with an aqueous solution of urea to which a large excess of acetic acid has been added and the mixture allowed to stand for two hours dioxanthidryl-urea $O(C_6H_4)_2CH\cdot NH\cdot CO$ will be deposited. The weight of this substance, after washing with alcohol and drying, may be used for estimating the amount of urea in a solution (Fosse, Hagene and Dubois, Compt. rend. 1924, 79, 214; J. Soc. Chem. Ind. 1924, 43, B. 731). Dulcin and saccharin also form crystalline condensation products with xanthydrol (cf Vol. vi. p. 4).

XARA. Trade name for acetyl-salicylic acid.

XAXAQUIN. Trade name for quinine acetyl-salicylate.

XENON. Sym. X. At.wt. 130.2.

An inert gas, discovered along with krypton in the final residues obtained after evaporating considerable quantities of liquid air (Ramsay and Travers, Proc. Roy. Soc. 1898, 63, 405). For the separation of xenon from these residues, see KRYPTON. Xenon may also be separated by passing a current of air through a spiral tube filled with glass wool and immersed in liquid air (Dewar, *ibid.* 1901, 68, 360). Xenon occurs in the gases evolved from many thermal springs (Moureu and Lepape, Compt. rend. 1909, 149, 1171).

Xenon is the least volatile and least abundant of the inert gases which exist in the atmosphere, being present only to the extent of 1 part in 170 million parts of air by volume (Ramsay,

Proc. Roy. Soc. 1903, 71, 421; 1906, 80, A, 599). It boils at -109.1° , at which temperature its density is 3.063 and its atomic volume 42.7. The critical temperature is $+16.6^{\circ}$, the critical pressure 58.2 atmospheres, and the critical density 1.115 grms. per c.c. The 'rectilinear diameter' is given by the equation

$$D_r = 1.205 - 0.003055t$$

where D_r = mean density of liquid and saturated vapour at $t^{\circ}C$. (Patterson, Cripps and Whytlaw-Gray, Proc. Roy. Soc. 1912, A, 579). At the temperature of liquid air xenon readily solidifies (Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329).

At N.T.P. 1 litre of xenon weighs 5.851 grms.; its density is therefore 65.35 ($\rho=16$) (Moore, Chem. Soc. Trans. 1908, 93, 2181; Watson, *ibid.* 1910, 97, 833). The refractive index at N.T.P. for the green mercury line ($\lambda=5461$) is 1.0007055 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1908, 81, A, 440; 1910, 84, A, 13). At 20° the absorption coefficient is 0.1109 (Antropoff, *ibid.* 1910, 83, A, 474; Zeitsch. Elektrochem. 1919, 25, 269). For the spectrum of xenon v. Baly (Phil. Trans. 1903, A, 202, 183); Livinge and Dewar (Proc. Roy. Soc. 1901, 68, 389; Merrill, Bur. Standards, Bull. 1919, 15, 251; Collic, Proc. Roy. Soc. 1920, [A] 97, 349).

Xenon is monatomic since the ratio of its specific heats is 1.66 (Ramsay). Xenon would appear to be a mixture of isotopes, with definite evidence of five isotopes of masses 129, 131, 132, 134 and 136, and with distinct indications of a sixth component, 128, present in smaller quantity. It is possible also that there is a seventh isotope of mass 130 (Aston). For regularities in the xenon spectrum, see Sommer, Zeitsch. Physik. 1923, 13, 85.

XENOTIME. Yttrium orthophosphate YPO_4 crystallised in the tetragonal system. The crystals resemble in habit and also closely in interfacial angles those of cassiterite, rutile, zircon, thorite, tapiolite, &c. Crystals of xenotime and zircon intergrown in parallel position have been observed. There is a good cleavage parallel to the faces of the square prism. Sp.gr. 4.4–4.6; H. 4–5; colour usually brownish with resinous lustre; insoluble in acids. The yttrium earths are rich in erbia, xenotime being one of the principal sources of this rare-earth. Cerium earths are also present in small amount, but only occasionally thorina (cf. MONAZITE). Curiously, however, a supposed new earth (afterwards proved to be basic yttrium phosphate) in xenotime was called thorina by Berzelius in 1815—a name later transferred to the earth that he discovered in 1829 in thorite. Sulphuric anhydride in small amount is sometimes present in xenotime. The mineral occurs as single crystals scattered in pegmatite and granitic rocks, and is of wide distribution, though less common than monazite. It is found in sands derived from these rocks, including monazite sands. Rough opaque crystals with the form of low tetragonal bipyramids, up to an inch across, are found in the felspar quarries at several places in the south of Norway. Small transparent crystals of prismatic habit are met with in the diamondiferous sands of Minas Geraes and Bahia in Brazil. L. J. S.

XYLAN $C_8H_8O_4$, a substance contained in wheat straw and corn cobs. To obtain it, air dried wheat straw is treated in the cold with a dilute solution of ammonia for 24 hours, and the ammoniacal solution removed by decantation. The residue, after washing with water, is immersed in a 7 p.c. solution of sodium hydroxide for 48 hours, and the extract filtered through a silk cloth. To the clear brown-coloured solution an equal volume of 98 p.c. alcohol is added with constant stirring, when the xylan is precipitated, collected and washed with dilute alcohol, again dissolved in 7 p.c. sodium hydroxide solution and reprecipitated with alcohol. The separated xylan is treated with dilute hydrochloric acid, washed with dilute alcohol, and subsequently with ether and dried over sulphuric acid *in vacuo*. The yield is about 16-17 p.c. (Allen and Tollens, Ann. 1890, 260, 290; Komatsu and Kashima, Mem. Coll. of Science, Kyoto Imp. Univ. 1922, 5, [5] 307; Heuser and Braden, J. pr. Chem. 1922, [ii.] 104, 250).

Xylan is a light yellow amorphous substance, easily soluble in alkaline solutions with a specific rotation $[\alpha]_D^{25} = -78^\circ$ in 2.5 p.c. sodium hydroxide solution. Insoluble in water and alcohol. Readily hydrolysed to *lævo*-xylose when heated with 1.5 p.c. hydrochloric acid (cf. Heuser and Brunner, J. pr. Chem. 1922, [ii.] 104, 264). Gives a monoacetyl ($C_8H_7O_4(CH_3CO)$) and diacetyl derivative ($C_8H_6O_4(CH_3CO)_2$) when treated with acetyl chloride, or with glacial acetic acid, and acetic anhydride in presence of a catalyst. They are light yellow amorphous powders, soluble in chloroform but insoluble in alcohol or ether. Soluble in sodium hydroxide solution (Komatsu and Kashima, *l.c.*; Böeseken, van der Berg, and Kerstjens, Rec. trav. chim. 1916, 35, 320; Bader, J. Chem. Soc. 1896, 70, 1335).

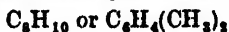
For methyl ethers of xylan, *see* Heuser and Ruppel, Ber. 1922, 55, 2084; acetyl derivatives, Heuser and Schlosser, Ber. 1923, 56, [B] 392.

For the constitution of xylan, *see* S. Komatsu, T. Inoue and R. Nakai, The Memoirs of the College of Science, Kyoto Imperial University, Series A. vol. vii. No. 1923.

For the products of its dry distillation, *see* Heuser and Scherer, Brennstoff Chem. 1923, 4, 97; J. Soc. Chem. Ind. May 11, 1923, 393 A.

For the hydrolysis of xylan by means of dilute nitric acid, *see* E. Heuser and G. Jayme, J. prakt. Chem. 1923, [ii.] 105, 232-242, 283-287.

XYLENES, Dimethylbenzenes,



A hydrocarbon C_8H_{10} , in reality a mixture, was isolated by various investigators from the fraction of coal tar, or wood tar, boiling between 137.5° and 142° (Cahours, Compt. rend. 1850, 30, 319; Voelckel, Ann. 1853, 86, 331; Reissig, Zeitsch. für anal. Chem. 1864, 3, 9; Ritthausen, J. pr. Chem. 1854, 61, 74; Church, Phil. Mag. (4), 9, 453; Warren and Storer, J. pr. Chem. 1867, 102, 436; Fittig, Koelbrich and Jilke, Ann. 1868, 145, 129; Bull. Soc. chim. 1869, 11, 78; de la Rue and Müller, J. pr. Chem. 1857, 70, 300; Bussenius and Eisenstuck, Ann. 1860, 113, 151; Müller, Zeitsch. f. Chem. 1864, 151).

Fittig (Ann. 1870, 153, 265; Bull. Soc. chim. 1869, 12, 306) showed that the crude xylene from coal tar contained two isomeric hydrocarbons: *m*-xylene, which he had previously obtained by distilling mesitylenic acid with lime, and *p*-xylene, which he had prepared by the action of sodium on a mixture of crude bromotoluene and methyl iodide. Later, Jacobsen (Ber. 1877, 10, 1010) isolated the third isomeride from coal tar, viz. *o*-xylene, which had previously been prepared by Fittig and Bieber (Ann. 1870, 156, 239), by distilling *p*-xylic acid with lime.

Of the xylenes found in coal tar and wood tar, the *m*-isomeride exists in the greatest quantity, although the relative proportions of the three isomerides varies both with the material distilled and the temperature at which the distillation is conducted.

o-Xylene with about 5 p.c. of *p*-xylene is formed when methyl chloride is passed into warm toluene in presence of aluminium chloride. Xylenes are formed also, together with other hydrocarbons, when the vapour of turpentine oil is passed through a red-hot tube or when cymene vapour is passed through a red-hot tube, a large quantity of naphthalene, benzene and other hydrocarbons being formed at the same time (Berthelot, Bull. Soc. chim. 1867, 7, 229). Toluene and xylene have been isolated from petroleum fractions by means of liquid sulphur dioxide (Taus and Stuber, Zeitsch. angew. Chem. 1919, 32, 175).

When cracked at 760° , 100 galls. of oil derived from Pennsylvania crude petroleum yielded 3.3 galls. of benzene, 3.2 galls. of toluene, and 2.5 galls. of xylene, the maximum amount of xylene in the recovered oil being 6.8 p.c. at 815° (Egloff and Twomey, Met. & Chem. Eng. 1916, 15, 15; J. Phys. Chem. 1916, 20, 121). For the formation of the xylenes in pyrogenic acetylene condensations, *see* Meyer and Fricke, Ber. 1914, 47, 2765; Meyer and Meyer, Ber. 1918, 51, 1571).

In order to separate the isomerides, a commercial xylene, boiling at about 140° , and freed from phenols and bases by treatment with alkali and acid, is used. If only the *m*-isomeride, which is of chief technical importance, is required, the mixture is boiled with dilute nitric acid (1 part of commercial acid, D 1.4, and 2 parts of water); the *o*- and *p*-xylenes are converted into acids, whilst the *m*-isomeride is scarcely attacked (Fittig and Velguth, Ann. 1868, 148, 10). The product is distilled with steam, the distillate shaken with alkali to remove acids and nitro-xylenes, then dried and distilled. *o*-Xylene is slowly attacked in open vessels by nitric acid (D 1.075), but more readily by nitric acid (D 1.1).

Under the same conditions *p*-xylene is attacked more readily, and *m*-xylene with greater difficulty. This behaviour leads to a modification of Fittig and Velguth's method for purifying *m*-xylene, which is best carried out by boiling and constantly stirring the crude xylene with nitric acid (D 1.075), the concentration being kept constant by addition of acid. The nitro groups are eliminated subsequently by treating the product with aqueous potassium hydroxide (Konowaloff, J. Russ. Phys. Chem. Soc. 1903, 37, 530, 537). Jacobsen (Ber. 1877, 10, 1000;

1876, 11, 17) has described a method by which the three isomerides may be isolated from coal-tar xylene. The crude xylene is shaken in the cold with concentrated sulphuric acid, when *p*-xylene is scarcely attacked, whilst the *o*- and *m*-isomerides are converted into their sulphonic acids and dissolve in the acid.

In order to obtain the *o*- and *m*-xylenes, the acid solution is treated with calcium carbonate, filtered from calcium sulphate, the filtrate, containing the calcium sulphonates, is precipitated with sodium carbonate, and the sodium sulphonates allowed to crystallise. Sodium *o*-xylene sulphonate separates first, whilst the sodium salts of the two isomeric *m*-xylene sulphonic acids remain in solution.

In order to purify the *p*-xylene, it is warmed gently with fuming sulphuric acid, in which it dissolves, leaving behind a paraffin and other impurities. The three xylenes are then regenerated from their sulphonic acids by hydrolysis with concentrated hydrochloric acid at 195° (cf. Armstrong and Miller, Chem. Soc. Trans. 1884, 45, 151).

Wroblewsky (Ber. 1879, 12, 1226; Ann. 1881, 207, 91) separated *o*-xylene from its *m*-isomeride by converting the mixture into the corresponding xylidines, followed by acetylation with glacial acetic acid for 3 days. The fraction, b.p. above 320°, consists of aceto-*m*-xylidide, and the fraction, distilling up to 310°, consists of water, acetic acid, and unchanged *o*-xylidene. This method of separation is stated to yield better results than that of Jacobsen.

Nölting and Palmer (Ber. 1891, 24, 1955) have shown that commercial xylene contains ethylbenzene, and that in Jacobsen's method of separation the *p*-xylene obtained is mixed with this hydrocarbon (see also Moore and Roaf, Proc. Roy. Soc. 1908, B, 77, 80; Ward, Proc. Cambridge Phil. Soc. 1905, 13, 81; Stohmann, J. pr. Chem. 1887, (2) 35, 41). Moreover, Crafts (Compt. rend. 1892, 114, 1110) and Clarke and Taylor (J. Amer. Chem. Soc. 1923, 45, 830) have found that *p*-xylene is sulphonated readily, even in the cold, by 95 p.c. sulphuric acid.

Levinstein (J. Soc. Chem. Ind. 1884, 3, 77, 354; Ber. 1884, 17, 444) has estimated *m*-xylene in crude xylene by heating 100 c.c. of the crude material at 100° with dilute nitric acid (40 c.c. acid 80°Tw., and 60 c.c. of water) for 1-1½ hours, or until red fumes are no longer evolved. The hydrocarbons are separated from the acid, treated with an excess of sodium hydroxide and steam distilled, or thoroughly washed with sodium hydroxide to remove the toluic acid or nitro-toluic acids formed. The *m*-xylene and paraffins contained in the distillate are separated from the aqueous layer, treated with 1½ times the volume of concentrated sulphuric acid, when the *m*-xylene is dissolved. In order to estimate *p*-xylene, 100 c.c. of the crude xylene are shaken with 120 c.c. of concentrated sulphuric acid to dissolve the *o*- and *m*-isomerides. The volume of the residual *p*-xylene and other hydrocarbons having been noted, the liquid is then treated with an equal bulk of fuming sulphuric acid (20 p.c. SO₃) to dissolve the *p*-xylene. The *p*-xylene may also be separated from the paraffins without converting the former into its sulphonic acid.

This is effected by steam distillation and fractionation, the fraction boiling below 138° on keeping in a freezing mixture deposits pure *p*-xylene. This method does not give good results with a very impure product, as toluene, cymene, &c., are all attacked by nitric acid and sulphuric acid; and in such cases it is better to convert the *o*- and *m*-xylene sulphonic acids into their sodium salts, which can be separated by recrystallisation.

The accuracy of the above methods has been questioned by Reuter (Ber. 1884, 17, 2028), for it has been shown by Brückner (Ber. 1876, 9, 406), Wroblewsky (Ber. 1879, 12, 1226), Ador and Rilliet (Ber. 1879, 12, 2300), that pure *m*-xylene cannot be obtained by treating a mixture of xylenes with dilute nitric acid, whilst stronger acid, as recommended by Levinstein, attacks *m*-xylene, although more slowly than the isomerides. A full account of Reuter's method (Chem. Zeit. 1889, 13, 830, 850) for separating *o*-, *m*-, and *p*-xylene is given in J. Soc. Chem. Ind. 1889, 8, 874. The method employed by Friedel and Crafts (Compt. rend. 1885, 101, 1218; 1891, 114, 1110; see also Eng. Pat. 8665 of 1898) for separating ethylbenzene and the three xylenes depends upon the fact that dry bromine containing 1 p.c. of iodine converts all the xylenes completely into tetrabromoderivatives, and ethylbenzene into a dibromoderivative, and the same authors give a method of separating the xylene by means of sulphuric acid, for the details of which the original communications should be consulted.

It is thus seen that the above methods for the separation of the xylenes are both contradictory and unsatisfactory. A more recent method of separation has been worked out by Clarke and Taylor (J. Amer. Chem. Soc. 1923, 45, 830), and consists of four series of operations: (1) fractional distillation; (2) selective sulphonation; (3) fractional crystallisation of sulphonic acids or their salts; (4) selective hydrolysis of the sulphonic acids at different temperatures. *m*-Xylene, which forms by far the largest proportion of coal-tar xylene, can be obtained in a high state of purity by distillation alone. The isomeric *o*- and *p*-xylenes may be removed by boiling the mixture with dilute nitric acid. The product is then washed with water and alkali, distilled first in a current of steam, and finally under atmospheric pressure with the use of a fractionating column. The hydrocarbon is then sulphonated by stirring at 95° with half its volume of concentrated sulphuric acid, the resulting acid solution separated from unsulphonated material, diluted with an equal volume of concentrated sulphuric acid and twice its volume of water, and distilled in a current of steam with the aid of heat to increase the concentration and raise the temperature. The first runnings consist of water and suspended unsulphonated hydrocarbons, the fraction distilling between 110°-120° is pure *m*-xylene, b.p. 138°-139°. Pure *o*-xylene may be obtained from commercial *o*-xylene (95 p.c. of which distils at 143°-144°) by treating 5 litres (4400 grs.) of the latter with 2½ litres of concentrated sulphuric acid at 95° for four hours with stirring. After cooling, the layer of unsulphonated material is removed, and the sulphonic acid layer is diluted with

3 litres of water and neutralised with 40 p.c. sodium hydroxide solution. The solution of the sodium salt is centrifuged, and the solid recrystallised three times from water, when the pure sodium salt, long flat needles, is obtained. To obtain the hydrocarbon, sodium *o*-xylene sulphonate is dissolved in the minimum amount of cold water to which an equal volume of concentrated sulphuric acid is added subsequently. The mixture is heated to 110° and steam distilled with external heating until the temperature rises to about 130°. Practically the whole of the *o*-xylene distils between 110° and 120°. The hydrocarbon is separated from the distillate and distilled, when a 45 p.c. yield (1980 grs.) of pure *o*-xylene, b.p. 144°–145°, is obtained. To prepare pure *p*-xylene, 10 kg. of commercial *p*-xylene (91 p.c. of which distils between 136° and 137°) are treated with an equal volume of concentrated sulphuric acid at a temperature of 15°–20° with stirring for 5–6 hours, the undissolved hydrocarbons (5–6 litres) being treated again in a similar manner. The portion which remains undissolved after this treatment is mixed with an equal volume of concentrated sulphuric acid and stirred for 5 hours at 95°. After cooling, the lower acid layer is separated and mixed cautiously with an equal volume of concentrated hydrochloric acid. Heat is evolved, and as the solution cools the *p*-xylene sulphonic acid crystallises in fine plates, which are recrystallised from a quarter of their weight of hot distilled water. The mother liquors contain *p*- and *m*-xylene sulphonic acids. The recrystallised *p*-acid, which still contains a little *m*-xylene sulphonic acid, is dissolved in the minimum amount of water and mixed with an equal weight of concentrated sulphuric acid, heated to 120° and steam distilled, allowing the temperature to rise to 145°, when *m*-xylene distils. The temperature is then raised gradually to 170°, the greater part of the *p*-xylene distilling at 150°–155°. The oil in the distillate is separated, dried over calcium chloride, and cooled to 5°, when the greater part solidifies. The supernatant liquor is removed and the crystalline *p*-xylene, m.p. 10°–12°, distils completely at 136.5°–137°. The yield from 20 kg. of the commercial product is 2847 grms. (14.2 p.c.). No evidence of the presence of ethylbenzene was obtained. The unsulphonated material present in xylene, usually referred to as consisting of paraffins, is probably a mixture of cyclohexane derivatives, such as the hexahydroxylenes. Patterson, McMillan and Somerville (Chem. Soc. Trans. 1925, 125, 2488) separate the three xylenes as follows: Coke-oven xylene-b.p. 137°–141°, is shaken with concentrated sulphuric acid for about three-quarters of an hour. The acid liquid contains *m*-xylene 4-sulphonic acid and *o*-xylene 4-sulphonic acid. *p*-Xylene remains undissolved. Water is added slowly to the acid and the pasty crystals formed are filtered and heated in a current of steam at 150°–200° when *m*-xylene distils. The mixed *o*- and *m*-xylene 4-sulphonic acids are separated by fractional crystallisation of their calcium salts from water. The solubility of calcium *o*-xylene sulphonic acid increases, whilst that of calcium *m*-xylene sulphonic acid decreases with rise of temperature. According to P. Dekker (Chem. Weekblad, 1923, 20, 575), samples of xylene

which, after boiling for 24 hours, left on distillation 5 grms. of residue per 100 c.c. gave strong reactions for aldehydes.

The three xylenes may also be separated by freezing with liquid air and allowing the solid to melt slowly under suction (Fischer, Zeitsch. Elektrochem. 1910, 16, 161). The commercial fractional separation of benzene, toluene, and the xylenes has been studied by Butler and Popham (J. Soc. Chem. Ind. 1918, 37, 220 T), and James (*ibid.* 1916, 35, 236).

Commercial xylene should have been previously washed with sulphuric acid, and should, therefore, give only a pale-brown coloration with concentrated sulphuric acid. The boiling-point of the product should lie within a few degrees; thus not more than 10 p.c. should distil below 130°, and not more than 10 p.c. above 140.5°, the remainder passing over between these temperatures.

The xylene of commerce is a product of very variable composition. The relative proportion of the three isomerides varies in different samples, and as these three compounds have almost identical boiling-points, the boiling-point of such a mixture affords no criterion of its composition. The value of a commercial xylene depends on the quantity of *m*-xylene which it contains.

To identify *m*- and *p*-xylenes in a mixture of the three isomerides, 50 c.c. of the mixture may be heated with a mixture of chromic and sulphuric acids, whereby *o*-xylene is completely oxidised to carbon dioxide, whereas *m*-xylene yields iso-phthalic acid and *p*-xylene yields terephthalic acid (Worstell and Burwell, Amer. Chem. J. 1897, 19, 830).

Methods for the quantitative estimation of the three xylenes in the commercial product have been devised by Levinstein (*l.c.*), Friedel and Crafts (*l.c.*), Reuter (Ber. 1884, 17, 2028; J. Soc. Chem. Ind. 1884, 3, 626; 1889, 8, 874; Chem. Zeit. 1889, 13, 830); in light oils by Egloff (Met. & Chem. Eng. 1917, 16, 259); in solvent naphtha by Spielmann and Jones (J. Soc. Chem. Ind. 1917, 36, 489); in gases by Davis, Davis and MacGregor (J. Ind. Eng. Chem. 1918, 10, 712).

The use of xylene for stripping illuminating gas to remove naphthalene has been investigated by Eitner (J. für Gasbeleucht. 1899, 42, (6) 89; (9) 148; (26) 425); Breithkopf (*ibid.* 1899, 42, (40) 671); Leather (J. Gas Lighting, 1899, 73, 1734); Irwin (J. Soc. Chem. Ind. 1899, 18, 109); Young (J. Gas Lighting, 1899, 74, 755).

For the degradation of xylene into lower homologues in the presence of catalysts, &c., see Houlehan (U.S. Pats. 1334033, 1337317 of 1920), Fischer and Niggemann (Ber. 1916, 49, 1475). When xylene is submitted in the form of vapour to a temperature of 600°–850° at a pressure capable of being reduced to half an atmosphere, a yield of 30 p.c. of toluene is obtained (Synthetic Hydro-Carbon Co., Fr. Pat. 479786 of 1915; see also Eng. Pats. 9163, 13100, of 1915; Fr. Pat. 479211 of 1915).

The xylenes and similar coal-tar hydrocarbons may be rendered miscible with water without separation by heating them with a suitable soap and a minimum quantity of water. Thus when 40 kg. of oleic acid, 40 kg. of potash

lye (20°B.) and 20 kg. of *o*-xylene are heated together with agitation until homogeneous, the product forms a clear solution containing up to 10 p.c. of xylene. The products are also soluble in sea water and may be used for washing and other purposes, including the drilling, turning, or other similar working of metals (Simon and Dürkheim, Fr. Pat. 422953 of 1910; J. Soc. Chem. Ind. 1911, 30, 610).

The autoxidation of xylene, in admixture with an aromatic nitro-hydrocarbon, in the presence of sunlight has been studied by Suida (Ber. 1914, 47, 467; Monatsh. 1912, 33, 1268), and the photobromination of xylene by Swenson (Zeitsch. wiss. Photochem. 1921, 20, 206).

When the xylenes are oxidised with chromic acid in the presence of acetic acid and sulphuric acid, the corresponding tetracetate of phthalaldehyde is formed (Thiele and Winter, Ann. 1900, 311, 353). Like other homologues of benzene, xylene reacts with cellulose forming desoxyxins (Nastukoff, Zeitsch. Farb. Ind. 1907, 6, 70), and the xylenes react with 96 p.c. selenic acid to form selenonic acids (Anschütz, Kallen and Riepenkröger, Ber. 1919, 52, 1860).

Crude coal-tar xylene, containing paraffins and other hydrocarbons, was formerly used only under the name of solvent naphtha. At present purified xylene is used for the preparation of xylidine for use in the manufacture of Xylidine Scarlet and other azo-dyes.

Ring substituted chloro-xylenes can be further chlorinated in the side-chain at high temperatures (100°–130°) in the presence of light. The products may be converted by concentrated sulphuric acid into chlorinated dialdehydes or aldehyde-carboxylic acids, which, on condensation with *o*-cresotinic acid, for example, yield leuco-compounds of the triphenylmethane series. On oxidation with sodium nitrite in concentrated sulphuric acid solution dyes are obtained which dye wool from an acid bath brownish-red, converted by after-chroming into bright violet-blue, very fast to washing and milling (Schmidlin and M. Fischer, U.S. Pat. 1219166 of 1917; cf. Ransford, Eng. Pat. 114645 of 1917).

o-Xylene, from coal-tar and wood-tar; by distilling *p*-xylic acid with lime (Fittig and Bieber, Ann. 1870, 156, 231; Bull. Soc. chim. 1870, (2) 13, 268); from *o*-bromotoluene and methyl iodide in presence of sodium, followed by fractionating the product over sodium (Jannasch and Hübner, Ann. 1873, 170, 117; Bull. Soc. chim. 1872, (2) 18, 334; Reymann, *ibid.* 1876, (2) 26, 532); by heating cantharidin with excess of phosphorus pentasulphide (Piccard, Ber. 1879, 12, 580); by passing methyl iodide through a mixture of toluene and aluminium chloride at 85° (Jacobsen, Ber. 1881, 14, 2628).

Liquid, b.p. 144° (corr.), m.p. –25° (Fischer, Zeitsch. Elektrochem. 1910, 16, 161), or –28.5° (Colson, Ann. Chim. Phys. 1885, (6) 6, 128); b.p. 141.9°; D_{20}^0 0.8932 (Pinette, Anp. 1888, 243, 50; cf. Hirsch, Ann. Phys. Chem. 1899, (2) 69, 456); b.p. 141°/756.2 mm.; D_{41}^{141} 0.7559; capillarity constant at b.p. $\alpha^2=4.437$ (Schiff, Ann. 1896, 236, 36; Rob and Feustel, Ann. der Phys. 1904, (4) 16, 61; cf. Neubeck, Zeitsch.

physikal. Chem. 1887, 1, 660); D_4^0 0.8903; D_{15}^{15} 0.818. For vapour tension, see Woringer (Zeitsch. physikal. Chem. 1900, 34, 263); critical temperature, Altschul (*ibid.* 1893, 11, 950), Brown (Chem. Soc. Trans. 1906, 89, 311); latent heat of vaporisation, Brown (*ibid.* 1906, 87, 2657); dielectric constant and refractive index, Landolt and Jahn (Zeitsch. physikal. Chem. 1892, 10, 300), Drude (*ibid.* 1897, 23, 309), Brühl (J. pr. Chem. 1894, (2) 50, 140); magnetic properties, Schönrock (Zeitsch. physikal. Chem. 1893, 11, 785), Perkin (Chem. Soc. Trans. 1896, 69, 1241; 1900, 77, 267); absorption spectrum, Groebe (Zeitsch. wiss. Photochem. 1905, 3, 376), Mies (*ibid.* 1910, 8, 287), Hartley (Chem. Soc. Trans. 1885, 47, 685), Baly and Ewbank (*ibid.* 1905, 87, 1347); molecular refraction and dispersion, Gladstone (Chem. Soc. Trans. 1891, 59, 290). *o*-Xylene when oxidised with dilute nitric acid yields *o*-toluic acid, and on treatment with a hot solution of potassium permanganate, phthalic acid is formed (Claus and Preszcek, Ber. 1886, 19, 3083), whilst chromic acid completely destroys it. For the oxidation of *o*-xylene, see also Thiele (Ann. 1900, 311, 358), Clausner (Ber. 1905, 38, 2860), Law and F. M. Perkin (Chem. Soc. Trans. 1907, 91, 258). When heated with hydrogen iodide at 250°–280°, *o*-xylene yields toluene, methyl- and dimethylcyclohexane and methylated pentamethylene (Markownikow, Ber. 1897, 30, 1218). *o*-Xylene, when treated with aluminium chloride at 100° in the presence of hydrogen chloride, yields principally *m*-xylene, together with smaller quantities of benzene, toluene, *p*-xylene, pseudocumene and mesitylene (Heise and Tohl, Ann. 1892, 270, 155; Friedel and Crafts, Compt. rend. 1885, 100, 100, 692; Jacobsen, Ber. 1881, 14, 2626; 1885, 18, 338; Anschütz and Immendorff, *ibid.* 1884, 17, 2816; 1885, 18, 657). Nitrogen peroxide reacts with *o*-xylene to yield nitro-*o*-xylene, *p*-toluic acid, phthalic acid, and oxalic acid (Leeds, Ber. 1881, 14, 482). On methylation, *o*-xylene yields exclusively pseudocumene (Jacobsen). Hot dilute nitric acid yields nitro-derivatives, substituted in the side-chain. When oxidised electrolytically in presence of acetone, *o*-xylene yields *o*-toluic aldehyde (Law and F. M. Perkin, Trans. Faraday Soc. 1904, 1), and when heated for several hours with hydroxylamine in the presence of aluminium chloride or ferric chloride, it yields *o*-4-xylidine (Graebe, Ber. 1901, 34, 1778). It also condenses with triphenylmethyl yielding a complex $[(C_6H_5)_3C]_2 + C_8H_9(CH_3)_2$ (Gomberg and Conc, Ber. 1905, 38, 1333).

Phosphorus pentachloride at 200° reacts with *o*-xylene forming $C_8H_4(CCl_2)_2CHCl_2$ (Colson and Gautier, Bull. Soc. chim. 1886, (2) 45, 507). Bromine in the dark forms 4-bromo-*o*-xylene, whilst in direct sunlight the products are xylid bromide and xylidene bromide (Schramm, Ber. 1885, 18, 1278).

o-Xylene when monobrominated at 130° yields chiefly monobromo-derivatives, together with a small quantity of unchanged material and *o*-dibromo-derivatives, whilst, on dibromination at 130°, the product consists chiefly of dibromo-, together with mono- and tribromo-derivatives. The method employed by Radziszewski and Wispek (Ber. 1882, 15, 1743), Löw (Ann. 1885,

231, 363), and Pellagrin (Rec. trav. chim. 1899, 18, 458), in which the vapour of the halogen was allowed to react with the boiling hydrocarbon, is not satisfactory, owing to the difficulty of preventing the hydrogen bromide evolved from carrying some of the bromine vapour away with it. The method adopted by Atkinson and Thorpe (Chem. Soc. Trans. 1907, 91, 1687) yields more satisfactory results. A litre Geissler flask with a ground-in air condenser is fitted with a dropping funnel fused into the neck of the flask and reaching below the level of the hydrocarbon to be brominated. *o*-Xylene when brominated with a mixture of nitric and hydrobromic acids, or preferably with a mixture of bromine and nitric acid, yields bromo-*o*-xylene and tetrabromo-*o*-xylene, together with *o*- and *p*-toluic acids (Datta and Chatterjee, J. Amer. Chem. Soc. 1916, 38, 2545). *o*-Xylene when treated with aqua regia yields a monochloro-, 4:5-dichloro-, and the tetrachloro-derivative (Datta and Fernandes, *ibid.* 1916, 38, 1809).

When *o*-xylene bromoacetyl bromide is treated with aluminium chloride in carbon disulphide solution, 4-*o*-xylyl bromomethyl ketone is obtained, which is probably identical with the substance prepared by Armstrong and Kipping (Chem. Soc. Trans. 1893, 63, 86) by brominating *o*-xylyl methyl ketone (Jacobs and Heideberger, J. Biol. Chem. 1915, 21, 819).

Well-cooled *o*-xylene, when treated with the vapours of sulphuric anhydride at a temperature below 30°, yields di-*o*-xylyl-*m*-(?)-sulphone, brilliant plates, m.p. 158°–159° (Zorn and Brunel, Compt. rend. 1894, 119, 1224).

4-Cyan-*o*-xylin $[C_6H_4(CH_3)_2CN]_2$ is formed from *o*-xylene by the action of cyanogen bromide in presence of aluminium chloride. It sinters at 204°, melts at 210° (decomp.), and on treatment with hydrochloric acid at 220° yields *p*-xylic acid (Scholl and Nörr, Ber. 1900, 33, 1052).

o-Xylyl boro-chloride melts at 0° and boils at 212°, and the corresponding acid forms colourless needles, m.p. 190°5', and the oxide melts at 226° (Michaelis and Thévenot, Ann. 1901, 315, 19).

o-Xylylene hydrazine $C_6H_4 \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} N \cdot NH_2$ is prepared by reducing nitroso-dihydro-isindole with zinc dust in dilute acetic acid solution (Fränkel, Ber. 1900, 33, 2808).

o-Chloro-*o*-xylene, *o*-xylyl chloride; by chlorinating boiling *o*-xylene (Reynian, Bull. Soc. chim. 1876, (2) 26, 534); in an impure condition by heating *o*-xylyl alcohol with concentrated hydrochloric acid (Colson, Ann. Chim. Phys. 1885, (6) 6, 117; Compt. rend. 1884, 98, 1543; 1884, 99, 40); by the action of chlorine on *o*-xylene in sunlight (Radziewanowski and Schramm, Akad. Wiss. Krakau, 1898, 61). Oil, b.p. 197°–199° (R.), or 195°–203° (R. and S.). When treated with aqueous lead nitrate it yields *o*-tolualdehyde.

o-o-Dichloro-*o*-xylene, *o*-xylylene chloride; from phthalyl alcohol and concentrated hydrochloric acid (Hessert, Ber. 1879, 12, 648; Colson, Bull. Soc. chim. 1885, (2) 43, 7; Ann. Chim. Phys. 1887, (6) 11, 25); in small yield by chlorinating 1 mol. of *o*-xylene with 1 mol. of chlorine in sunlight, or as chief product when 2 mols. of chlorine are used (R. and S.); by heating *o*-xylene with phosphorus pentachloride

at 180°–200° (Colson and Gautier, Bull. Soc. chim. 1886, (2) 45, 6; Compt. rend. 1885, 101, 1064; 1887, 104, 428; Strassmann, Ber. 1888, 21, 578).

Triclinic crystals (Wilk, Ber. 1885, 18, 2879), or long prisms, m.p. 55°, b.p. 240°–260° (R. and S.), or m.p. 54°6'–54°8', b.p. 239°–241°, D_0^{20} 1.393.

Tolyldene chloride $CH_3 \cdot C_6H_4 \cdot CHCl_2$ (?); by chlorinating heated *o*-xylene (Rayman). Tables, m.p. 103°; b.p. 225°, converted into phthalaldehyde (?) by boiling with lead nitrate solution. This compound, however, is stated by Colson (Compt. rend. 1884, 98, 1543) to be more probably 1:4-dichloro-xylene.

Symm.-o-tetrachloro-o-xylene $C_6H_4(CHCl_2)_2$; by the action of chlorine on *o*-xylene, initially at 140° and finally at 160°–170° (Hjelt, Ber. 1885, 18, 2879); from *o*-xylene and 4 mols. of phosphorus pentachloride at 150° (Colson and Gautier, Ann. Chim. Phys. 1887, (6) 11, 25). Triclinic crystals (Wilk), m.p. 89°, b.p. 273°–274° (H.); m.p. 86° (C. and G.); D_0^{20} 1.601 (Colson, Bull. Soc. chim. 1886, 46, 2). When heated with water at 200°–210° it yields phthalaldehyde.

Penta-o-chloro-o-xylene, $C_6H_4(CCl_2)(CHCl_2)$; as the chief product when *o*-xylene is heated in a sealed tube at 100° with a large excess of phosphorus pentachloride (Colson and Gautier, *l.c.*; Compt. rend. 1886, 102, 689). Monoclinic crystals, m.p. 53°6'. When left in contact with dilute aqueous potassium hydroxide it loses the whole of its chlorine and is converted into phthalaldehydic acid.

o-Xylene hexachloride $C_6H_4(CH_2)_2Cl_6$; by chlorinating *o*-xylene in sunlight (R. and S.). Rhombic crystals, m.p. 194°5', b.p. 260°–266°.

3-Chloro-*o*-xylene; together with the 4-chloro-isomeride by chlorinating ice-cold *o*-xylene in presence of 5 p.c. of iodine (Krüger, Ber. 1885, 18, 1755), or iron (Claus and Bayer, Ann. 1893, 274, 304). The isomerides may be separated by means of their barium sulphonates (K.). Colourless refractive oil, b.p. 189°5'.

4-Chloro-*o*-xylene; *see* above. Oil, b.p. 191°5'; D_{15}^{15} 1.0692 (K.); or b.p. 195° (Claus and Gronweg, J. pr. Chem. 1891, (2) 43, 252; *cf.* Claus and Kautz, Ber. 1885, 18, 1367). Its barium sulphonate is more soluble than that of 3-chloro-*o*-xylene (K.).

3:5-Dichloro-*o*-xylene; together with 3:5:6-trichloro-*o*-xylene when 3:5-dichloro-1:1-dimethyl- Δ^2 :4-cyclohexadiene is treated in cold chloroform solution with chlorine, followed by heating the product to 150°–180° for 1 hour (Hinkel, Chem. Soc. Trans. 1920, 117, 1296); by the action of excess of phosphorus pentachloride on 3:5-dichloro-1:1-dimethyl- Δ^2 :4-dihydrobenzene in chloroform solution (Crossley and Le Sueur, Chem. Soc. Trans. 1902, 81, 1533); in small quantities together with the above dichlorodimethyldihydrobenzene by the action of phosphorus pentachloride on dimethyldihydroresorcinol (Crossley and Le Sueur, Chem. Soc. Trans. 1903, 83, 110); together with 3:5-dichloro-6-bromo-*o*-xylene by treating 3:5-dichloro-1:1-dimethyl- Δ^2 :4-dihydrobenzene with 1 mol. of bromine in chloroform solution (Crossley, *ibid.* 1904, 85, 264); together with dimethylmalonic

acid, isobutyric acid, 3:5-dichlorophthalic acid, dichlorotribromo - dimethyltetrahydrobenzene and 3:5-dichloro-6-bromo-*o*-xylene by oxidising dichlorodibromo - dimethyltetrahydrobenzene with potassium permanganate (C.).

Faintly yellow, highly refractive liquid, b.p. 129°/23 mm. or 226°/atm., which on cooling solidifies to flaky needles, m.p. 3°-4°. On oxidation with dilute nitric acid under pressure it yields a dichlorotoluic acid, long glistening needles, m.p. 184°-185°, and 3:5-dichlorophthalic acid (C.; C. and S.).

4:5-Dichloro-*o*-xylene; together with higher chlorinated homologues by passing dry chlorine through well-cooled *o*-xylene containing 10 p.c. of iodine (Claus and Kautz; Claus and Gronweg). Oil, b.p. 227°, solidifying on cooling to crystals, m.p. 3°. When heated at 200° with nitric acid (D 1.15) in a sealed tube it yields 4:5-dichlorophthalic acid. Koch (Ber. 1890, 23, 2318) states that a solid dichloro-*o*-xylene, long hard needles, m.p. 73°, is obtained together with the liquid isomeride when *o*-xylene is chlorinated.

Trichloro-*o*-xylene (Claus and Kautz), long colourless needles which sublime, m.p. 93°, b.p. 265° (decomp.). When oxidised with nitric acid (D 1.15) at 200° in a sealed tube it yields trichlorophthalic acid.

3:4:5-Trichloro-*o*-xylene; by heating pentachlorodimethylcyclohexene; together with other substances when 3:5-dichloro-1:1-dimethyl-Δ²:4-cyclohexadiene is treated in chloroform solution with excess of chlorine at low temperatures. Felt-like needles, m.p. 96° (Hinkel, Chem. Soc. Trans. 1920, 117, 1296).

3:5:6-Trichloro-*o*-xylene; see 3:5-dichloro-*o*-xylene; together with the 3:4:5-trichloroisomeride, 3:4:5:6-tetrachloro-*o*-xylene and 2:3:3:4:5-pentachloro-1:1-dimethyl-Δ⁵-cyclohexene, by chlorinating 3:5-dichloro-1:1-dimethyl-Δ²:4-cyclohexadiene in chloroform solution at low temperatures (Hinkel). Short colourless crystals, m.p. 47.5°.

3:4:5:6-Tetrachloro-*o*-xylene; see above; by chlorinating well-cooled *o*-xylene containing 10 p.c. of iodine (C. and K.); by chlorinating 3:4:5- or 3:5:6-trichloro-*o*-xylene in chloroform solution in presence of iron (H.); by heating pentachlorodimethylcyclohexene on the water-bath with fuming nitric acid (H.). Long slender glistening needles, m.p. 223°-224° (H.), or 215° (C. and K.). It is not oxidised when heated at 200° with nitric acid in a sealed tube; chromic acid mixture completely destroys it. It sublimes, and is non-volatile with steam (C. and K.).

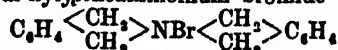
Tetrachloroxylylene oxide; by reducing tetrachlorophthalic acid with hydriodic acid and red phosphorus (Graebe, Ann. 1887, 238, 318). Long needles, m.p. 218°.

ω-Bromo-*o*-xylene, *o*-xylyl bromide; by brominating boiling *o*-xylene (Radziszewski and Wispek, Ber. 1882, 15, 1747; 1885, 18, 1281; Atkinson and Thorpe, Chem. Soc. Trans. 1907, 91, 1687); or by brominating cold *o*-xylene exposed to direct sunlight (Schramm, Ber. 1885, 18, 1278; Colson, Ann. Chim. Phys. 1885, (6) 6, 115; Bull. Soc. chim. 1885, (2) 43, 6). Prisms or quadratic plates m.p. 21°, b.p. 216°-217°/742 mm.; D₂₅ 1.3811. With potassium thiocyanate it yields *o*-xylyl thiocyanate (Strzelecka, Bull. Acad. Sci. Cracow, 1909, 731). With

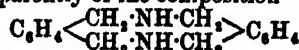
methylaniline it yields *o*-xylylmethylaniline, m.p. 34°, b.p. 200°/35 mm. (von Braun, Ber. 1910, 43, 1353), and with potassium phthalimide it yields *o*-xylyl-phthalimide, m.p. 148°-149° (Strassmann, Ber. 1888, 21, 576). The chief product obtained when magnesium acts on an ethereal solution of a xylyl bromide is the corresponding dimethyldibenzyl, and only a small amount of organo-magnesium compound is formed (Carré, Compt. rend. 1909, 148, 1108; Bull. Soc. chim. 1909, (4) 5, 486).

ω-Dibromo-*o*-xylene, *o*-xylylene bromide; by heating *o*-xylene with 2 mols. of bromine at 150°-155°, or better at 125°-130° (Bacayer and Perkin, Ber. 1884, 17, 123; Perkin, Chem. Soc. Trans. 1888, 53, 5; cf. Atkinson and Thorpe, *ibid.* 1907, 91, 1687; Radziszewski and Wispek, Ber. 1882, 15, 1743; 1885, 18, 1278 by the action of 2 mols. of bromine on cold *o*-xylene in presence of direct sunlight (Schramm, Ber. 1885, 18, 1278; Colson, Ann. Chim. Phys. 1885, (6) 6, 105; Compt. rend. 1887, 104, 428; 1884, 98, 1543).

It melts at 94.5°-94.0°, or 93° (B.), and forms large glistening rhombic crystals, *a*:*b*:*c* = 0.8581:1:0.5014. It reacts with triethylphosphine forming *o*-xylylenetriethylphosphonium bromide, colourless crystals, m.p. 250°-250.5° (Partheil and Gronover, Ber. 1900, 33, 606); with alcoholic potassium hydrosulphide to yield *o*-xylylene hydrosulphide, m.p. 45°-46°, b.p. 160°/20 mm., which is converted by methylene iodide and sodium ethoxide into *o*-xylylene-methylene mercaptal, m.p. 152°-153° (Kötz and Sevin, Ber. 1900, 33, 729); with aniline in chloroform solution to yield 2'-phenyldihydroisindole C₈H₄:(CH₂)₂:NC₆H₅, m.p. 165°; with secondary amines NHR₂' or NH-R'' it forms substituted ammonium bromides of the type C₈H₄:(CH₂)₂:NR', Br or C₈H₄:(CH₂)₂:NBr·R'', and these react with a molecule of the same or another amine at 200° yielding diacid bases of the type NR'₂·CH₂·C₈H₄·CH₂·N·R''; with tertiary amines, it forms substituted diammonium bromides of the type C₈H₄(CH₂)₂·NR'''·Br₂ (Leser, Ber. 1884, 17, 1824; Scholtz, Ber. 1898, 31, 414, 627, 1154, 1700, 1707; Partheil and Schumacher, *ibid.* 591). When treated with potassium hydroxide, *o*-xylylene bromide yields *o*-xylylene oxide C₈H₄<CH₂>O, b.p. 192° (Willstätter and Veraguth, Ber. 1907, 40, 957), and when heated at 120° with ten times its weight of concentrated ammonia for 6 hours it yields di-xylyleneammonium bromide



whilst at temperatures above 120°, preferably at 170° for 8 hours in a sealed tube, a secondary base, apparently of the composition



m.p. 79°-80°, b.p. 130°-135°/12 mm., is formed (Scholtz, Ber. 1891, 24, 2402). An alcoholic solution of *ω*-dibromo-*o*-xylene on treatment with an aqueous solution of potassium sulphide yields *o*-xylylene sulphide C₈H₄<CH₂>S, and on boiling with a large excess of alcoholic potassium hydroxide for 1½ hours it yields *o*-xylylene diethyl-ether C₈H₄(CH₂OC₂H₅)₂ (Leser, Ber. 1884, 17, 1824). When boiled for a

long time with excess of potassium iodide, it is *o*-xylene di-iodide (Leser).

When *o*-xylene bromide and *o*-xylene mercaptan are boiled with alcoholic sodium ethoxide cyclo-diithiodi-*o*-xylene, colourless slender needles, m.p. 234°–236°, is formed (Autenrieth and Brüning, Ber. 1903, 36, 183). For further condensations of *o*-xylene bromide, see Scholtz (Ber. 1910, 43, 2304; 1914, 47, 2162). With potassium thiocyanate it yields *o*-xylene thiocyanate (Strzelecka, Bull. Acad. Sci., Cracow, 1909, 731); with allylamine it yields allyl-dihydroisindole (von Braun, Ber. 1910, 43, 1353); with sodium iodide in acetone solution it yields *o*-xylylenedi-iodide, m.p. 109° (Finkelstein, Ber. 1910, 43, 1528).

ω-ω'-Tribromo-o-xylene; by brominating heated *o*-xylene. Colourless glistening plates, m.p. 97° (Atkinson and Thorpe).

Symm.-ω-tetrabromo-o-xylene, $C_8H_4(Br)_4$; by the gradual addition of 4 mols. of bromine to *o*-xylene heated to 140° (Gabriel and Muller, Ber. 1895, 28, 1830). Crystals, m.p. 115°–117°, which form an addition product with methyl iodide, pointed yellow needles, m.p. 235°–240° (G. and M.). When boiled with potassium oxalate and dilute alcohol for 24 hours it forms *o*-phthalaldehyde, yellow needles, m.p. 56°–56.5° (Thiele and Gunther, Ann. 1906, 347, 106).

3-Bromo-o-xylene; by the steam distillation of a solution of barium 3- or 6-bromo-*o*-xylene 4-sulphonate in excess of sulphuric acid. The product is purified by resulphonation and regeneration from the sodium salt (Stallard, Chem. Soc. Trans. 1906, 89, 808). Colourless highly refractive liquid, b.p. 213.8°; D_{15}^{25} 1.382.

4-Bromo-o-xylene; formed by the action of bromine on cold *o*-xylene in the presence of iodine in the dark (Jacobsen, Ber. 1884, 17, 2372; Schramm, *ibid.* 1885, 18, 1278). The product is purified by conversion into the barium sulphonate. Liquid, solidifying below 0° to a brown mass, m.p. –0.2°, b.p. 214.5°/760 mm.; D_{15}^{25} 1.3693 (J.). When boiled with dilute nitric acid it yields bromo-*o*-toluic acid, and with the lead salt of thiophenol it yields *α*-phenyl-*o*-xylyl sulphide $[(CH_3)_2S=1:2:4]$. Oil, b.p. 181.5°/11 mm.; D_4^{20} 1.0962 (Bourgeois, Ber. 1895, 28, 2312).

3(?)4-Dibromo-o-xylene; together with the 4, 5-dibromo-isomeride by the action of bromine on 4-bromo-*o*-xylene in the presence of iodine (Jacobsen, Ber. 1884, 17, 2372). Oil, solidifying on cooling to a hard crystalline mass, m.p. 6.8°, b.p. 277°; D_{15}^{25} 1.7842. The isomerides may be separated by crystallisation from alcohol.

4:5-Dibromo-o-xylene; as the chief product in the above reaction (J.); together with 4-bromo-*o*-xylene and 5- or 3-bromo-*o*-xylene 4-sulphonic acid by treating an aqueous solution of *o*-xylene 4-sulphonic acid at about 40° with a solution of bromine in hydrochloric acid (Kelbe and Stein, Ber. 1886, 19, 2137). Large rhombic tables or long needles, subliming to large thin plates, m.p. 88°, b.p. 278° (cf. Crossley and Smith, Chem. Soc. Trans. 1913, 103, 989). *4:5-Dibromo-o-xylene*, when heated with concentrated sulphuric acid at 215°, yields *3:4-dibromo-o-xylene* (Koch, Ber. 1890, 23, 2318).

3:4:5-Tribromo-o-xylene; from *3:5-*

dibromo-o-4-xylylene by the Sandmeyer reaction (Jaeger and Blanksma, Proc. K. Acad. Wetensch. Amsterdam, 1905, 8, 153). It melts at 105°.

3:4:6-Tribromo-o-xylene; from *4:6-dibromo-o-3-xylylene* by the Sandmeyer reaction (J. and B.). It melts at 86.5°.

Tetrabromo-o-xylene; from *o*-xylene and bromine (Jacobsen, Ber. 1884, 17, 2378), in presence of aluminium bromide (Blümlein, *ibid.* 2402). Long glistening needles, m.p. 262° (J.) or 254°–255° (B.), b.p. 374°–375° (B.); on oxidation at 170° with nitric acid (D 1.15) in the presence of bromine it yields tetrabromophthalic acid.

4-Chloro-5-bromo-o-xylene; by brominating 4-chloro-*o*-xylene in chloroform solution in the presence of iron, followed by distillation in a current of steam. Long colourless needles, m.p. 75° (Claus and Gronweg, J. pr. Chem. 1891, [2] 43, 252).

4:5-Dichloro-3-bromo-o-xylene; in a similar manner from *4:5-dichloro-o-xylene* (C. and G.). Colourless felted crystals, m.p. 90°.

3:5-Dichloro-4-bromo-o-xylene; together with dichlorotribromodimethyl-tetrahydrobenzene when *3:5-dichloro-1:1-dimethyl-Δ2:4-dihydrobenzene*, dissolved in a small amount of chloroform, is treated with about 2 mols. of bromine; by heating *3:5-dichloro-2:4:5-tribromo-1:1-dimethyl-Δ5-tetrahydrobenzene*; from *3:5-dichloro-o-4-xylylene* by the Sandmeyer reaction; together with *3:5-dichloro-4:6-dibromo-o-xylene* by brominating *3:5-dichloro-o-xylene* (Crossley, Chem. Soc. Trans. 1904, 85, 264). Felted needles, m.p. 100°, b.p. 170°–175°/30 mm., or 265°–270°/atm. It is volatile with steam and when heated with dilute nitric acid (D 1.15) at 180°–200° for 7 hours it yields *3:5-dinitro-phthalic acid* (C.).

3:5-Dichloro-6-bromo-o-xylene; together with *3:5-dichloro-o-xylene* by heating dichlorodibromodimethyltetrahydrobenzene, or by treating *3:5-dichloro-1:1-dimethyl-Δ2:4-dihydrobenzene* with 1 mol. of bromine and distilling the product, when the fraction, b.p. 220°–230°, consists of *3:5-dichloro-o-xylene*, whilst the intermediate fractions and that of b.p. 240°–250° contain *3:5-dichloro-6-bromo-o-xylene*; also together with other products (see *3:5-dichloro-o-xylene*) by oxidising dichlorodibromodimethyltetrahydrobenzene with potassium permanganate (C.). It forms long slender glistening needles, m.p. 42°. When brominated in presence of iron it yields the *4:6-dibromo-derivative*, whilst on heating with fuming nitric acid on the water-bath for 10 minutes it yields *3:5-dichloro-4:6-dinitro-o-xylene*. When heated with dilute nitric acid (D 1.15) at 180°–190° for 6 hours it yields *3:5-dichloro-6-nitro-o-toluic acid*.

3:5-Dichloro-4:6-dibromo-o-xylene; by brominating a warm solution of *3:5:6-trichloro-o-xylene* in chloroform in presence of iron (Hinkel, Chem. Soc. Trans. 1920, 117, 1296); by heating dichlorotribromodimethyltetrahydrobenzene with concentrated nitric acid (D 1.42) on the water-bath for 10 minutes; by brominating *3:5-dichloro-o-xylene*, or *3:5-dichloro-4- or 6-bromo-o-xylene* in presence of iron (C.). Slender glistening needles, m.p. 233°–233.5°, subliming in stout needles.

3:4:5-Trichloro-6-bromo-o-xylene; by brominating *3:4:5-trichloro-o-xylene* in presence

of iron (Hinkel, Chem. Soc. Trans. 1920, 117, 1296). Slender glistening needles, m.p. 226°.

For the iodo-derivatives of *o*-xylene, see Læser (Ber. 1884, 17, 1826), Klages and Liecke (J. pr. Chem. 1900, (2) 61, 307, 323), Edinger and Goldberg (Ber. 1900, 33, 2880), Datta and Chondhuri (J. Amer. Chem. Soc. 1916, 38, 1079), Knoll & Co. (D. R. P. 230172 of 1908), Finkelstein (Ber. 1910, 43, 1528).

The nitration of o-xylene. As the result of numerous experiments on the nitration of *o*-xylene under varied conditions, Crossley and Renouf (Chem. Soc. Trans. 1909, 95, 202), have arrived at the following conclusions. When fuming nitric acid alone is used and the nitration is effected below -4°, unchanged *o*-xylene is always recovered if less nitric acid is used than 6 times the weight of *o*-xylene. In all cases, however small an amount of nitric acid is used, dinitro-*o*-xylenes are obtained, and if the amount of nitric acid is increased to 15 times the weight of *o*-xylene, the amount of dinitro-*o*-xylene continually increases, but some mononitro-*o*-xylenes are always formed. When, however, *o*-xylene is nitrated with 10 times its weight of fuming nitric acid at 22°-25° an almost theoretical yield of dinitro-*o*-xylenes is produced. These results only hold good when the *o*-xylene is added to the nitric acid, for when nitric acid is added to *o*-xylene, a small amount of the latter is converted into mononitro-*o*-xylenes, together with a substance $C_{16}H_{17}O_2N$.

When the nitration is effected with nitric acid alone, about equal proportions of 3- and 4-nitro-*o*-xylene are produced, but with nitric and acetic acids, however, the proportion of the former to the latter is 1.5 : 1. Moreover, under these conditions no dinitro-*o*-xylenes are formed.

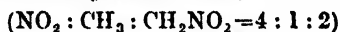
If the nitration is carried out with nitric and sulphuric acids below 0°, and the nitrating mixture is added to *o*-xylene, the proportion of 3-nitro-*o*-xylene obtained is about 8 times that of the 4-nitro-isomeride. If, on the other hand, *o*-xylene is added to the mixed acids, no mononitro-*o*-xylenes are produced, but a theoretical yield of dinitro-*o*-xylenes is obtained. Although this method gives rather better yields of dinitro-*o*-xylenes than when nitric acid is used alone, it is not to be recommended for their preparation, because a larger proportion of 4 : 5-dinitro-*o*-xylene, m.p. 115°, is formed, and this crystallises from sulphuric acid together with 3 : 4-dinitro-*o*-xylene, m.p. 82°, and the constituents of this mixture can be separated only by prolonged fractionation involving the use of large amounts of alcohol. To ensure the results described, it is not advisable to nitrate more than 50 grms. of *o*-xylene at one time.

ω-Nitro-o-xylene, o-tolyl-nitromethane; by dissolving *o*-nitro-*o*-xylyl phthalide in aqueous sodium hydroxide and precipitating with oxalic acid (Goldberg, Ber. 1900, 33, 2820); by boiling sodium-*o*-tolylisnitroacetoneitrile with aqueous sodium hydroxide (Wishlencus and Wren, Ber. 1905, 38, 502); by heating *o*-xylene with nitric acid (D 1075) in a sealed tube at 110° (Konowaloff, J. Russ. Phys. Chem. Soc. 1905, 37, 530). Oil (G.), or yellow oil, b.p. 137°-139°/23 mm. (W. and W.), or needles, m.p. 12°-14°, b.p. 145°-146°/23 mm.; D_4^{15} 1.423; n_D^{15} 1.54387 at 18° (K.). The corresponding iso-nitro derivative

melts at 61°-65° (K.). When kept, *o*-tolyl-nitromethane becomes red and deposits a crystalline substance which contains more nitrogen than the original compound and melts at 238°-242° (K.). The potassium derivative of *o*-tolyl-nitromethane, $C_8H_7KNO_2$, forms shining scales and its aqueous solution gives the following reactions: with copper sulphate, a dark green precipitate, soluble in ether or benzene with a red colour; with silver nitrate, a yellow precipitate, soluble in benzene, with a dark red colour; with mercuric chloride or stannic chloride, a white precipitate. Nitration with nitric acid (D 15) results in nuclear substitution. Its 5-bromo-*o*-toluic acid, m.p. 175°, and a liquid nitro-compound by the action of dilute nitric acid on bromo-*o*-xylene, melts at 65° (Konowaloff, &c., and J. Russ. Phys. Chem. Soc. 1904, 36, 537).

A nitro-*o*-tolyl-nitromethane, yellow leaflets, sintering at 170° and melting at 183°-185° (decomp.), has been obtained by Simonsen (Chem. Soc. Trans. 1913, 103, 1144), together with 3-nitro-*o*-xylene 4- and 5-sulphonic acids, and 4-nitro-*o*-xylene 5-sulphonic acid by gradually adding *o*-xylene 4-sulphonic acid to well-cooled fuming nitric acid (D 15) and then keeping the mixture at 30° for 2 days.

4-Nitro-*o*-tolyl-nitromethane,



forms crystals, m.p. 58°-59° (Konowaloff and Sentschikowski, J. Russ. Phys. Chem. Soc. 1904, 36, 462).

3-Nitro-*o*-xylene; in 90 p.c. yield together with 4-nitro-*o*-xylene by treating *o*-xylene with a mixture of nitric acid (D 1397) and sulphuric acid (D 184) below 0° and distilling the washed product with steam, or together with 4-nitro-*o*-xylene in the proportion of 2 : 1 by using nitric acid alone (Nölting and Forel, Ber. 1885, 18, 2668; Crossley and Renouf, Chem. Soc. Trans. 1909, 95, 202); from 3-nitro-*o*-4-xylylene by the diazo-reaction (Crossley and Wren, Chem. Soc. Trans. 1911, 99, 2341). Pale yellow refractive liquid, b.p. 240°/760 mm., solidifying on cooling to crystals, m.p. 15° (C. and W.); b.p. 250°/739 mm.; D_4^{15} 1.147 (N. and F.). When heated with nitric acid (D 115) in a sealed tube for 4 hours at 170°-180°, it yields 3-nitrophthalic acid, yellow transparent prisms, m.p. 217° (C. and R.; cf. Miller, Ann. 1881, 208, 240; Graeff, Ber. 1882, 15, 1127). When reduced with zinc dust and a dilute alcoholic solution of ammonium chloride it yields *o*-xylene-3-hydroxylaniline, white leaflets, m.p. 74° (Bamberger and Rising, Ann. 1901, 316, 257).

4-Nitro-*o*-xylene; see above; by nitrating 1 part of *o*-xylene with 8-10 parts of cold nitric acid (Jacobsen, Ber. 1884, 17, 159), or better with fuming nitric acid in presence of acetic acid at a temperature of 20°-25°. The yield of mononitro-derivatives obtained when *o*-xylene is nitrated with 8 times its weight of nitric acid is only half of that obtained when 6 times its weight of fuming nitric acid is used, and even in the latter case the yield is not as good as when nitric and acetic acids are used (C. and R.); from 5-nitro-*o*-4-xylylene by the diazo-reaction (Diepolder, Ber. 1909, 42, 2916). Long transparent glistening yellow prisms, m.p. 30°, b.p. 254°/748 mm. (slight decomp.), or 143°/21 mm.

(C. and R.); D¹⁰⁰ 1.139 (J.). On oxidation with dilute nitric acid it yields two nitrotoluic acids, and 4-nitrophthalic acid. When treated with caustic alkalis in the presence of air, it yields 4:4'-dinitro-2:2'-dimethyldibenzyl, lemon-yellow needles, m.p. 222°-224° (Green, Davies and Horsfall, Chem. Soc. Trans. 1907, 91, 2076). For electrolytic reduction, see Elbs and Kopp (Zeit. Elektrochem. 1898, 5, 108). When reduced with zinc dust and a dilute alcoholic solution of ammonium chloride 4-nitro-*o*-xylene yields *o*-xylene-4-hydroxylamine, white needles, m.p. 98°-101° (Bamberger and Rising, Ann. 1901, 316, 257).

3:4-Dinitro-*o*-xylene; from 3:4-dinitro-*o*-xylidine by the diazo-reaction (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345); by the action of fuming nitric acid on *o*-xylene at 22°-25°; also together with its isomerides by nitrating *o*-xylene or 4-nitro-*o*-xylene with fuming nitric acid or with mixed acids (C. and R.). Small silky needles, m.p. 82°. When heated in a sealed tube with nitric acid it yields 3:4-dinitrophthalic acid, m.p. 204°-205° (decomp.), and 3:4-dinitro-*o*-toluic acid, m.p. 182° (Warner, Chem. Soc. Proc. 1913, 29, 60).

3:6-Dinitro-*o*-xylene; by nitrating *o*-xylene; together with 4:6- and 3:4-dinitro-*o*-xylenes by nitrating 3-nitro-*o*-xylene with fuming nitric acid; as a by-product in the preparation of 3:4-dinitro-*o*-xylene (C. and R.; Crossley and Wren, Chem. Soc. Trans. 1911, 99, 2341). Sheaves of small needles, m.p. 89°-90°.

4:5-Dinitro-*o*-xylene; from 4:5-dinitro-*o*-xylidine by the diazo-reaction (C. and M.); together with 4:6- and 3:4-dinitro-*o*-xylene by nitrating 4-nitro-*o*-xylene in sulphuric acid solution with a mixture of nitric and sulphuric acids at the ordinary temperature and completing the reaction by heating for 10 minutes on the water-bath; also, but less conveniently, by nitrating 4-nitro-*o*-xylene with fuming nitric acid alone, the products being separated by fractional crystallisation from alcohol (Nölting and Thesmar, Ber. 1902, 35, 628), or by alternate crystallisation from sulphuric acid and alcohol (C. and R.). Long white glistening needles, m.p. 115°. It is more sparingly soluble in alcohol than 4:6-dinitro-*o*-xylene, and also differs from the latter in being readily converted into 5-nitro-4-amino-*o*-xylene by alcoholic ammonia at 150° (N. and T.).

4:6-Dinitro-*o*-xylene; see above; from 3:5-dinitro-*o*-xylidine by the diazo-reaction (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345); in largest quantity together with its isomerides by the action of fuming nitric acid on *o*-xylene at 22°-25° (C. and R.; cf. N. and T.); by heating 4:6-dinitro-*o*-tolylacetic acid (Borsche and Fiedler, Ber. 1913, 46, 2117). It crystallises from alcohol in faintly yellow, stout leafy needles, or long transparent needles, and from chloroform and light petroleum in stellar aggregates of long glistening needles, m.p. 75°-76° (C. and R.). It is reduced by ammonium sulphide to 6-nitro-*o*-4-xylidine, m.p. 74°-75°, and by tin and hydrochloric acid to the diamine (N. and T.). On oxidation with dilute nitric acid in a sealed tube it yields 3:5-dinitro-*o*-toluic acid, m.p. 206°, and 3:5-dinitrophthalic acid, m.p. 225° (W.).

3:4:5-Trinitro-*o*-xylene; together with

3:4:6-Trinitro-*o*-xylene by nitrating the mixture of the two isomeric dimethylcyclohexenes, obtained by eliminating 2 mols. of hydrogen bromide from 3:5-dibromo-1:1-dimethylcyclohexane, or by adding *o*-xylene to a cold mixture of nitric acid (D 1.5) and concentrated sulphuric acid and completing the nitration by heating the mixture on the water-bath for 15 hours; or the same mixture is obtained by the further nitration of 3:4- or 4:6-dinitro-*o*-xylene, whereas 4:5-dinitro-*o*-xylene on further nitration yields only 3:4:5-trinitro-*o*-xylene. It forms long colourless needles, m.p. 115° (Crossley and Renouf, Chem. Soc. Trans. 1908, 93, 629; 1909, 95, 202; cf. Harries and Antoni, Ann. 1903, 328, 88; Marquoyrol and Lorient, Bull. Soc. chim. 1920, [iv.] 27, 424).

3:4:6-Trinitro-*o*-xylene; see above; also as the sole product of the further nitration of 3:6-dinitro-*o*-xylene with fuming nitric acid and sulphuric acid (C. and R.). It forms faintly yellow glistening flat needles, m.p. 72°.

No tetranitro-derivatives are formed in the above nitrations. The 'dinitro-*o*-xylene,' m.p. 71°, obtained by Drossbach (Ber. 1886, 19, 2518), and erroneously considered by Nölting and Thesmar (l.c.) to be 4:6-dinitro-*o*-xylene, m.p. 75°-76°, has been shown by Crossley and Renouf (l.c.) to be actually 3:4:6-trinitro-*o*-xylene, m.p. 72°.

For the manufacture of trinitroxylene for use as a substitute for T.N.T. in bursting charges for high explosive shells, see Marshall (J. Ind. Eng. Chem. 1920, 12, 248).

When 50 grms. of commercial xylene, containing only the three isomerides, is nitrated with 500 grms. of mixed acids (2 parts of nitric acid, D 1.52 to 3 parts of sulphuric acid, D 1.84), 52 grms. of a solid trinitroxylene and 17 grms. of a yellow liquid nitroxylene are obtained. The presence of a small amount of dinitroxylens renders the product useless as an explosive, but by a second nitration a trinitroxylene capable of detonation by 0.15-0.2 gm. of silver azide is obtained in the form of white crystals, melting between 120° and 177° (Schweizer, Z. ges. Schiess- u. Sprengstoffw. 1919, 14, 24).

***o*-(2)-Chloro-4-nitro-*o*-xylene**; by treating a mixture of *p*-nitrotoluene and *s*-dichloromethyl-ether with fuming sulphuric acid (20 p.c. SO₃) and allowing the whole to stand (Stephen, Short and Gladding, Chem. Soc. Trans. 1920, 117, 510). Needles, m.p. 50°. On reduction with tin and hydrochloric acid it yields *o*-4-xylidine, and on oxidation with potassium permanganate it yields 4-nitrophthalic acid.

4-Chloro-5-nitro-*o*-xylene; by the action of nitric acid on 4-chloro-*o*-xylene (Claus and Groneweg, J. pr. Chem. 1891, (2) 43, 257). Needles, m.p. 73°.

3:5-Dichloro-4:6-dinitro-*o*-xylene; by nitrating 3:5-dichloro-*o*-xylene with fuming nitric acid and sulphuric acid for 10 minutes on the water-bath; or by dissolving 3:5-dichloro-6-bromo-*o*-xylene in fuming nitric acid and heating the solution on the water-bath for 20 minutes; by warming dichlorotribromodimethyltetrahydrobenzene with concentrated nitric acid (Crossley, Chem. Soc. Trans. 1904, 85, 264); by adding 3:5:6-trichloro-*o*-xylene to fuming nitric acid, and warming for a short time (Hinkel, Chem. Soc. Trans. 1920, 117,

1296). Attempts to obtain 3:5-dichloro-4:6-dinitro-*o*-xylene by chlorinating 4:6-dinitro-*o*-xylene failed (Crossley and Renouf, Chem. Soc. Trans. 1909, 95, 202). Faintly yellow glistening four-sided crystals, m.p. 175°–176° (C.).

4:5-Dichloro-3:6-dinitro-*o*-xylene; by nitrating 4:5-dichloro-*o*-xylene with fuming nitric acid and sulphuric acid (Claus and Berkefeld, J. pr. Chem. 1891, (2) 43, 583). Colourless transparent needles, m.p. 155°.

3:4:5-Trichloro-6-nitro-*o*-xylene; by the gradual addition of 3:4:5-trichloro-*o*-xylene to fuming nitric acid and warming on the water-bath for 20 minutes (Hinkel). Stout transparent crystals with a faint yellow tint, m.p. 149°.

3-Bromo-5-nitro-*o*-xylene; from 5-nitro-*o*-3-xylidine (Crossley and Bartlett, Chem. Soc. Trans. 1913, 103, 1297). Long colourless glistening needles, m.p. 101°.

Nitro-5-bromo-4-chloro-*o*-xylene; small colourless prisms, m.p. 223° (Claus and Groneweg, J. pr. Chem. 1891, (2) 43, 252).

3:5-Dichloro-4-bromo-6-nitro-*o*-xylene; by heating 3:5-dichloro-4-bromo-*o*-xylene for 20 minutes on the water-bath with fuming nitric acid (Crossley). Faintly yellow glistening needles, m.p. 175°–176.5°.

3-Nitro-4:5-dibromo-*o*-xylene; by nitrating 4:5-dibromo-*o*-xylene with fuming nitric acid in presence of glacial acetic acid (Crossley and Smith, Chem. Soc. Trans. 1913, 103, 989; Töhl, Ber. 1885, 18, 2651). Colourless needles, m.p. 141° (T.), or 143°–144° (C. and S.).

3:6-Dinitro-4:5-dibromo-*o*-xylene; together with the above compound by adding 4:5-dibromo-*o*-xylene to cold fuming nitric acid (Töhl). Small needles, m.p. about 250°.

o-Xylene 3-sulphinic acid; melts at 105° (Moschner, Ber. 1901, 34, 1257).

o-Xylene 4-sulphinic acid; by the action of zinc dust on *o*-xylene 4-sulphonylchloride (Jacobsen, Ber. 1877, 10, 1011); by treating *o*-xylene in carbon disulphide solution with sulphur dioxide in presence of aluminium chloride and hydrogen chloride at 0° (Knocvenagel and Kenner, Ber. 1908, 41, 3315). Large thin crystalline plates, m.p. 83° (J.), or 75° (K. and K.).

o-Xylene 3-sulphonic acid; by treating 6-chloro-*o*-xylene 3-sulphonic acid with sodium amalgam (Krüger, Ber. 1885, 18, 1760); by oxidising *o*-xylene 3-sulphinic acid (Moschner); by treating sodium 4:5-dibromo-*o*-xylene sulphionate with zinc dust and sodium hydroxide (Moody, Chem. Soc. Proc. 1892, 8, 213); by prolonged treatment of 3-bromo-*o*-xylene 6-sulphonic acid with sodium amalgam (Stallard, Chem. Soc. Trans. 1906, 89, 808). $\text{NaA}' + \text{H}_2\text{O}$, long flat plates. When heated at 115°–120° for 2 hours *o*-xylene 3-sulphonic acid is completely isomerised to *o*-xylene 4-sulphonic acid (Moody).

Chloride; prisms, m.p. 47° (Moody; Moschner), or 41.5°–43.5° (S.).

Sulphonamide; needles, m.p. 167°.

o-Xylene 4-sulphonic acid; by warming *o*-xylene with sulphuric acid (Jacobsen, Ber. 1877, 10, 1011; 1878, 11, 22). Long flat prisms or rectangular tables $+ 2\text{H}_2\text{O}$. Melts at 64° (Patterson, McMillan and Somerville, Chem. Soc. Trans. 1924, 126, 2489). $\text{NaA}' + 5\text{H}_2\text{O}$, long flat prisms, $\text{BaA}' + \text{H}_2\text{O}$, large rhombic plates. The barium salt may be obtained by oxidising

o-xylene 4-sulphinic acid with barium peroxide.

Chloride; large prismatic crystals, m.p. 51°–52°.

Amide; prisms, m.p. 144°.

The oxidation of *o*-xylene 4-sulphonic acid with permanganate yields two acids, and when treated at 40° with a solution of bromine in hydrochloric acid a mixture of 4-bromo-*o*-xylene, 4:5-dibromo-*o*-xylene and two bromo-*o*-xylene sulphonic acids is obtained (Kelbe and Stein, Ber. 1886, 19, 2137). *o*-Xylene 4-sulphonic acid on fusion with lead peroxide and potassium hydroxide gives phthalic acid in a yield of 70.5 p.c. (Graebe and Krafft, Ber. 1906, 39, 2507).

o-Xylene 4:6(?)-disulphonic acid; from *o*-xylene 4-sulphonic acid and chlorosulphonic acid at 150° (Pfannenstill, J. pr. Chem. 1892, (2) 46, 155). $\text{K}_2\text{A}'' + \text{H}_2\text{O}$, needles; $\text{BaA}'' + 3\text{H}_2\text{O}$; $\text{PbA}'' + 3\text{H}_2\text{O}$, large prisms.

Chloride; large prisms, m.p. 70°.

Amide; irregular crystals, m.p. 239°.

3-Chloro-*o*-xylene 6-sulphonic acid; small prismatic needles $+ 2\text{H}_2\text{O}$ (Claus and Bayer, Ann. 1893, 274, 304; Krüger, Ber. 1885, 18, 1755). $\text{NaA}' + \text{H}_2\text{O}$, large plates; $\text{BaA}' + \text{H}_2\text{O}$.

Amide; long prisms, m.p. 199° (K.). On treatment with sodium amalgam the free acid yields *o*-xylene 3-sulphonic acid (K.).

4-Chloro-*o*-xylene 5-sulphonic acid; colourless needles or nacreous plates $+ 5\text{H}_2\text{O}$ (C. and B.; K.). $\text{NaA}' + 5\text{H}_2\text{O}$, needles or flat prisms; KA' , vitreous needles; $\text{BaA}' + 4\text{H}_2\text{O}$, needles. The barium salt is more soluble than that of 3-chloro-*o*-xylene 6-sulphonic acid.

Amide; long needles, m.p. 207° (K.).

4-Bromo-*o*-xylene 5-sulphonic acid; by dissolving 4-bromo-*o*-xylene in slightly fuming sulphuric acid (Jacobsen, Ber. 1877, 10, 1011; 1878, 11, 22; 1884, 17, 2372; Stallard, Chem. Soc. Trans. 1906, 89, 808). Fibrous crystalline mass $+ x\text{H}_2\text{O}$. $\text{BaA}' + 3\text{H}_2\text{O}$, long hard prisms; $\text{NaA}' + 1\frac{1}{2}\text{H}_2\text{O}$, long slender needles; $\text{KA}' + \text{H}_2\text{O}$, thin vitreous prisms.

Amide; long hair-like needles, m.p. 213° (J.).

6- or 3-Bromo-*o*-xylene 4-sulphonic acid; together with 4:5-dibromo-*o*-xylene and 4-bromo-*o*-xylene by treating an aqueous solution of *o*-xylene 4-sulphonic acid at 40° with a solution of bromine in hydrochloric acid (Kelbe and Stein, Ber. 1886, 19, 2137); or better, by brominating barium *o*-xylene 4-sulphonic acid (Stallard). $\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, needles; $\text{NaA}' + \text{H}_2\text{O}$, thin plates; KA' , stout needles (S.); BaA' , needles $+ 4\text{H}_2\text{O}$ (K. and S.).

Chloride; large six-sided plates, m.p. 85.5° (S.).

Amide; m.p. 191.5° (S.), or 186.5° (K. and S.).

When the sodium salt of the free sulphonic acid is dissolved in sulphuric acid and distilled with steam, 3-bromo-*o*-xylene is obtained (S.).

3-Bromo-*o*-xylene 6-sulphonic acid; together with the above compound by sulphonating 3-bromo-*o*-xylene (S.). BaA' , small plates or powder; $\text{NaA}' + \text{H}_2\text{O}$, thin plates; KA' , long flat needles.

Chloride; six-sided plates, m.p. 68.5°.

Amide; arborescent crystals, m.p. 195°.

The sodium salt of 3-bromo-*o*-xylene 6-sulphonic acid on prolonged treatment with

sodium amalgam yields sodium *o*-xylene 3-sulphonate.

3-Nitro-*o*-xylene 4-sulphonic acid; together with 3-nitro-*o*-xylene 5-sulphonic acid, 4-nitro-*o*-xylene 5-sulphonic acid and a dinitro-*o*-xylene by gradually adding *o*-xylene 4-sulphonic acid to well-cooled fuming nitric acid (D 1.5) and keeping the mixture for 6 hours at 0° and then at 30° for 2 days. The 3-nitro-*o*-xylene 5-sulphonic acid is isolated by means of its barium salt, and the remaining sulphonic acids are isolated as their sulphonamides (Simonsen, Chem. Soc. Trans. 1913, 103, 1144). Needles, BaA', glistening needles + H₂O.

Amide; large prismatic needles, m.p. 214°.

3-Nitro-*o*-xylene 5-sulphonic acid; hygroscopic slender needles (S.). BaA' + 3H₂O, glistening prismatic needles.

Chloride; large irregular glistening plates, m.p. 69°-70°.

Amide; fine hairlike needles, m.p. 180°.

4-Nitro-*o*-xylene 5-sulphonic acid; bayonet-shaped, somewhat hygroscopic needles (S.)

Amide; small hard prismatic needles, m.p. 157°-158°.

***m*-Xylene or isoxylene**; in lignite tar (Oehler, Zeitsch. angew. Chem. 1899, 12, 561) and in coal tar; together with a little *o*- and *p*-isomerides by the action of methyl chloride on toluene in presence of aluminium chloride (Ador and Rilliet, Ber. 1878, 11, 1627; Friedel and Crafts, Ann. Chim. Phys. 1884, (6) 1, 461); from *m*-iodotoluene (but not from *m*-bromotoluene) with methyl iodide and sodium (Wroblewsky, Ann. 1878, 192, 200); together with a little *p*-xylene by heating toluene with methyl iodide in the presence of iodine (Raymann and Preis, Ann. 1884, 223, 315); by distilling mesitylenic and xylylic acids with lime (Fittig, Ann. 1868, 148, 10; 1870, 156, 236; Zeit. für Chem. 1867, 526; Bull. Soc. chim. 1867, (2) 8, 268, 424); from pseudocumene or mesitylene by the action of aluminium chloride (Jacobsen, Ber. 1885, 18, 338). The fact that *m*-xylene is more slowly attacked by oxidising agents than are its *o*- and *p*-isomerides has been employed to obtain this hydrocarbon in a pure condition (Tawildarow, Zeit. für Chem. 1870, 418; Gundelach, Bull. Soc. chim. 1876, (2) 20, 43; Lako, Ann. 1876, 182, 30; Brückner, Ber. 1876, 9, 405; Bull. Soc. chim. 1876, (2) 26, 463).

For the separation of *m*-xylene from its *o*- and *p*-isomerides, see under *o*-xylene. According to a recent patent *m*-xylene may be separated from the mixture by means of 75 p.c. sulphuric acid in presence of *m*-xylene sulphonic acid. The *m*-xylene sulphonic acid thus produced is separated from the unchanged hydrocarbons and is subsequently desulphonated (Lepers, U.S. P. 1311848 of 1919).

Liquid, b.p. 139° (corr.), m.p. -50° (Fischer, Zeitsch. Elektrochem. 1910, 16, 161). It is stated by Pictet (Compt. rend. 1894, 119, 955) that *m*-xylene does not solidify at -100°. M.p. -54° to -53° (Colson, Ann. Chim. Phys. 1885, (6) 6, 128); b.p. 138.9°; D₄⁰ 0.8812 (Pinette, Ann. 1888, 243, 50); b.p. 139.2/759.2 mm.; D₄^{15.5} 0.8715, D₄^{19.2} 0.7572 (Schiff, Ann. 1883, 220, 92; cf. Neuback, Zeitsch. physikal. Chem. 1887, 1, 660); m.p. -45° (Altschul and Schneider, Zeitsch. physikal. Chem. 1895, 16, 24); b.p.

142.6°; D₄⁰ 0.8779, D₁₅¹⁵ 0.8691, D₂₅²⁵ 0.8625, D₄^{8.4} 0.87397 (Perkin, Chem. Soc. Trans. 1896, 1, 1241; 1900, 77, 278); D₄²⁰ 0.8655 (Brühl,

Ann. 1886, 235, 12; cf. von Hirsch, Ann. Phys. Chem. 1899, (2) 69, 456). Critical pressure and temperature (Altschul, Zeitsch. physikal. Chem. 1893, 11, 590); refractive power (Brühl; Landolt and Jahn, Zeitsch. physikal. Chem. 1892, 10, 303); capillarity constant (Schiff, Ann. 1884, 223, 104); electromagnetic property (Schönrock, Zeitsch. physikal. Chem. 1893, 11, 785); dielectric constant (Drude, *ibid.* 1897, 23, 309; Turner, *ibid.* 1901, 35, 427); other physical constants (von Auwers, Ann. 1919, 419, 92; Gladstone, Chem. Soc. Trans. 1891, 59, 290; Flusin, Compt. rend. 1898, 126, 1497); absorption spectrum in ultra-violet (Mies, Zeitsch. wiss. Photochem. 1910, 8, 287). It is not attacked by dilute nitric acid, and is only oxidised very slowly by potassium dichromate, forming isophthalic acid (Fittig and Velguth, Ann. 1868, 148, 11), but after conversion into the diethyl-ether, a colourless mobile oil, b.p. 246°-247°/712 mm., an almost theoretical yield of isophthalic acid is obtained on oxidation in a similar manner (Kipping, Chem. Soc. Trans. 1888, 53, 21). For other methods of oxidation in presence of catalysts, &c., see under *o*-Xylene.

When heated with phosphonium iodide it forms a hydrocarbon C₈H₁₄ (Bayer, Zeit. für Chem. (2) 4, 455).

The degradation of alkylbenzenes by means of anhydrous aluminium chloride was first noticed by Friedel and Crafts (Compt. rend. 1885, 100, 692). Anschütz (Ber. 1884, 17, 2816; 1885, 18, 657; Ann. 1886, 235, 182, 323) obtained toluene from *m*-xylene by heating the latter with anhydrous aluminium chloride. Jacobsen (Ber. 1885, 18, 338) obtained toluene from *m*-xylene in a similar manner, by boiling the mixture for 4 hours. On boiling with aluminium chloride the products are benzene, toluene, a little *p*-xylene, pseudocumene, mesitylene, and durene (Anschütz, Ann. 1886, 235, 182). Heise and Töhl (Ann. 1892, 270, 155), on passing dry hydrogen chloride through a mixture of 70 grms. of *m*-xylene and 20 p.c. of aluminium chloride heated for 6 hours at 100°, obtained only 2 grms. of hydrocarbon of lower boiling-point than *m*-xylene, together with benzene, mesitylene, some *p*-xylene and pseudocumene. Fischer and Niggemann (Ber. 1916, 49, 1475) found that for the most productive degradation of *m*-xylene to toluene, the reaction should be carried out at the boiling point of *m*-xylene for 2 hours in the presence of 2.4 p.c. of aluminium chloride. Under these conditions *m*-xylene yields approximately 12 p.c. of toluene together with benzene and polymethylated benzenes.

***m*-Xylene**, when treated with hydroxylamine hydrochloride in presence of aluminium chloride, yields 4-amino-*m*-xylene (Graebe, Ber. 1901, 34, 1778), and on heating with methyl iodide and iodine at 250° it yields pseudocumene, mesitylene, and a hydrocarbon C₁₀H₁₄ (Rayman and Preis, Ann. 1884, 223, 320). When treated with benzoyl peroxide *m*-xylene forms dixylylene (Lippman, Monatsch. 1886, 7, 528).

In the presence of aluminium chloride, *m*-xylene reacts with acetyl chloride to form

m-xylyl-4-methylketone (Verley, Bull. Soc. chim. 1897, (3) 17, 906); Claus and Gärtner, Ber. 1886, 19, 230; Ishzaka, Ber. 1914, 47, 2460), which, on oxidation with potassium permanganate, yields dimethylphenylglyoxylic acid, and on reduction with sodium amalgam yields *m*-xylyl-4-methylcarbinol (Claus, J. pr. Chem. 1890, (2) 41, 483). *m*-Xylyl-4-methylketone, on nitration with nitric acid (D 1.52) at temperatures below 30°, yields two mononitro-derivatives, but when the ketone is added slowly to a mixture of nitric acid (D 1.52) and sulphuric acid, a dinitro- and a dinitronitroso-ketone are obtained, the latter being formed in greater quantity at higher temperatures (Claus). *m*-Xylyl-4-methylketone when treated with sodium ethoxide and amyl nitrite yields xylylformoxime (Söderbaum, Ber. 1892, 25, 3459). *m*-Xylene condenses with bromoacetyl bromide in presence of aluminium chloride, forming *m*-xylyl-4-bromomethylketone (Jacobs and Heidelberger, J. Biol. Chem. 1915, 21, 455), whilst 5-methoxy-*m*-xylene with acetyl chloride yields 5-methoxy-*m*-xylyl-2-methylketone, and the xylenyl acetate in a similar manner yields 5-hydroxy-*m*-xylyl-2-methylketone (Auwers, Ber. 1915, 48, 90). *m*-Xylyl propyl ketone on oxidation with permanganate yields *o*-*p*-dimethylbenzoylformic acid (*m*-xylyl-glyoxylic acid), and on reduction in alkaline solution yields *m*-xylylpropylcarbinol; *m*-xylyl isopropyl ketone on oxidation with potassium permanganate also yields *m*-xylyl-glyoxylic acid. The ketones on heating with yellow ammonium sulphide, containing sulphur, yield the corresponding butyramides (Claus, J. pr. Chem. 1892, (2) 46, 474). *m*-Xylyl-3-chloromethylketone forms large white plates, m.p. 62°-63° (Kuncell, Ber. 1897, 30, 577; Ber. Deut. Pharm. Ges. 1912, 22, 242), whilst *m*-xylyl-4-bromoethylketone, prepared by gradually adding aluminium chloride to a mixture of α -bromopropionic chloride and *m*-xylene, is an oil, b.p. 160°-163°/20-25 mm. (Collet, Compt. rend. 1897, 125, 305). *m*-Xylyl-6-butylketone is obtained by the action of valeryl chloride on *m*-xylene in presence of aluminium chloride. It boils at 149°/16 mm., and forms an oxime, b.p. 184°-187°/21 mm., and a semi-carbazone, m.p. 188° (Layraud, Bull. Soc. chim. 1906, (3) 35, 223). 5-Butyl-*m*-xylyl-4-methylketone, obtained by slowly adding acetyl chloride to butylxylene and aluminium chloride, forms large plates, m.p. 48°, b.p. 265°, and does not react with hydroxylamine or phenylhydrazine. On oxidation with permanganate below 65° it yields butylxylyl-glyoxylic acid; when heated with aniline and *p*-toluidine by Bouveault's method butylxylylaldehyde is formed; on nitration the ketone yields a dinitro-derivative, which does not form an oxime or a phenylhydrazone, but yields a benzylidene-derivative, m.p. 140°, and a trichloroethylidene-derivative, m.p. 179° (Baur-Thurgau, Ber. 1898, 31, 1344; 1899, 32, 3647; 1900, 33, 2562). *m*-Xylene condenses with phthalic anhydride in presence of aluminium chloride forming *m*-xylene-phthalic acid (Meyer, Ber. 1882, 15, 636), with benzoyl chloride forming dimethylbenzophenone, and with phenylacetyl chloride forming dimethyl-desoxybenzoin (Söllicher, Ber. 1882, 15, 1680). Unsymm. *m*-xyleneoxyacetal boils at 273° and has D₂₀ 0.995; the hydrate melts at 62°. The

derived *o*-*p*-dimethylcoumarone is an oil, b.p. 221°-222°, D₁₅ 1.036, refractive index 1.5412 at 16°; with concentrated sulphuric acid it produces a violet coloration. It forms a picrate, m.p. 78°-79° (Stoermer and Schroeder, Ber. 1897, 30, 1700). Di-*m*-xylyl ethylene diketone C₂H₄[CO·C₆H₄(CH₃)₂]₂(CO·CH₃; CH₃=1:2:4) colourless needles, m.p. 129°, is obtained by the action of succinyl chloride on *m*-xylene in presence of aluminium chloride (Claus and Werner, Ber. 1887, 20, 1375).

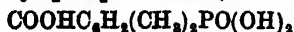
When 4 mols. *m*-xylene, 1 mol. nickel carbonyl, and 4 mols. aluminium chloride are allowed to react for several days at the ordinary temperature, or when the mixture is heated for several hours in a sealed tube at 100°, a 20 p.c. yield of 2:4-dimethylbenzaldehyde is obtained. Under the latter conditions, 2:4:6:8-tetramethylantracene, identical with the product obtained by Anschütz (Ann. 1886, 235, 174) by the action of acetylene tetrabromide and aluminium chloride on *m*-xylene, is also formed (Dewar and Jones, Chem. Soc. Trans. 1904, 85, 217). 2:4-Dimethylbenzaldehyde has also been prepared by treating *m*-xylene in presence of aluminium chloride and cuprous chloride with carbon monoxide and hydrogen chloride (Gattermann and Koch, Ber. 1897, 30, 1622; 1898, 31, 1149; Gattermann, Ann. 1906, 347, 347), and from the phenylimide derived from *m*-xylyl-glyoxylic acid by boiling with dilute sulphuric acid (Bouveault, Compt. rend. 1896, 122, 1543). The tetramethylantracene obtained by Friedel and Crafts (Ann. Chim. Phys. 1887, (6) 11, 268) by the action of methylene chloride and aluminium chloride on *m*-xylene differs from the tetramethylantracene described above, and must be 1:3:6:8-tetramethylantracene.

m-Xylene is converted into *m*-tolualdehyde by Étard's reaction (Bornemann, Ber. 1884, 17, 1462). *m*-Xylylamide, lustrous needles, m.p. 180°, is formed when *m*-xylene and chloro-carbonylamide are heated gently; *m*-xylyl-anilide is prepared by heating a mixture of phenyl cyanate and *m*-xylene in presence of aluminium chloride (Leuchart, J. pr. Chem. 1890 (2), 41, 301).

When *m*-xylene is treated with mercury fulminate, sublimed aluminium chloride, aluminium hydroxide and hydrated aluminium chloride, a mixture of *aa*-*m*-xylylaldoxime, *m*-xylo-2-nitrile, m.p. 90°-91°, and *m*-xylo-4-nitrile, m.p. 24°, is formed; *m*-xylyl-4-aldoxime is separated from the nitriles by means of sodium hydroxide. The *syn*-form, m.p. 126°, is purified by precipitation from its ethereal solution with hydrochloric acid, and is converted into the *anti*-form, m.p. 85°-86°, by warming under water (Scholl and Kafer, Ber. 1903, 36, 322).

By the action of phosphorus chloride on *m*-xylene in presence of aluminium chloride, a mixture of *m*-xylyl-4- and 5(?)-chlorophosphines is obtained, the former being also formed by the action of phosphorus chloride on mercury dixylyl (Hg·CH₃; CH₃=4:1:3) at 230°-240°. The mixture on treatment with chlorine yields a mixture of the tetrachlorides, which with sulphur dioxide yields a mixture of oxy-chlorides (Weller, Ber. 1887, 20, 1718), whilst the chlorophosphines react with zinc-methyl to form xylylphosphine C₆H₄(CH₃)₂P(CH₃)₂H

b.p. 233°, and a little dimethylphosphine oxide (Conan, Ber. 1898, 31, 2919). The oxy-chlorides on prolonged boiling with water are converted into the corresponding *m*-xylylphosphinic acids (W.). *m*-Xylophosphonic acid,



(1:2:4:5) is obtained by oxidising pseudo-oumyl-phosphonic acid with potassium permanganate. It melts at 258°, and when heated above this temperature yields metaphosphoric acid and xylene carboxylic acid (Michaelis, Rothe, Ulster and Hecker, Ann. 1896, 293, 261). *m*-Xylene reacts with diphenylcarbamide in presence of aluminium chloride, forming *m*-xylyldiphenylamide, yellowish monoclinic prisms, m.p. 141°–142° (Lellmann and Bonhöffer).

When *m*-xylene is treated with ethyl bromide and aluminium chloride, both unsymm. and symm. ethyl *m*-xylenes are obtained and are separated by means of their sulphonamides. After these have been separated there remains an uncrystallisable sulphonamide from which, by heating with concentrated hydrochloric acid at 180°, 4-ethyl-*o*-xylene is obtained, molecular transformation having occurred (Töhl and Geyger, Ber. 1892, 25, 1533). *m*-Xylene, on treatment with aluminium chloride at 100°, yields a small amount of benzene, *p*-xylene and trimethyl-benzene, but for the greater part remains unchanged (Heise and Töhl, Ann. 1892, 270, 155). *m*-Xylene reacts with potassium thiocyanate, forming *m*-xylene thiocyanate, m.p. 160°–161° (Wheeler and Merriam, J. Amer. Chem. Soc. 1902, 24, 439). Aqua regia converts *m*-xylene into monochloro-, dichloro-, trichloro-, and tetrachloro-derivatives (Datta and Fernandes, J. Amer. Chem. Soc. 1916, 38, 1809).

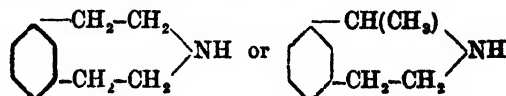
When treated with 1 mol. of chlorosulphonic acid *m*-xylene yields chiefly *m*-xylene 4-sulphonic acid (amide, m.p. 137°), identical with that described by Jacobsen (Ber. 1877, 10, 1014) as 'erste metaxylyl-sulfonsäure' (Beckurts and Otto, Ber. 1878, 11, 2061). When *m*-mercury dixylyl is heated with boron chloride at 200° for 24 hours, *m*-xylylborochloride, colourless fuming liquid, b.p. 218°, is obtained, which is converted by pouring into water into *m*-xylylborooxide, white needles, m.p. 202°, and this yields *m*-xylylboric acid when boiled with water. *m*-Xylylborobromide is a colourless refractive liquid, b.p. 125°/15 mm.; D_4^{20} 1.57 (Michaelis, Thevenot, and Richter, Ann. 1901, 315, 19). Sulphuryl chloride reacts with *m*-xylene in presence of sunlight, forming a chloro-derivative, substituted in the side-chain, whilst in the absence of sunlight a good yield of 4-chloro-*m*-xylene is obtained. Similar results are obtained with sulphuryl chloride at 160°, but in the presence of aluminium chloride a sulphonyl chloride is obtained together with the above chloro-*m*-xylene (Töhl and Eberhard, Ber. 1893, 26, 2940). For arsenic derivatives of *m*-xylene, see Michael and Seemann (Ann. 1902, 320, 271), and for the hydrogenated derivatives of *m*-xylene, see Wallach (Ann. 1890, 258, 326); Tiemann and Semmler (Ber. 1895, 28, 2136); Verley (Bull. Soc. chim. 1897, (3) 17, 180); Wreden (Ber. 1872, 5, 608; 1873, 6, 1379; Ann. 1872, 163, 336; 1877, 187, 157); Putochin (J. Russ. Phys. Chem. Soc. 1884, 16, (2) 295); Lossen (Ann. 1884, 225, 110); Wallach (Ber. 1892, 25, 923);

Beilstein and Kurbatow (Ber. 1880, 13, 1820); Markownikoff and Spady (Ber. 1887, 20, 1850); Renard (Ann. Chim. Phys. 1884, (6) 1, 229); Aschan (Ber. 1891, 24, 2718); Schiff (Ber. 1880, 13, 1417; Gazz. chim. ital. 1880, 10, 320); Baeyer (Ann. 1870, 155, 272); Klages and Knoevenagel (Ber. 1894, 27, 3023); Ballo (Ann. 1879, 197, 322); Jakowkin (J. Russ. Phys. Chem. Soc. 1884, 16, (2) 294).

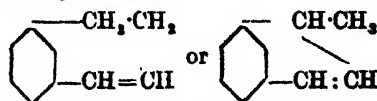
When sulphur chloride acts upon *m*-xylene in presence of the aluminium-mercury couple it is probable that dixylylene disulphide is first formed, and this yields *m*-xylyl hydrosulphide, or thioxyleneol when distilled (Cohen and Skirrow, Chem. Soc. Trans. 1899, 75, 890). The thioxyleneol obtained by Yssel (Zeit. für Chem. 1865, (2) 1, 360) by the action of zinc and sulphuric acid on xylene sulphonyl chloride is described as a liquid boiling at 213°. When treated with sulphur, *m*-xylene yields dimethyl-dibenzyl and *m*-dimethylstilbene (Aronheim and van Merop, Rec. trav. chim. 1903, 21, 448), and with triphenylmethyl, *m*-xylene forms the complex $\text{C}_6\text{H}_4(\text{CH}_2)_2 + 2[(\text{C}_6\text{H}_5)_3\text{C}]$ (Gomberg and Kone, Ber. 1905, 38, 1333).

5-Chloro-2:3-dihydro-*m*-xylene, oil, b.p. 78°–80°/15 mm., or 176°–178°/atm., is obtained by the action of phosphorus pentachloride on 3:5-dimethyl- Δ -ketotetrahydro-benzene (Klages and Knoevenagel, Ber. 1894, 27, 3019).

m-Xylylene cyanide on reduction with sodium and alcohol produces only about one-seventh of the normal reduction product, *m*-di- β -aminoethylbenzene $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$, b.p. 165°–170°/20 mm., the chief product being a saturated secondary amine



b.p. 97°–98°/16 mm. The quaternary ammonium hydroxide, obtained from this base on treatment with methyl iodide, loses water and dimethylamine when distilled, forming an unsaturated hydrocarbon



b.p. 62°–63°/18 mm., D_4^{19} 0.900. Both these compounds yield isophthalic acid on oxidation. These reactions indicate the important fact that two meta-carbon atoms in a benzene ring may be connected not only by a nitrogen-containing chain, but also by a simple carbon chain (von Braun, Karpf and von Garn, Ber. 1920, 53, 98).

ω -Chloro-*m*-xylene, *m*-xylyl chloride,

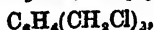


by the action of chlorine on boiling *m*-xylene (Vollrath, Zeit. für Chem. 1866, 2, 488; Lauth and Grimaux, Bull. Soc. chim. 1867, (2) 7, 233; Ann. 1868, 145, 115; Gundelach, Bull. Soc. chim. 1876, (2) 26, 43; Compt. rend. 1876, 82, 1444); by the action of chlorine on *m*-xylene in sunlight (Radziewanowski and Schramm, Akad. Wiss. Krakau, 1898, 61); by the action of hydrogen chloride on *m*-xylyl alcohol



(Colson, Ann. Chim. Phys. 1885, (6) 6, 118). It boils at 196°; D_{20}^{20} 1.079.

ω-Dichloro-*m*-xylene, *m*-xylene chloride,



from the glycol $C_8H_6(CH_2OH)_2$, and hydrogen chloride (Colson, Bull. Soc. chim. 1885, (2) 43, 7; Compt. rend. 1884, 99, 42); by heating *m*-xylene with an equivalent amount of phosphorus pentachloride at 180°. The yield is not good, and to obtain a pure product it is necessary to hydrolyse it to the glycol, which is then treated as above (Colson and Gautier, Bull. Soc. chim. 1886, (2) 45, 6; Ann. Chim. Phys. 1885, (6) 6, 114; 1887, (6) 11, 23). *ω*-Dichloro-*o*-xylene is also obtained by the action of chlorine on *m*-xylene in sunlight (Radziewanowski and Schramm). It forms crystals, m.p. 34.2°, b.p. 253°, D_{20}^{20} 1.302.

Symm.-ω tetrachloro-m-xylene $C_8H_4(CHCl_2)_2$; by the action of chlorine on boiling *m*-xylene in presence of aluminium chloride (Bielecki, Bull. Acad. Sci. Cracow, 1908, 29).

It forms slender silky needles, m.p. 223°–223.5° (B.), whereas, according to Colson and Gautier (Bull. Soc. chim. 1886, (2) 45, 509; Compt. rend. 1886, 102, 689), it boils at 273°; D 1.536.

Hexachloro-m-xylene; by heating *m*-xylene with excess of phosphorus pentachloride in a sealed tube at 100° (Colson and Gautier, Compt. rend. 1886, 102, 689).

It boils at 286°, and is converted by dilute alkalis into complex acids containing chlorine. In this case, phosphorus pentachloride has attacked the nucleus, and, in this respect, *m*-xylene differs from its isomerides.

4-Chloro-m-xylene; from *m*-4-xylidine (Klages, Ber. 1896, 29, 310); by chlorinating *m*-xylene at 0° in presence of 5 p.c. of iodine (Jacobsen, Ber. 1885, 18, 1760; Vollrath, Zeit. für Chem. 1866, 488), or in chloroform solution in presence of iron (Claus and Burstert, J. pr. Chem. 1890, (2) 41, 532). The crude product may be purified by sulphonation (J.) or by fractional distillation (C. and B.).

Oil, which does not solidify at –20°, b.p. 186.5°/767 mm., D_{20}^{20} 1.0598 (J.); b.p. 180°–181° (uncorr., C. and B.), or 187–188/755 mm. (K.). On oxidation with chromic acid mixture it yields 6-chloro-*m*-toluic acid (J.).

4-Chloro-m-xylene is also obtained in good yield by the action of sulphuryl chloride on *m*-xylene in the absence of sunlight (Toll and Eberhard, Ber. 1893, 26, 2940).

5'-Chloro-2-m-xyloylbenzoic acid, m.p. 162°, obtained by the interaction of phthalic anhydride and *o*-chloro-*m*-xylene, on treatment with ammonium hydroxide in the presence of copper powder is converted into an amino-acid, m.p. 140° (decomp.), and subsequently into 1-amino-2:4-dimethylantraquinone, m.p. 293° (B. A. S. E., D. R. P. 234917 of 1910).

5-Chloro-m-xylene; from *m*-5-xylidine by the Sandmeyer reaction (Klages, Ber. 1896, 29, 310); from the bromide of 5-chloro-dihydro-*m*-xylene by the elimination of hydrogen bromide; by oxidising 5-chlorodihydro-*m*-xylene with cold potassium permanganate, potassium dichromate, or chromic acid in glacial acetic acid (Klages and Knoevenagel, Ber. 1894,

27, 3024; 1895, 28, 2044). Oil, b.p. 190°–191°/755 mm.

2:4-Dichloro-m-xylene; by heating *m*-xylene-2:4-disulphonylchloride with phosphorus pentachloride for 10 hours at 180° (Wischn, Ber. 1890, 23, 3113); together with the 4:6-isomeride by chlorinating cold *m*-xylene in presence of iodine (Koch, Ber. 1890, 23, 2318; cf. Hollemann, Zeit. für Chem. 1865, 554; Ann. 1867, 144, 268). Liquid, solidifying at –20°, b.p. 221.5°. When treated with methyl iodide and sodium it yields *v*-tetramethylbenzene.

4:5-Dichloro-m-xylene; from 4-chloro-*m*-5-xylidine by the Sandmeyer reaction (Klages). Oil, b.p. 231°–232°, readily volatile with steam.

4:6-Dichloro-m-xylene; see above; together with the mono- and trichloro-derivatives by chlorinating *m*-xylene in chloroform solution in the presence of iron (Claus and Burstert, J. pr. Chem. 1890, (2) 41, 552); together with the mono- and the tetrachloro-derivatives by treating *m*-xylene with *aqua regia* (Datta and Fernandes, J. Amer. Chem. Soc. 1916, 38, 1809).

Large pearly plates, which sublime, m.p. 68°, b.p. 222°–224°. On heating in a sealed tube with nitric acid (D 1.15) for 5–6 hours at 150° it yields 4:6-dichloro-3-methylbenzoic acid, whereas on heating with nitric acid (D 1.18) in a sealed tube at 220° for several hours, or with chromic acid, 4:6-dichloro-isophthalic acid is formed (C. and B.). Treatment with methyl iodide and sodium yields durenene, and when heated with concentrated sulphuric acid at 220° a 12 p.c. yield of 2:4-dichloro-*m*-xylene is obtained (Koch).

Trichloro-m-xylene (?); by chlorinating *m*-xylene in presence of iodine (Hollemann, Ann. 1867, 144, 270). Silky needles, m.p. 150°, b.p. 255°.

Trichloro-m-xylene; together with the mono-chloro-, 4:6-dichloro-, and the tetrachloro-derivatives by the action of *aqua regia* on *m*-xylene (Datta and Fernandes, J. Amer. Chem. Soc. 1916, 38, 1809); by chlorinating *m*-xylene in chloroform solution in presence of iron (C. and B.). Colourless, lustrous needles, m.p. 117°. It sublimes and on oxidation with nitric acid or chromic acid yields only trichloro-isophthalic acid. This trichloro-derivative is also formed by the method of Datta and Fernandes (l.c.).

Tetrachloro-m-xylene; see above. White brittle needles, m.p. 210° (C. and B.), or 212° (K.). Very resistant to oxidising agents.

ω-Bromo-m-xylene, *m*-xylyl bromide; by brominating boiling *m*-xylene (Radziszewski and Wispek, Ber. 1882, 15, 1743; 1885, 18, 1279; Atkinson and Thorpe, Chem. Soc. Trans. 1907, 91, 1687; Colson, Compt. rend. 1884, 99, 42; Bull. Soc. chim. 1885, (2) 43, 6); by the action of 1 mol. of bromine on cold *m*-xylene in the presence of indirect sunlight (Schramm, Ber. 1885, 18, 1277).

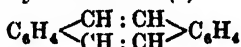
Colourless liquid, b.p. 215°/735 mm. (R. and W.); 212°–218° (C.); D_{20}^{20} 1.3711; b.p. 185°/340 mm. (Poppe, Ber. 1890, 23, 109); b.p. 212°–214° (A. and T.). When treated with potassium thiocyanate in dilute alcohol it yields *m*-xylyl thiocyanate, b.p. 170°/30 mm. (Strzelecka, Bull. Acad. Sci. Cracow, 1909, 731), and may be converted into *m*-tolylcarbinol, b.p. 216°–217.5°/758 mm.; D_{20}^{20} 1.028 (C.). When

treated with the sodium derivative of ethyl-acetoacetate it yields ethyl *m*-xylylacetoacetate, a yellowish oil, b.p. 195°/36 mm., which, when treated with nitrous acid under varied conditions, yields isonitroso-*m*-xylylacetic acid, $C_8H_4(CH_3)_2CH_2C(ONH)COOH$, and isonitroso-*m*-xylylacetone (Ryan, Ber. 1898, 31, 2129).

ω-*Dibromo-m-xylene*, *m*-xylene bromide $C_8H_4(CH_2Br)_2$; by brominating heated *m*-xylene (R. and W.; A. and T.; C.; Kipping, Chem. Soc. Trans. 1888, 53, 21; Pellegrin, Rec. trav. chim. 1899, 18, 458); by the action of bromine on *m*-xylene in direct sunlight (S.); from the glycol and hydrogen bromide.

Long prismatic, monoclinic needles, m.p. 77°; D_4^{20} 1.734; D^{20} 1.61 (C.); b.p. 135°–140°/20 mm. (P.).

On hydrolysis with aqueous potassium carbonate, *m*-xylene glycol, m.p. 45°–46° 2', is formed (C.), and with alkaline permanganate it yields isophthalic acid. With ethyl chloromalonate in presence of sodium ethylate it yields ethyl *m*-xylylenedichlorodimalonate (K.). With alcoholic potassium hydrosulphide it yields *m*-xylylene hydrosulphide, b.p. 157°/15 mm. (Kötz and Sevin, Ber. 1900, 33, 729); with potassium thiocyanate it yields *m*-xylylene thiocyanate, m.p. 60° (Strzelecka, Bull. Acad. Sci. Cracow, 1909, 731); by the action of bromobenzene in presence of sodium it yields diphenyl *m*-di-xylylene (?), $C_{12}H_{16}$, m.p. 131° 5', and di-*m*-phenylenediethene (?)



m.p. 191°, b.p. 260°/12 mm. (Pellegrin). *m*-Xylylene dibromide is converted into *m*-xylylene diiodide, m.p. 106°, when treated in acetone solution with sodium iodide (Finkelstein, Ber. 1910, 43, 1528; Knoll & Co., D. R. P. 230172 of 1908). For the action on primary, secondary, and tertiary amines, &c., see Halfpaap (Ber. 1903, 36, 1672). It reacts with ethyl acetoacetate in presence of sodium ethoxide to form ethyl *m*-xylylenedi-acetoacetate, a colourless viscous oil, which on treatment with 80 p.c. sulphuric acid is converted into ethyl hydrogen dimethylindacene dicarboxylate, m.p. 165°–166° (Ephraim, Ber. 1901, 34, 2779).

ω-ω-ω'-Tribromo-m-xylene, forms large prisms, m.p. 118° (A. and T.).

Symm. ω-tetrabromo-m-xylene $C_8H_4(CHBr)_2$; by the action of 200 c.c. of bromine on 100 grms. of *m*-xylene in direct sunlight at 90°–150° (Thiele, Gunther and Leopold, Ann. 1906, 347, 106). Colourless needles, or monoclinic plates, m.p. 107°. On treatment with concentrated sulphuric acid, or better, with potassium oxalate, *m*-phthalaldehyde is formed.

2-Bromo-m-xylene; by treating a hot solution of sodium *m*-xylene 2-sulphonate with a solution of bromine in hydrochloric acid (Jacobsen and Deike, Ber. 1887, 20, 904). Liquid at –10°, b.p. 206°. On treatment with methyl iodide and sodium, 1:2:3-trimethylbenzene is formed.

4-Bromo-m-xylene; by the action of bromine on cold *m*-xylene in the dark (Fittig, Ann. 1868, 147, 31; Schramm, Ber. 1885, 18, 1277), or in the presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1899, 75, 984); by the action of sulphur bromide and

nitric acid (D 1.4) on *m*-xylene in benzene solution (Edinger and Goldberg, Ber. 1900, 33, 2883). Oil, b.p. 203°–204° (F.), or 205° (E. and G.). When treated with the lead salt of thiophenol, it yields *as*-phenyl-*m*-xylyl sulphide $C_8H_4S-C_6H_5(CH_3)_2$ (Bourgeois, Ber. 1895, 28, 2312).

5-Bromo-m-xylene; from *m*-4-xylylidine by acetylation, bromination, hydrolysis, and elimination of the amino-group (Wroblewsky, Ann. 1878, 192, 215; Ber. 1876, 9, 497); from 5-bromo-*m*-4-xylylidine (E. Fischer and Windaus, Ber. 1900, 33, 1973). Liquid at –20°, b.p. 204°, D^{20} 1.362 (W.). When boiled for three-quarters of an hour with aluminium chloride and acetyl chloride in carbon disulphide solution, it is converted into 4-acetyl-5-bromo-*m*-xylene, b.p. 272°–276°, which, on oxidation with warm alkaline permanganate, yields 5-bromo-*m*-xylyl-4-glyoxylic acid (Noyes, Amer. Chem. J. 1898, 20, 789).

2:4-Dibromo-m-xylene; together with the 4:6-dibromo-isomeride by treating *m*-xylene with bromine (Jacobsen, Ber. 1888, 21, 2821); by heating 4:6-dibromo-*m*-xylene with sulphuric acid for a quarter of an hour at 240° (J.). Only liquid, solidifying on cooling to a hard crystalline mass, m.p. –8°, b.p. 269°/760 mm. It forms a 5:6-dinitro-derivative, almost colourless microscopic crystals, m.p. 191°, and on treatment with chlorosulphonic acid, 2:4-dibromo-*m*-xylene 6-sulphonic acid is obtained.

2:5-Dibromo-m-xylene; from 5-bromo-*m*-2-xylylidine (Blanksma, Rec. trav. chim. 1906, 25, 165). Colourless crystals, m.p. 28°.

4:5-Dibromo-m-xylene; from brominated *m*-xylylidine by the diazo-reaction (Wroblewsky, Ann. 1878, 192, 216); from 5:6-dibromo-*m*-4-xylylidine and 5-bromo-*m*-4-xylylidine (Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153). Crystals, m.p. 11°, b.p. 256° (J. & G.); b.p. 252° (W.).

4:6-Dibromo-m-xylene; see above; from 6-bromo-*m*-4-xylylidine (Jaeger and Blanksma, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153; Rec. trav. chim. 1906, 25, 352); by brominating *m*-xylene (Fittig, Ann. 1867, 147, 25; 1870, 156, 236); by treating *m*-xylene with an excess of bromine in presence of iodine (Auwers and Traun, Ber. 1899, 32, 3312); by warming 6-bromo-*m*-xylene 4-sulphonic acid with bromine (Kelbe and Stein, Ber. 1886, 19, 2139). Crystals, m.p. 72°, b.p. 255°–256°, or m.p. 69° (J. and B.); b.p. 132°/12 mm. (Auwers and Traun). On heating with sulphuric acid at 240° it is converted into the 2:6-dibromo-isomeride. By the action of magnesium on an ethereal solution of 4:6-dibromo-*m*-xylene an organo-magnesium compound is obtained, which reacts readily with carbon dioxide, forming 5-bromo-2:4-dimethylbenzoic acid, and with chloral forming an alcohol, b.p. 197°–199°/15 mm. (Iocitsch, J. Russ. Phys. Chem. Soc. 1904, 36, 8).

2:4:5-Tribromo-m-xylene; from 4:5-dibromo-*m*-2-xylylidine by the Sandmeyer reaction (J. and B.). Colourless crystals, m.p. 87°.

2:4:6-Tribromo-m-xylene; from 2:4:6-dibromo-*m*-5-xylylidine by the elimination of the amino-group; from 4:6-dibromo-*m*-2-xylylidine and 2:6-dibromo-*m*-4-xylylidine, by

the Saadmeier reaction (J. and B.). Colourless prisms, m.p. 85°.

4:5:6-Tribromo-*m*-xylene; from 4:5:6-tribromo-*m*-2-xylydine and 5:6-dibromo-*m*-4-xylydine (J. and B.). Colourless crystals, m.p. 105°.

Tetrabromo-*m*-xylene; by keeping *m*-xylene in contact with an excess of bromine for a long time (Fittig and Bieher, Ann. 1870, 156, 235); by the action of bromine on *s*-tertiary butyl-*m*-xylene (Bodroux, Bull. Soc. chim. 1898, (3) 19, 889). Fine needles, m.p. 241° (F. and B.).

The bromination of *m*-xylene in presence of nitric acid yields a mixture of mono-, di-, and tetrabromo-*m*-xylenes (Datta and Chatterjee, J. Amer. Chem. Soc. 1916, 38, 2545).

4-Chloro-2-bromo-*m*-xylene; from bromo-*m*-xylydine by conversion into the hydrazine and boiling this with copper sulphate in hydrochloric acid solution (Noyes, Amer. Chem. J. 1898, 20, 789; Genz, Ber. 1870, 3, 225). White leaflets, m.p. 68°, b.p. 244°.

4:6-Dichloro-2:5-dibromo-*m*-xylene; by brominating an acetic acid solution of 4:6-dichloro-*m*-xylene in presence of iron (Claus and Runschke, J. pr. Chem. 1890, (2) 42, 125). Long silky needles which sublime, m.p. 230°.

2:4-Dichloro-5:6-dibromo-*m*-xylene; by the action of bromine on cold 2:4-dichloro-*m*-xylene (Koch, Ber. 1890, 23, 2318; Wischin, Ber. 1890, 23, 3113). Silky needles, m.p. 215°.

For the iodo-derivatives, *etc.*, of *m*-xylene, see Hammerich (Ber. 1890, 23, 1634); Töhl and Bauch (*ibid.* 1893, 26, 1105); Klages and Luecke (J. pr. Chem. 1900, (2) 61, 307, 324); Willgerodt and Howells (Ber. 1900, 33, 841); Noyes (Amer. Chem. J. 1898, 20, 789); Ortoleva (Gazz. chim. ital. 1900, 30, ii, 9); Edinger and Goldberg (Ber. 1900, 33, 2875); Willgerodt and Schmierer (Ber. 1905, 38, 1472); Datta and Choudhury (J. Amer. Chem. Soc. 1916, 38, 1079); Blankama (Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70); Töhl and Bauch (Ber. 1893, 26, 1115).

ω -Nitro-*m*-xylene, *m*-toluene-nitromethane; by decomposing a solution of nitro-*m*-xylene-phthalide with hydrochloric acid (Heilmann, Ber. 1890, 23, 3165); by heating *m*-xylene with nitric acid (D 1-075), either in open or closed vessels (Konowaloff, J. Russ. Phys. Chem. Soc. 1899, 31, 254). Yellowish liquid, b.p. 140°/35 mm. (decomp.); D_0^{20} 1.137, D_0^{20} 1.1197 (K.). When kept in presence of calcium chloride, it yields *m*-toluic acid. The potassium salt of ω -nitro-*m*-xylene forms yellow leaflets, and the sodium, calcium, barium, and strontium salts are white stable powders (K.).

(c) or 2-Nitro-*m*-xylene; together with 4-nitro-*m*-xylene by nitrating *m*-xylene with sulphuric and nitric acids (Nölting and Forel, Bull. Soc. chim. 1884, (2) 42, 332, 338); from 2-nitro-*m*-4-xylydine by the diazo-reaction (Grevingk, Ber. 1884, 17, 2340); from 2:4:6-trinitro-*m*-xylene by reduction with ammonium sulphide and treatment of a boiling alcoholic solution of the diamine formed with nitrous fumes (Miolati and Lotti, Gazz. chim. ital. 1897, 27, i, 297; cf. Pechmann and Nold, Ber. 1898, 31, 560). Liquid, b.p. 225°/744 mm; D_0^{20} 1.112 (G.); b.p. 225° (N. and F.); m.p. 13° (Auwers and Pechmann, Ber. 1906, 41, 2337). When oxidised

with potassium permanganate in presence of magnesium sulphate, it yields 2-nitroisophthalic acid, and when boiled with nitric acid (D 1.4) *v*-dinitro-*m*-xylene, a substance,



and 2-nitro-*m*-toluic acid are formed (Nölting and Gachot, Ber. 1906, 39, 73). When reduced in alcoholic solution with zinc dust and ammonium chloride it yields *m*-xylene-2-hydroxylamine, white lustrous needles, m.p. 97°-98.5° (Bamberger and Rising, Ann. 1901, 316, 292; Pechmann and Nold, Ber. 1898, 31, 557), which is converted on oxidation into 2-nitroso-*m*-xylene, m.p. 144°-145° (P. and N.).

(i) or 4-Nitro-*m*-xylene; from dinitro-*m*-xylene, m.p. 93°, by partial reduction and elimination of the amino-group (Tawildarow, Zeitsch. fur Chem. 1870, 6, 418); by nitrating *m*-xylene (Harmsen, Ber. 1880, 13, 1658; N. and F.) or its dihydride (Wallach, Ann. 1898, 258, 330); from nitroxylidine, m.p. 123° (G.). Crystals, m.p. 2°, b.p. 237°-239°; D_0^{20} 1.126 (T.); b.p. 238° or 243°-244° (corr.), remaining liquid at -20° (Neubeck, Zeitsch. physikal. Chem. 1887, 1, 661; Harmsen). On reduction in alcoholic solution with zinc dust and ammonium chloride at about 60°-65° it yields *m*-4-xylydine, 4-azoxy-*m*-xylene, and *m*-xylene-4-hydroxylamine, glistening white plates, m.p. 64.5° (Bamberger and Brady, Ber. 1900, 33, 3642; cf. Bamberger, Ann. 1921, 424, 297; or m.p. 66° (Pechmann and Nold, Ber. 1898, 31, 560). For a further study of the reactions of *m*-xylyl-4-hydroxylamine, see Bamberger and collaborators (Ber. 1907, 40, 1893, 1906, 1918, 1932; 1900, 33, 3643).

(s) or 5-Nitro-*m*-xylene; from 5-nitro-*m*-4-xylydine by the elimination of the amino-group (Wroblewski, Ann. 1881, 207, 94; Bull. Soc. chim. 1880, (2) 34, 332). Large, flat needles, m.p. 74°-75°, b.p. 273°/739 mm. (Nölting and Forel, Ber. 1885, 18, 2678); m.p. 71°, b.p. 255° (Töhl, *ibid.* 360); m.p. 74° (Blankama, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). When oxidised with potassium permanganate and acetic acid it yields 5-nitro-*m*-toluic acid. 5-Nitro-*m*-xylene is also formed together with 5-nitro-*m*-4-xylylnitroamine, by oxidising potassium-5-nitro-*m*-xyleneisodiazooxide with potassium ferricyanide (Bamberger and von Goldberger, Ber. 1920, 53, 2321).

ω -4-Dinitro-*m*-xylene; together with ω -6-dinitro-*m*-xylene by nitrating *o*-nitro-*m*-xylene at high temperatures with 70 p.c. nitric acid. It melts at 64° (Soc. Chim. Usines du Rhône, Eng. Pats. 6076 of 1911, 17985 of 1911; U.S. Pats. 1015496, 1015491; Fr. Pat. 426635; D. R. P. 239953 of 1910).

ω -6-Dinitro-*m*-xylene melts at 86.5°.

2:4-Dinitro-*m*-xylene; together with 4:6-dinitro-*m*-xylene, by nitrating *m*-xylene with a mixture of sulphuric acid (D 1.84), and nitric acid (D 1.498) at 5°. The yield of the 2:4-dinitro-compound diminishes the higher the temperature used in nitration (Grevingk, Ber. 1884, 17, 2423; cf. Errera and Maltose, Gazz. chim. ital. 1903, 33, ii, 277; cf. Nölting and Gachot, Ber. 1906, 39, 73; Morgan, Chem. Soc. Trans. 1902, 81, 86); by nitrating 2-nitro-*m*-xylene (Nölting, Braun and Thann, Ber. 1893,

34, 2243). The products are separated by crystallisation from alcohol or acetic acid in which 2:4-dinitro-*m*-xylene is more soluble than the 4:6-dinitro-isomeride. Glistening white plates, m.p. 83°-84° (N. B. and T.).

2:5-Dinitro-*m*-xylene; from 2:5-dinitro-*m*-4-xylydine by elimination of the amino-group (Blanksma, Rec. trav. chim. 1909, 28, 92; cf. Klages, Ber. 1896, 29, 310). Colourless needles, m.p. 101°, which become yellow on exposure to light (B.).

4:5-Dinitro-*m*-xylene; by nitrating 5-nitro-*m*-xylene with nitric acid (D 1.52) (Blanksma, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70); by the nitration of 5-nitroaceto-*m*-xylydide, followed by hydrolysis and removal of the amino-group (Blanksma, Rec. trav. chim. 1909, 28, 92). Klages (Ber. 1896, 29, 310) regarded this compound as the 2:5-dinitro-isomeride. It forms flat needles, m.p. 132° (B.; K.).

4:6-Dinitro-*m*-xylene; by nitrating *m*-xylene or its dihydride (Luhmann, Ann. 1867, 144, 274; Fittig and Velguth, Ann. 1868, 148, 5; Wallach, Ann. 1890, 258, 332; Errera and Maltese, Gazz. chim. ital. 1903, 33, ii, 277; Morgan, Chem. Soc. Trans. 1902, 81, 86); from 4:6-dinitro-*m*-5-xylydine (Blanksma, Rec. trav. chim. 1909, 28, 92; *ibid.* 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). Crystals, m.p. 93°. It is very resistant to oxidation and on treatment with nitric acid (D 1.15) at 155°-160° for 3 hours only $\frac{1}{2}$ is transformed into 4:6-dinitro-*m*-toluic acid, m.p. 171°-171.5° (Errera and Maltese, Gazz. chim. ital. 1903, 33, ii, 277). It condenses with 2 mols. of benzaldehyde at 190° in presence of a little piperidine to form 4:6-dinitro-1:3-distyrylbenzene, m.p. 186°, and a little 4:6-dinitro-3-methylstilbene, m.p. 145° (Borsche, Ann. 1912, 386, 351). On partial reduction it yields 6-nitro-*m*-4-xylydine (Morgan, Micklethwait and Couzens, Chem. Soc. Trans. 1906, 89, 1289; Blanksma, Rec. trav. chim. 1909, 28, 92).

5:6-Dinitro-*m*-xylene; from 5:6-dinitro-*m*-4-xylydine (Blanksma, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70).

2:5:6-Trinitro-*m*-xylene; by nitrating 2:5-dinitro-*m*-xylene (B.); together with 4:5:6-trinitro-*m*-xylene by treating 5-nitro-*m*-xylene with nitric acid (D 1.52) and sulphuric acid (B.). Triclinic crystals, m.p. 90°.

2:4:6-Trinitro-*m*-xylene; by nitrating *m*-xylene, its dihydride or tetrahydride (Luhmann; Grevingk; Tilden, Chem. Soc. Trans. 1884, 45, 416; Wallach, Ann. 1890, 258, 333; Knoevenagel, Ann. 1896, 289, 159; Bussonius and Eisenstuck, Ann. 1860, 114, 156; Molatti and Lotti, Gazz. chim. ital. 1897, 27, i, 293); by nitrating 4-iodo-6-nitro-*m*-xylene (B.). Large thick prismatic bipyramidal rhombic crystals, m.p. 182° (B.). It condenses with benzaldehyde in amyl alcoholic solution in the presence of a little piperidine to form 2:4:6-trinitro-1:3-distyrylbenzene (Borsche). When reduced with ammonium sulphide it yields a mixture of a monoamine and 6-nitro-4:6-diamino-*m*-xylene (M. and L.), but when reduced with stannous chloride it yields 2:4:6-triamino-*m*-xylene, white needles, decomposing between 140°-150° (Grevingk, Ber. 1896, 17, 2489).

4:5:6-Trinitro-*m*-xylene; by heating 4-iodo-5-nitro-*m*-xylene with nitric acid and sulphuric acid (B.); together with a little 2:5:6-trinitro-*m*-xylene by treating 5-nitro-*m*-xylene with nitric acid (D 1.52) and sulphuric acid (B.); by nitrating 4:5-dinitro-*m*-xylene with mixed acids (Blanksma, Rec. trav. chim. 1909, 28, 92). Long colourless monoclinic needles or rods, m.p. 125° (B.).

For nitroso-derivatives, etc., see Pechmann and Nold (Ber. 1898, 31, 560); Zincke and Schwarz (Ann. 1899, 307, 47); Zincke (J. pr. Chem. 1896, (2) 53, 340); Bamberger and Rising (Ann. 1901, 316, 292).

5-Chloro-2- (or 4-) nitro-*m*-xylene; together with other products by heating chlorodihydro-*m*-xylene with 30 p.c. nitric acid for 24 hours (Klages and Knoevenagel, Ber. 1895, 28, 2044). It is volatile with steam and melts at 48°-49°.

4-Chloro-6-nitro-*m*-xylene; from the corresponding nitroxyldine (Ahrens, Ann. 1892, 271, 17; Bamberger and Reber, Ber. 1913, 46, 787). Needles, m.p. 42°.

4-Chloro-5-nitro-*m*-xylene; from 5-nitro-*m*-4-xylydine (B.; Klages, Ber. 1896, 20, 310). Long colourless needles, m.p. 52°, b.p. 278° or 161°/20 mm.; volatile with steam.

4-Chloro-2:5-dinitro-*m*-xylene; from 2:5-dinitro-*m*-4-xylydine (Klages). Yellow crystals, m.p. 61°, b.p. 290°-291°.

4:6-Dichloro-2:5-dinitro-*m*-xylene; by nitrating 4:6-dichloro-*m*-xylene (Koch, Ber. 1890, 23, 2318; Claus and Runsche, J. pr. Chem. 1890, (2) 42, 110). Pale yellow cubes, m.p. 223° (C. and R.), or short hard prisms, m.p. 215° (K.).

4:6-Dichloro-2- (or 5-) nitro-*m*-xylene; by nitrating 4:6-dichloro-*m*-xylene in cold acetic acid solution (C. and R.). Long prisms, m.p. 118°-119°. An isomeride, m.p. 106°, is obtained under somewhat different conditions.

2:4-Dichloro-5:6-dinitro-*m*-xylene; by treating 2:4-dichloro-*m*-xylene with a warm mixture of nitric and sulphuric acids (K.). Pale yellow needles, m.p. 155°.

4-Chloro-2:5:6-trinitro-*m*-xylene; by heating 4-chloro-5-nitro-*m*-xylene with a mixture of sulphuric acid and nitric acid for 1 hour on the water-bath (Blanksma, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). It melts at 165°.

5-Chloro-2:4:6-trinitro-*m*-xylene; by dissolving 5-chlorodihydro-*m*-xylene in ice-cold fuming nitric acid, keeping the mixture for some time at the ordinary temperature and then boiling with equal parts of fuming nitric acid and 15 p.c. fuming sulphuric acid for $\frac{1}{2}$ hour (Klages and Knoevenagel); by boiling 5-chloro-*m*-xylene with a mixture of nitric and sulphuric acids (Klages, Ber. 1896, 29, 310); by heating ethyl chlorotrinitrophenyleneacetic malonate with concentrated hydrochloric acid at 160°-170° in a sealed tube (Jackson and Smith, Amer. Chem. J. 1904, 32, 168). White needles, m.p. 218° (K.), or 215°-220° (J. and S.). When heated with ammonia it is converted into 2:4:6-trinitro-*m*-5-xylydine, m.p. 206°, and with aniline it forms 2:4:6-trinitro-5-phenylamino-*m*-xylene, m.p. 175°.

4-Bromo-2-nitro-*m*-xylene; by brominating 2-nitro-*m*-xylene in presence of iron powder (Anvers and Markovits, Ber. 1906, 41, 2332);

from 2-nitro-*m*-4-xylydine (Nölting, Braun and Thesmar, Ber. 1901, 34, 2242). Yellowish prisms or needles, m.p. 70°-71°.

4-Bromonitro-*m*-xylene; by dissolving 4-bromo-*m*-xylene in cold fuming nitric acid (Fittig, Ahrens and Mattheides, Ann. 1867, 147, 31). Liquid, b.p. 260°-265° with partial decomposition.

2-Bromo-4-nitro-*m*-xylene; from 4-nitro-*m*-2-xylydine (Nölting, Braun and Thesmar, Ber. 1901, 34, 2242). Bright yellow needles, m.p. 57°-58°.

4-Bromo-6-nitro-*m*-xylene; from 6-nitro-*m*-4-xylydine (Ahrens, Ann. 1892, 271, 17; Nölting, Braun and Thesmar, Ber. 1901, 34, 2242; Bamberger and Reber, Ber. 1913, 46, 787). Needles, m.p. 57°.

4-Bromo-5-nitro-*m*-xylene; from 5-nitro-*m*-4-xylydine (Blanksma). Colourless crystals, m.p. 56°. On nitration with nitric and sulphuric acids it yields 4-bromo-2 : 5 : 6-trinitro-*m*-xylene.

5-Bromo-6-nitro-*m*-xylene; from 5-bromo-6-nitro-*m*-4-xylydine by elimination of the amino-group (N., B. and T.). Faintly yellow needles, m.p. 39°-40°.

4-Bromo-2 : 6-dinitro-*m*-xylene; by the action of fuming nitric acid on 4-bromo-*m*-xylene (Lellmann and Just, Ber. 1891, 24, 2099). Small yellow needles, m.p. 89°.

4 : 6 : Dibromo-2-nitro-*m*-xylene; by nitrating 4 : 6-dibromo-*m*-xylene (Auwers and Traun, Ber. 1899, 32, 3309; F., A. and M.). Long needles, m.p. 108° (F., A. and M.), or 106° (A. and T.).

4 : 5 : Dibromo-2 : 6-dinitro-*m*-xylene; by nitrating 4 : 5-dibromo-*m*-xylene with nitric acid (D 152) and sulphuric acid (Blanksma, Rec. trav. chim. 1906, 25, 165; Jaeger and Blanksma, *ibid.* 352; Blanksma, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70, 153; cf. Jacobsen, Ber. 1888, 21, 2821). It melts at 193°.

4 : 6 : Dibromo-2 : 5-dinitro-*m*-xylene; by nitrating 4 : 6-dibromo-*m*-xylene with nitric acid in presence of sulphuric acid (J. and B.; cf. Jacobsen). It melts at 252°.

4-Bromo-2 : 5 : 6-trinitro-*m*-xylene; by nitrating 4-bromo-5-nitro-*m*-xylene in presence of sulphuric acid with nitric acid (D 152) (Blanksma). It melts at 183°.

5-Bromo-2 : 4 : 6-trinitro-*m*-xylene; by nitrating 5-bromo-*m*-xylene (Blanksma, Rec. trav. chim. 1906, 25, 373). Colourless crystals, m.p. 224°. When heated with *m*-xylydine in alcoholic solution it is converted into 2 : 4 : 6-trinitro-di-1 : 3 : 5-xylylamine, which, on nitration, yields *s*-hexanitro-di-1 : 3 : 5-xylylamine, m.p. 222° (B.).

m-Xylene 4-sulphinic acid; from *m*-xylene 4-sulphonyl chloride (Jacobsen, Ber. 1877, 10, 1011); by the action of sulphur dioxide on the diazoesulphate of *m*-4-xylydine in excess of sulphuric acid, followed by the gradual addition of copper powder, until the evolution of nitrogen ceases (Gattermann, Ber. 1899, 32, 1136); by the action of sulphur dioxide on *m*-xylene in presence of hydrogen chloride, and aluminium chloride (Knoevenagel and Kenner, Ber. 1908, 41, 3315). Long colourless needles, m.p. 77°-78° (G.). On reduction it yields *m*-xylylmercaptan, b.p. 207°-208° (G.), and with alkyl haloids, sodium *m*-xylene 4-sulphinate forms alkyl xylyl sulphones (Tröger, Budde and Hill,

m-Xylene 5-sulphinic acid; from *s*-*m*-xylydine by Gattermann's method (Moschner, Ber. 1901, 34, 1257). It melts at 75°-76°.

(β)-*m*-xylene 2-sulphonic acid; by reducing dibromo-*m*-xylene 2-sulphonic acid with zinc dust and sodium hydroxide (Moody, Chem. Soc. Proc. 1888, 4, 77); by reducing 5-chloro-*m*-xylene 2-sulphonic acid with sodium amalgam (Klages, Ber. 1896, 29, 310); together with a larger quantity of the 4-sulphonic acid, by dissolving *m*-xylene in fuming sulphuric acid. It remains in the acid liquor after precipitating the 4-isomeride with water (Jacobsen, Ann. 1876, 184, 188; Ber. 1877, 10, 1015; 1878, 11, 17; cf. Beckurts and Otto, Ber. 1878, 11, 2061). Moody states that the sulphonation of pure *m*-xylene yields only one sulphonic acid, viz. *m*-xylene 4-sulphonic acid. KA', needles (J.); BaA', microscopic needles (J.); the potassium salt when heated with sodium formate yields an acid, C₈H₁₀O₂, m.p. 99° (J.).

m-Xylene 2-sulphonic acid is readily isomerised into *m*-xylene 4-sulphonic acid by heating at 100° (M.).

Chloride; oil (J.), or prisms, m.p. 30° (M.).

Amide; slender brittle needles, m.p. 113° (M.; cf. Jacobsen and Weinberg, Ber. 1878, 11, 1534), or m.p. 95°-96° (J.; K.). Moody states that Jacobsen's sulphonamide, m.p. 95°-96°, is not a pure derivative of *m*-xylene, but is a mixture containing a considerable quantity of *p*-xylene sulphonamide.

(α)-*m*-xylene 4-sulphonic acid; see above; by reducing sodium diiodo-*m*-xylene sulphonate with zinc dust and ammonia (Töhl and Bauch, Ber. 1893, 26, 1105). Long flat prisms + 2H₂O. Melts at 62°. The calcium salt is less soluble in hot than in cold water (Patterson, McMillan and Somerville, Chem. Soc. Trans. 1924, 125, 2489). NaA', small anhydrous scales (J.); BaA', small rhombic anhydrous plates (J.), or anorthic (?) tables + 1H₂O; ZnA', + 9H₂O; CuA', + 6H₂O.

Chloride; large prismatic crystals, m.p. 34° (J.) or 32° (Schreinmakers, Rec. trav. chim. 1897, 16, 411).

Amide; m.p. 137° (J.; cf. Töhl and Eberhard, Ber. 1893, 26, 2940; Beckurts and Otto, *l.c.*); methylamide, m.p. 43°; dimethylamide, m.p. 35° (Schreinmakers). Chloroacetamide reacts with sodium *m*-xylene 4-sulphonate forming *m*-xylene 4-sulphonacetamide, m.p. 149°, and with chloroacetonitrile forming *m*-xylene 4-sulphonacetoneitrile, m.p. 79°-80°. The latter on treatment with alcoholic ammonia and hydrogen sulphide is converted into *m*-xylene-4-sulphonthioacetamide, m.p. 118° (Tröger, Hill and Volkner, J. pr. Chem. 1904, (2) 70, 315; 1905, (2) 71, 201, 236). *m*-Xylene 4-sulphonic acid condenses with *p*-nitroaniline in pyridine solution forming *m*-xylene 4-sulphonyl-*p*-nitroaniline, which, when freed from benzene of crystallisation, melts at 117°-119°. On reduction, the latter yields the corresponding diamine, m.p. 156°-157°, the diazonium chloride of which yields *m*-xylene 4-sulphonyl-*p*-phenylenediazoamide on treatment with sodium acetate (Morgan and Micklethwait, Chem. Soc. Trans. 1906, 17, 1302). *m*-Xylene 4-sulphonic acid, when treated at about 40° with a solution of bromine

in hydrochloric acid, yields monobromo-*m*-xylene, 4:6-dibromo-*m*-xylene, and an acid m.p. 130° (Kelbe and Stein, Ber. 1886, 19, 2137). When fused with lead peroxide and potassium hydroxide it is oxidised with difficulty, forming isophthalic acid, and traces of benzoic and *m*-toluic acids (Graebe and Krafft, Ber. 1906, 39 2507).

m-Xylene 5-sulphonic acid; by diazotising potassium *m*-4-xylylene 5-sulphonate and boiling with alcohol, or by means of the hydrazine (Armstrong and Wilson, Chem. Soc. Proc. 1900 16, 229). The acid forms thin flat needles $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, colourless leaflet (A. and W.).

Chloride, needles or massive crystals, m.p. 94° (A. and W.), or 89°–90° (Moschner, Ber. 1901, 34, 1257); *bromide*, m.p. 92°–93° (A. and W.).

Sulphonamide, colourless flakes or very fine needles, m.p. 134° (A. and W.), or 135° (M.; Jungmann, Ber. 1902, 35, 3747). *Anilide*, large monosymmetric crystals, m.p. 119; *p*-toluidide, monosymmetric crystals, m.p. 121°–122° (A. and W.).

m-Xylene 4:6-disulphonic acid, formerly believed to be the 2:4-disulphonic acid but shown to be the 4:6-disulphonic acid by Pollak and Lustig (Ann. 1923, 433, 191; Pollak and Rudich, Monatsh. 1922, 43, 206); by heating 1 part of *m*-xylene with 4 parts of fuming sulphuric acid at 150° (Wischn, Ber. 1894, 23, 3113; Pollak and Schädler, Monatsh. 1911, 39, 129); by heating *m*-xylene 4-sulphonic acid with chlorosulphonic acid at 150° (Pfannenstill, J. pr. Chem. 1892, (2) 46, 152); from crude xylylene by sulphonation, diazotisation, conversion into thioxylenol sulphonic acid, and oxidation of the latter (Pfannenstill, Ber. 1894, 27, 1888). Deliquescent needles, $(\text{NH}_4)_2\text{A}'$, tab.; NaHA'' (W.), $+3\text{H}_2\text{O}$ (P); $\text{K}_2\text{A}'' + 2\text{H}_2\text{O}$; $\text{BaA}'' + 3\text{H}_2\text{O}$, needles; $\text{PbA}'' + 3\text{H}_2\text{O}$; Cu'' , gummy mass.

Diethyl-ester; leaflets (P.).

Chloride; conveniently by heating *m*-xylene or *m*-xylene 4-sulphonic acid (or its sodium salt) with seven times its weight of chlorosulphonic acid at 150°–160° (Pollak and Lustig). Needles, m.p. 129° (W.; P.), 130° (P. and L.) or 131° (Pfannenstill, Ber. 1894, 27, ref. 888).

Amide; glistening needles, m.p. 249° (W.; L.); *ethylamide*, needles, m.p. 135° (W.).

The 4:6-disulphonyl chloride, on reduction with tin and hydrochloric acid, yields 4:6-dithiol-*m*-xylene, m.p. 123°–125°, which reacts with chloroacetic acid and ethyl chloroformate, forming *m*-xylene-4:6-dithiolacetic acid, m.p. 185°–189°, and 4:6-diethylthiocarbonat-*m*-xylene, m.p. 61°–63°.

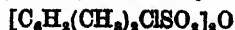
m-Xylene 2:5-disulphonic acid, or possibly *m*-xylene 2:4-disulphonic acid (Pollak and Lustig), together with *m*-xylene 4:6-disulphonic acid by sulphonating *m*-xylene (Pollak and Schädler); in small quantity, together with the 4:6-disulphonic acid, by heating barium *m*-xylene 2-sulphonate with chlorosulphonic acid at 150° (P.). Needles. The potassium, barium and lead salts are crystalline and readily soluble in water.

Chloride; brown viscous oil.

Amide; m.p. 210° (P.).

The 2:5-disulphonyl chloride gives rise to

2:5-dithiol-*m*-xylene, b.p. 142°–144°/9 mm., and from this *m*-xylene-2:5-dithiolacetic acid, m.p. 158°–161°, is obtained (Pollak and Schädler), 5-Chloro-*m*-xylene 2-sulphonic acid; together with a small quantity of its anhydride,



by sulphonating 5-chloro-*m*-xylene with 10 times its weight of fuming sulphuric acid (15 p.c. SO_3) at 30°–40° (Klages, Ber. 1896, 29, 310; Klages and Knoevenagel, Ber. 1894, 27, 3019). Colourless crystals, m.p. 52°.

Chloride; large rhombic crystals, m.p. 56°–58° (K.).

Amide; colourless needles, m.p. 192° (K.).

4-Chloro-*m*-xylene 6-sulphonic acid; by sulphonating 4-chloro-*m*-xylene (Gundelach, Bull. Soc. chim. 1877, (2) 28, 343. On reduction with sodium amalgam it yields *m*-xylene 4-sulphonic acid (Jacobsen, Ber. 1885, 18, 1762). $\text{NaA}' + \text{H}_2\text{O}$, long needles; $\text{KA}' + \text{H}_2\text{O}$, needles.

Amide; vitreous prisms, m.p. 195° (J.).

2:4-Dichloro-*m*-xylene 6-sulphonic acid; by treating 2:4-dichloro-*m*-xylene with chlorosulphonic acid (Koch, Ber. 1890, 23, 2318).

Amide; small white plates, melting with decomposition above 300°.

4:6-Dichloro-*m*-xylene 2-sulphonic acid; in a similar manner to the above isomeride from 4:6-dichloro-*m*-xylene (K.).

Amide; small plates, melting with decomposition above 250°.

4-Chloro-*m*-xylene 2:6-disulphonic acid; by sulphonating 4-chloro-*m*-xylene with fuming sulphuric acid (Wischn, Ber. 1890, 23, 3117).

Chloride; white needles, m.p. 155°.

Amide; silky needles, m.p. 270°. The free acid on fusion with potassium hydroxide yields the corresponding dihydroxy-derivative, white needles, which sublime, m.p. 106°, and produce an intense violet coloration with ferric chloride.

6-Bromo-*m*-xylene 2-sulphonic acid; by reducing dibromo-*m*-xylene sulphonamide with sodium amalgam (Jacobsen and Weinberg, Ber. 1878, 11, 1535).

Amide; long needles, m.p. 161°.

6-Bromo-*m*-xylene 4-sulphonic acid; by brominating barium *m*-xylene 4-sulphonate, or by sulphonating 6-bromo-*m*-xylene with fuming sulphuric acid (Weinberg, Ber. 1878, 11, 1062) from *m*-4-xylylene 6-sulphonic acid by the diazo-reaction (Sartig, Ann. 1885, 230, 335; Nölting and Kohn, Ber. 1886, 19, 139; Limpricht, Ber. 1885, 18, 2188; Moody, Chem. Soc. Proc. 1891, 7, 189). Leaflets or needles, which do not melt at 270° (M.), readily soluble in water.

$\text{NaA}' + \text{H}_2\text{O}$; $\text{BaA}' + \text{H}_2\text{O}$, scales;

$\text{ZnA}' + 9\text{H}_2\text{O}$; $\text{CuA}' + 7\text{H}_2\text{O}$.

Chloride; oblique prisms, m.p. 62°–63° (M.), or 61° (W.; L.).

Amide; small rhombic prisms, m.p. 194° (W.; L.), or 189°–190° (N. and K.; M.); *anilide*, m.p. 152° (Jungmann, Ber. 1902, 35, 3747).

4-Bromo-*m*-xylene 5-sulphonic acid; from *m*-4-xylylene 5-sulphonic acid by the Sandmeyer reaction (Jungmann). Colourless needles.

$\text{NaA}' + \text{H}_2\text{O}$; BaA' , anhydrous.

Chloride; pale yellow plates, m.p. 75°.

Amide; colourless prisms, m.p. 158°, converted by reduction with sodium amalgam and alcohol into *m*-xylene 5-sulphonamide.

Anilide; colourless needles, m.p. 179°.

2:4-Dibromo-*m*-xylene 6-sulphonic acid; by treating 2,4-dibromo-*m*-xylene with chlorosulphonic acid (Jacobsen, Ber. 1888, 21, 2825) $\text{NaA}' + \text{H}_2\text{O}$, needles, converted on reduction with zinc dust and ammonia into sodium *m*-xylene 4-sulphonate; $\text{KA}' + \text{H}_2\text{O}$, leaflets BaA'_2 , small prisms.

Amide; small prisms, melting with decomposition about 300° (J.).

4:6-Dibromo-*m*-xylene 2-sulphonic acid; by adding water to a solution of 4:6-dibromo-*m*-xylene in fuming sulphuric acid (Jacobsen and Weinberg). Leaflets (anhydrous), melting with decomposition at 165° ; converted by reduction with sodium amalgam into 6-bromo-*m*-xylene 2-sulphonic acid and *m*-xylene 2-sulphonic acid $\text{NaA}' + 2\text{H}_2\text{O}$, colourless pearly plates; BaA'_2 crystals.

Chloride; colourless rhombic plates, m.p. 107° .

Amide; woolly needles, melting at 220° and decomposing at 230° (J. and W.).

4-Bromo-*m*-xylene 2:6-disulphonic acid; by sulphonating 4-bromo-*m*-xylene (Wischn, Ber. 1890, 23, 3113). On reduction with zinc dust and ammonia it yields *m*-xylene 2:4-disulphonic acid.

Chloride; long white needles, m.p. 160° , converted on fusion with potassium hydroxide into 4-bromo-2:6-dihydroxy-*m*-xylene, needles, which sublime, m.p. 126° .

Amide; needles, m.p. 265° (Wischn).

2-Nitro-*m*-xylene 4-sulphonic acid; together with 5-nitro- and 6-nitro-*m*-xylene 4-sulphonic acids by nitrating *m*-xylene 4-sulphonic acid (Claus and Schmidt, Ber. 1886, 19, 1418). Small plates $+ \text{H}_2\text{O}$, m.p. 144° (anhydrous). $\text{NaA}' + \text{H}_2\text{O}$, colourless plates; $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, small colourless leaflets; BaA'_2 , large plates; $\text{CuA}'_2 + 2\text{H}_2\text{O}$, blue tables; $\text{AgA}' + \frac{1}{2}\text{H}_2\text{O}$, small white leaflets.

Chloride; long colourless prisms, m.p. 96° (C. and S.).

Amide; colourless needles or prisms, m.p. 172° (C. and S.).

5-Nitro-*m*-xylene 4-sulphonic acid; see above; formed only in small quantity. Small nodules of colourless plates, m.p. 95° – 100° . The salts are very soluble in water, and the much greater solubility of the barium salt is utilised for the separation of this acid from its isomerides. $\text{NaA}' + \text{H}_2\text{O}$, small needles; KA' , leaflets; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$; $\text{CaA}'_2 + 6\text{H}_2\text{O}$, small white needles; $\text{CuA}'_2 + 6\text{H}_2\text{O}$, bluish-green needles; $\text{AgA}' + \text{H}_2\text{O}$, small pale yellow prisms.

Chloride; colourless plates, m.p. 97° (C. and S.).

Amide; small colourless needles, m.p. 108° (C. and S.).

6-Nitro-*m*-xylene 4-sulphonic acid; by nitrating *m*-xylene 4-sulphonic acid (C. and S.; Pollak and Lustig, Ann. 1923, 433, 191; Karlsake and Bond, J. Amer. Chem. Soc. 1909, 31, 405; Riessen, Ber. 1885, 18, 2174; Limpriht, *ibid.* 2172, 2191); by sulphonating nitro-*m*-xylene at 70° (Harmen, Ber. 1890, 13, 1558). Long colourless needles, m.p. 122° (H.), or long thick prisms, m.p. 132° (B.). KA' , yellow needles (L.); $\text{NaA}' + 2\text{H}_2\text{O}$, yellow needles (L.), or $+ \text{H}_2\text{O}$ (H.); $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, long white needles (L.); M octagonal plates (H.); $\text{CaA}'_2 + 6\text{H}_2\text{O}$, pale yellow prisms H.; $\text{CuA}'_2 + 6\text{H}_2\text{O}$,

green tables (C. and S.); AgA' , fine white needles (C. and S.).

Chloride; m.p. 98° (L.; R.).

Amide; needles, m.p. 179° (L.), or 187° (C. and S.).

When oxidised with cold alkaline permanganate, potassium 6-nitro-*m*-xylene 4-sulphonate yields 6-nitro-3-methyl-4-sulpho-benzoic acid monopotassium salt, 4-nitro-5-methyl-2-sulpho-benzoic acid dipotassium salt, and 6-nitro-4-sulpho isophthalic acid monopotassium salt (K. and B.).

2:6-Dinitro-*m*-xylene 4-sulphonic acid; by prolonged heating of *m*-xylene 4-sulphonic acid with concentrated nitric acid (Limpriht), or by the action of cold nitric acid (D 152) on *m*-xylene 4-sulphonic acid (Pollak and Lustig, Ann. 1923, 433, 191); by nitrating 2- and 6-nitro-*m*-xylene 4-sulphonic acids (Claus and Schmidt). Crystals $+ 2\text{H}_2\text{O}$ (L.). $\text{NaA}' + \text{H}_2\text{O}$, leaflets (C. and S.); KA' , slender prisms (L.); $\text{BaA}'_2 + 3\text{H}_2\text{O}$, concentric needles (L.); $\text{CaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles (C. and S.), or $+ 2\text{H}_2\text{O}$, leaflets (C. and S.); $\text{CuA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, bluish-green leaflets (C. and S.).

Chloride; large yellow prisms, m.p. 123° (L.; C. and S.; Karlsake and Morgan, J. Amer. Chem. Soc. 1908, 30, 828).

Amide; white lustrous prisms, m.p. 193° (L.; C. and S.); **anilide**, yellow needles, m.p. 154° (K. and M.); **o-toluidide**, white needles, m.p. 135° (K. and M.).

By the action of the sulphonyl chloride on benzene in the presence of aluminum chloride, 2:6-dinitro-1:3-dimethylphenyl phenyl sulphone, large lustrous plates, m.p. 178° , is obtained (K. and M.).

5:6-Dinitro-*m*-xylene 4-sulphonic acid; together with the 2:6-dinitro-derivative by treating a solution of *m*-xylene 4-sulphonic acid in acetic acid with a mixture of 3 parts of fuming nitric acid, 3 parts of fuming sulphuric acid, and 1 part of phosphorus pentoxide and heating the mixture on the water-bath until the evolution of red fumes ceases; by nitrating 5-nitro- and 6-nitro-*m*-xylene 4-sulphonic acids (Claus and Schmidt, Ber. 1886, 19, 1418). It crystallises in microscopic plates. KA' ; $\text{NaA}' + \text{H}_2\text{O}$, needles; $\text{BaA}'_2 + \frac{1}{2}\text{H}_2\text{O}$, colourless needles, or $+ 2\frac{1}{2}\text{H}_2\text{O}$, prisms; $\text{CuA}'_2 + 4\text{H}_2\text{O}$, bluish-green leaflets; $\text{PbA}'_2 + 4\frac{1}{2}\text{H}_2\text{O}$, tables.

Chloride; irregular crystals, m.p. 117° – 118° (C. and S.).

Amide; small colourless needles, m.p. 158° (C. and S.).

6-Bromo-2- (or 5-) nitro-*m*-xylene 4-sulphonic acid; from nitro-*m*-xylylidine 4-sulphonic acid by the Sandmeyer reaction (Sartig, Ann. 1885, 230, 333; Limpriht, Ber. 1885, 18, 2172). Colourless rhombic plates. $\text{KA}' + \text{H}_2\text{O}$, yellow prisms; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, yellow crystals, or fine needles.

p-Xylene; see *o*- and *m*-xylene; in coal tar; in Galician petroleum (Pawlewski, Ber. 1885, 18, 1915); by the action of methyl iodide and sodium on *p*-bromotoluene (Fittig and Glimmer, Ann. 1865, 136, 303; Bull. Soc. chim. 1865, (2) 4, 36; Jannasch, Ann. 1874, 171, 79; Bull. Soc. chim. 1871, (2) 15, 275; 1874, 22, 306); from *p*-dibromobenzene, methyl iodide and sodium (von Meyer, Ann. 1870, 166, 265; Bull. Soc. chim. 1870, 14, 405; Ber. 1870, 3, 753; Jannasch,

Ber. 1877, 10, 1354); from *p*-tolylmagnesium bromide and methyl sulphate in a yield of 75 p.c. (Werner and Zilkens, Ber. 1903, 36, 2116; Houben, *ibid.* 3083).

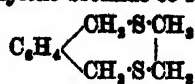
Monoclinic prisms, $a:b:c=2.32:1:2.34$, $\beta=69.5^\circ$ (Baeyer, Ann. 1888, 245, 141), m.p. 15° (Jannasch, Ann. 1874, 171, 80), or 13° (Reissert, Ber. 1890, 23, 2242); b.p. 138° ; D_4^{20} 0.8801 (Pinette, Ann. 1888, 243, 51); D_{25}^{20} 0.860 (Gladstone, Chem. Soc. Trans. 1891, 59, 290; cf. Neubeck, Zeitsch. physikal. Chem. 1887, 1, 601; von Hirsch, Ann. Phys. Chem. 1899 (ii), 69, 456); b.p. 137.5° ; D_{15}^{15} 0.8661; D_{25}^{15} 0.8593; $D_4^{14.4}$ 0.86619 (Perkin, Chem. Soc. Trans. 1896, 69, 1241; 1900, 77, 278); critical temperature 344.4° ; critical pressure, 35.0 (Altschul, Zeitsch. physikal. Chem. 1893, 11, 590); dielectric constant, density, refractive power (Landolt and Jahn, Zeitsch. physikal. Chem. 1892, 10, 300; Drude, *ibid.* 1897, 23, 309; Bruhl, J. pr. Chem. 1894, (2) 50, 140); capillarity constant (Schiff, Ann. 1884, 223, 67); magnetic behaviour (Schönrock, Zeitsch. physikal. Chem. 1893, 11, 785; Perkin); cryoscopic behaviour (Ampola and Rimatori, Gazz. chim. ital. 1897, 27, i, 38, 54) absorption spectrum in ultra violet (Mies, Zeitsch. wiss. Photochem. 1910, 8, 287); other physical constants (von Auwers, Ann. 1919, 419, 92).

For separation from its isomerides, see *o* and *m*-xylene. On oxidation with dilute nitric acid *p*-xylene yields *p* toluic acid, and with chromic acid terephthalic acid. For oxidation in presence of catalysts, &c., see *o*-xylene. When heated with concentrated hydriodic acid at 250° – 280° , *p*-xylene yields benzene, toluene, methylcyclohexane, and methylated penta methylene (Markownikow, Ber. 1897, 30, 1218). In separating *p*-xylene from coal-tar xylene by Jacobsen's method, Nölting and Palmer (Ber. 1891, 24, 1955) obtained ethylbenzene to the extent of two-thirds of the supposed *p* xylene content, and corresponding to an approximate proportion of 10 p.c. in the crude xylene, but Clarke and Taylor (J. Amer. Chem. Soc. 1923, 45, 830) did not find any evidence of the presence of ethylbenzene during the purification of commercial *p*-xylene.

p-Xylene on treatment with aluminium chloride at 100° in presence of hydrogen chloride yields mainly *m*-xylene (Heisse and Töhl, Ann. 1892, 270, 155). When *p*-xylene is heated with phenylcyanate in presence of aluminium chloride, the corresponding xylylanilide is obtained (Leuckart, J. pr. Chem. 1890, (2) 41, 301). By heating a mixture of benzhydro *p*-xylene, and phosphoric anhydride for 4 hours diphenyl-*p*-xylyl-methane, prismatic crystal m.p. 92° – 92.5° , is obtained. Like triphenyl methane, this yields dyes, similar to rosaniline by successive nitration, reduction, and oxidation (Hemilian, Ber. 1893, 16, 2360; Elbs, J. pr. Chem. 1887, (2) 35, 465). Unlike *o*- and *m*-xylene *p*-xylene does not react with diphenylcarbamic chloride in the presence of aluminium chloride (Lehmann and Bonhöffer, Ber. 1896, 19, 3231).

p-Xylene is converted into *p*-tolualdehyde, b.p. 204° – 205° , by means of Etard's reagent (Bornemann, Ber. 1894, 17, 1462). *p*-Xylene condenses with phthalic anhydride forming *p*-xylene-phthalic acid (Meyer, Ber. 1892, 15, 224). *p*-Xylylmercaptol condenses with methyl

ene iodide to form the *p*-mercaptal, m.p. 149° – 150° ; with ethylene bromide to form



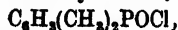
m.p. 113° – 114° ; and with *p*-xylylene bromide to form $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{S} \cdot \text{CH}_2 \end{array} \text{C}_6\text{H}_4$, m.p. 192° – 193° (Kötz and Sevin, J. pr. Chem. 1901, (2) 64, 518). When *p*-xylene is heated with hydroxylamine hydrochloride in presence of aluminium chloride, a small amount of *p*-2-xylylidine is obtained (Graebe, Ber. 1901, 34, 1778). Ethyl chloroglyoxylate in presence of aluminium chloride converts *p*-xylene into ethyl *p*-xylyl-glyoxylate, colourless liquid, b.p. 155° – $156^\circ/10$ mm. The free acid, m.p. 75° , on heating with sulphuric acid at 100° , is converted into *p*-xylyl-carboxylic acid, and when heated with aniline it forms 2:5-dimethylbenzylideneaniline (Bouveau, Bull. Soc. chim. 1897, (3) 17, 363, 940). *p*-Xylene-2-oxyacetal, prepared similarly to the corresponding *o*- and *m*-compounds, boils at 278° – 279° , and has D_{15}^{15} 0.972; the aldehyde hydrate melts at 63° – 64° ; the oxime at 114° ; the semi-carbazone at 104° ; the derived *o*-*m*-dimethylcoumarone boils at 216° , and has D_{15}^{15} 1.041, and refractive index at 16° 1.549 (Stoermer and Schroeder, Ber. 1897, 30, 1700). Well-cooled *p*-xylene, subjected to the vapours of sulphuric anhydride at temperatures below 25° , yields di-*p*-xylylsulphone (in which the SO_2 group is in the meta-position), prismatic needles, m.p. 141° – 142° (Zorn and Brunel, Compt. rend. 1894, 119, 1224). This sulphone is obtained also together with chloro-*p*-xylene and *p*-xylene-sulphonyl chloride by the action of sulphuryl chloride on *p*-xylene in presence of aluminium chloride (Töhl and Eberhard, Ber. 1893, 26, 2940). When heated with sulphur, *p*-xylene forms 4:4'-dimethylstilbene and 4:4'-dimethyldibenzyl, the former being probably the primary product, and reduced to the latter by the hydrogen sulphide evolved (Aronstein and Nierop, Proc. K. Akad. Wetensch. Amsterdam, 1902, 5, 288; Rec. trav. chim. 1902, 21, 448). When oxidised electrochemically in dilute sulphuric acid at a lead dioxide anode, *p*-xylene yields *p*-tolualdehyde, *p*-xyloquinone, and *p*-xylylene dioxide (?), silky needles, m.p. 161° (Fichter and Stocker, Ber. 1914, 47, 2603; cf. Law and F. M. Perkin, Chem. Soc. Trans. 1907, 91, 258).

2:6-Dithiol-*p*-xylene, b.p. $145.5^\circ/11.5$ mm. (diacetyl-derivative, needles, m.p. 79.5° – 82.5° ; dipicryl-derivative, yellow crystalline solid, m.p. 251° – 255° ; dimethyl-derivative, needles, m.p. 92° – 94° ; *p*-xylene-2:6-diethylacetic acid, needles, m.p. 170.5° – 174.5°) is obtained from *p*-xylene through the disulphonyl derivative as in the case of *m*-xylene (Pollak and Schädler, Monatsh. 1918, 39, 129).

p-Xylene when heated to 700° by means of an electrically heated wire yields di-*p*-xylyl and products converted on oxidation into terephthalic and *p*-toluic acids, whilst at 800° *p*-dimethylstilbene is formed (H. Meyer and A. Hofmann, Monatsh. 1916, 37, 821). When treated with aqua regia *p*-xylene yields monochloro-, 2:5-dichloro-, and tetrachloro-*p*-xylene (Datta and Fernandes, J. Amer. Chem.

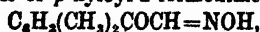
Soc. 1918, 38, 1809), and when brominated in presence of nitric acid a similar mixture of bromo-derivatives is obtained, together with *p*-toluic acid (Datta and Chatterjee, *ibid.* 2545).

p-Xylene reacts with phosphorus chloride in presence of aluminium chloride forming *p*-xylyl phosphorus chloride $C_6H_4(CH_2)_2PCl_2$, b.p. 253°–254°, m.p. –30°. The latter on treatment with chlorine yields the corresponding tetrachloride, m.p. 60°, which, on treatment with water or sulphur dioxide, is converted into *p*-xylyl phosphorus oxychloride,



b.p. 280°–281°. *p*-Xylene phosphinous acid, $C_6H_4(CH_2)_2PO_2H_2$, is formed when the corresponding chloride is treated with warm water. *p*-Xylene phosphonic acid, $C_6H_4(CH_2)_2PO(OH)_2$, colourless needles, m.p. 179°–180°, is obtained when either the tetrachloride or oxychloride is decomposed with water, and when heated it decomposes, forming metaphosphoric acid and *p*-xylene (Weller, Ber. 1888, 21, 1492; Michaelis and Panek, Ber. 1880, 13, 656). *p*-Xylene borochloride is a colourless fuming liquid, b.p. 205°; *p*-xylyl boric acid forms slender needles, m.p. 186°, and the oxide melts at 176° (Michaelis and Thévenot, Ann. 1901, 315, 19). For arsenic derivatives of *p*-xylene, see Michaelis and Pasel (J. pr. Chem. 1902, (2) 66, 130); Jacobs, Heidelberger and Rolf (J. Amer. Chem. Soc. 1918, 40, 1580); for hydrogenated derivatives of *p*-xylene, see Bayer (Ber. 1892, 25, 2122); Schiff (Ber. 1880, 13, 1407; Gazz. chim. ital. 1880, 10, 317); Renard (Ann. Chim. Phys. 1884, (6) 1, 223); Zelinsky and Naumow (Ber. 1898, 31, 3206).

p-Xylene when treated with acetyl chloride in presence of aluminium chloride yields *p*-xylyl methyl ketone, b.p. 224°–225°, $D_{20}^{25} 0.9962$ (Claus and Wollner), or b.p. 232°–233° (Errera). When heated in presence of 95 p.c. alcoholic ammonium hydrosulphide and sulphur, for 48 hours at 200°, the ketone yields *p*-xylyl-acetamide, m.p. 154°, which is converted on hydrolysis with 33 p.c. alcoholic potash into *p*-xylyl-acetic acid. The ketone when mixed with sodium, amyl nitrite and alcohol, forms the sodium salt of *p*-xylyl-2-formoxime,



together with isoxylylic acid (Claus and Wollner, Ber. 1895, 18, 1856; Errera, Gazz. chim. ital. 1891, 21, 94; Guerbet, Compt. rend. 1897, 125, 34; Söderbaum, Ber. 1894, 27, 658). *p*-Xylyl ethyl ketone, obtained similarly to the methyl-compound, is a highly refractive liquid, b.p. 237°–238° (Claus and Fickert, Ber. 1886, 19, 3182; Claus, J. pr. Chem. 1891, (2) 43, 138); for further information regarding ketones derived from *p*-xylene, see Elbs and Olberg (Ber. 1886, 19, 408); Elbs (J. pr. Chem. 1887, (2) 35, 465); Hemilian (Ber. 1883, 16, 2360); Claus and Murtfeldt (Ber. 1887, 20, 1377); Schopff (Ber. 1891, 24, 3766); Wege (*ibid.* 3540); Strzelecki (Bull. Acad. Sci. Cracow, 1902, 12); Straßmann (Ber. 1889, 22, 1229); Collet (Bull. Soc. chim. 1897, (3) 17, 506; Compt. rend. 1897, 125, 305); Klages and Allendorf (Ber. 1898, 31, 1298); Kunckell (Ber. 1897, 30, 577); Limpricht (Ann. 1895, 286, 306); Claus (J. pr. Chem. 1892, (2) 46, 474); Layraud (Bull. Soc. chim. 1906, (3) 35, 223).

Antimony trichloride may be substituted for aluminium chloride in condensing acid chlorides of moderately high boiling-point with hydrocarbons (Comstock, Amer. Chem. J. 1896, 18, 547).

o-Chloro-*p*-xylene; by chlorinating boiling *p*-xylene (Lauth and Grimaux, Zeit. für Chem. 1867, 3, 381); by chlorinating *p*-xylene in sunlight (Radziewanowski and Schramm, Akad. Wiss. Krakau, 1898, 61); from the corresponding alcohol by distillation with hydrochloric acid (Curtius and Sprenger, J. pr. Chem. 1900, (2) 62, 111); by the action of *s*-dichloromethylether on toluene in the presence of anhydrous zinc chloride, di-*p*-tolylmethane being formed also (Stephen, Short and Gladding, Chem. Soc. Trans. 1920, 117, 510). Oil, b.p. 192° (L. and G.), 200°–202° (R. and S.), 90°/20 mm. (C. and S.), 92°–94°/20 mm., or 192°/760 mm. (S., S. and G.).

o-Dichloro-*p*-xylene, *p*-xylylene chloride $C_6H_4(CH_2Cl)_2$; by chlorinating boiling *p*-xylene (L. and G.); by chlorinating *p*-xylene in sunlight (R. and S.); by distilling the glycol, $C_6H_4(CH_2OH)_2$, with hydrochloric acid (Grimaux, Zeit. für Chem. 1870, 6, 394); from *p*-xylene and phosphorus pentachloride at 190° (Colson and Gautier, Ann. Chim. Phys. 1887, (6) 11, 22; Bull. Soc. chim. 1886, (2) 45, 6; Colson, Compt. rend. 1884, 99, 40; Bull. Soc. chim. 1886, (2) 46, 2); together with benzyl chloride by warming a mixture of benzene, *s*-dichloromethylether and anhydrous zinc chloride for 10 hours (S., S. and G.); from benzyl chloride similarly, by heating for 18 hours at 30°–35° (S., S. and G.). Leaflets or rhombic tables, m.p. 100° (L. and G.), or 100.5° (S., S. and G.); b.p. when slightly impure, 120°/20 mm. (S., S. and G.), or b.p. 240°–258° with decomposition; $D_{20}^{25} 1.417$ (C.). On oxidation it yields terephthalaldehyde, m.p. 116°–117°, and terephthalic acid, m.p. 140° (S., S. and G.; Hönlitz, Monatsh. 1889, 9, 1153), and when heated with water at 170°–180° the corresponding glycol is formed.

2-*o*-(4-)Dichloro-*p*-xylene,



by keeping a mixture of *o*-chlorotoluene, *s*-dichloromethylether and zinc chloride monohydrate for 24 hours (S., S. and G.). Colourless oil, b.p. 124°/20 mm.

*Symm.-tetra-*o*-chloro-*p*-xylene*, $C_6H_4(CHCl)_2$; by heating *p*-xylene with phosphorus pentachloride at 190° (Colson and Gautier, Bull. Soc. chim. 1886, (2) 45, 9; Ann. Chim. Phys. 1887, (6) 11, 24; Colson, Bull. Soc. chim. 1886, (2) 46, 2). Crystals, m.p. 93°, $D_{20}^{25} 1.006$. On hydrolysis with water it yields terephthalaldehyde (Colson and Gautier, Compt. rend. 1886, 102, 689).

o-Pentachloro-*p*-xylene; together with the *o*-hexachloro-derivative by heating *p*-xylene with excess of phosphorus pentachloride in a sealed tube at 100° (Colson and Gautier).

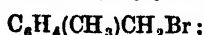
o-Hexachloro-*p*-xylene; from *p*-xylene in a similar manner to the pentachloro-compound (Colson and Gautier, Ann. Chim. Phys. 1887, (6) 11, 27; Compt. rend. 1886, 102, 689; Bull. Soc. chim. 1886, (2) 45, 507). Transparent matted crystals, m.p. 111°. When heated with water or sodium hydroxide solution it yields terephthalic acid.

2-Chloro-*p*-xylene; by chlorinating *p*-xylene in presence of iodine (Kluge, Ber. 1885, 18, 2099); together with the 2:5 dichloro- and the tetrachloro-derivative by treating *p*-xylene with *aqua regia* (Datta and Fernandes, J. Amer. Chem. Soc. 1916, 38, 1809). Oil, b.p. 186°/767 mm., solidifying to crystals, m.p. 2° (K.).

2:5-Dichloro-*p*-xylene; by treating *p*-xylene with *aqua regia* (D. and F.); by chlorinating *p*-xylene or its monochloro-derivative (K.); from 2-chloro-*p*-5-xylidine (K.). Plates or flat needles, m.p. 71°, b.p. 221°.

Tetrachloro-*p*-xylene; by chlorinating *p*-xylene in chloroform solution in presence of iron (Rupp, Ber. 1896, 29, 1628); by treating *p*-xylene with *aqua regia* (D. and F.). Colourless silky needles, m.p. 218°. When heated with nitric acid and potassium permanganate for 8 hours in a sealed tube at 180° tetrachloro-*p*-toluic acid, needles, m.p. 212°, is formed.

***ω*-Bromo-*p*-xylene**, *p*-xylyl bromide,



by treating toluene with *s*-dibromomethylether in presence of zinc chloride monohydrate (Stephen, Short and Gladding, Chem. Soc. Trans. 1920, 117, 510); by brominating heated *p*-xylene (Radziszewski and Wispek, Ber. 1882, 15, 1743; 1885, 18, 1279; Atkinson and Thorpe, Chem. Soc. Trans. 1907, 91, 1687); by brominating *p*-xylene in presence of sunlight (Schramm, Ber. 1885, 18, 1277). Colourless needles, m.p. 35.5°, b.p. 218°–220°/740 mm (R. and W.), or m.p. 38°, b.p. 109°/15 mm. (S., S. and G.). When treated with alcoholic potassium thiocyanate it yields *p*-xylyl thiocyanate, m.p. 21.5°–22.5° (Strzelecka, Bull. Acad. Sci. Cracow, 1909, 731; cf. Kosmos, 1910, 35, Radziszewski-Festband, 585), and with alcoholic potassium sulphide it yields *p*-xylyl sulphide, m.p. 76°, which, on oxidation, yields the corresponding sulfoxide, m.p. 117°, whilst both the sulphide and the sulfoxide are oxidised by potassium permanganate to *p*-xylyl-sulphone, m.p. 197° (Martynowicz, Kosmos, 1910, 35, Radziszewski-Festband, 594). *p*-Xylyl bromide, when treated with potassium cyanide, yields *p*-xylyl cyanide, m.p. 18°, b.p. 242°–243°, $D_{20}^{25} 0.9922$, which is converted by treatment with hydrogen peroxide and potassium hydroxide into the acetamide, m.p. 184° (R. and W.).

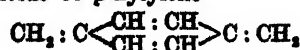
***ω*-Dibromo-*p*-xylene**, *p*-xylylene bromide,



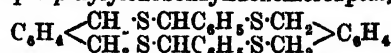
together with benzyl bromide by treating benzene with *s*-dibromomethylether in presence of anhydrous zinc chloride with cooling (Stephen, Short and Gladding); or by the action of bromine on heated *p*-xylene (Grimaux, Zeit. für Chem. 1870, 6, 394; Radziszewski and Wispek; Kipping, Chem. Soc. Trans. 1888, 53, 21; Atkinson and Thorpe; Colson, Bull. Soc. chim. 1886, (2) 46, 2; Compt. rend. 1884, 99, 40; 1887, 104, 428; Ann. Chim. Phys. 1885, (6) 6, 119); by the action of bromine on cold *p*-xylene in presence of sunlight (Schramm, Ber. 1885, 18, 1277; Allain-Le Canu, Compt. rend. 1893, 118, 534). Needles, rhomboidal plates, or large prisms, m.p. 143.5°, b.p. 340°–350° (R. and W.), $D_{20}^{25} 2.012$ (C.; A. and T.; A.-Le C.), or m.p. 144° (S., S. and G.).

When reduced with zinc dust in glacial

acetic acid solution, a mixture of *p*-xylene and a polymeride of *p*-xylylene



is obtained, but on reduction with stannous chloride in acetic acid solution, *p*-xylyl acetate, b.p. 227°, is formed (Thiele and Balhorn, Ber. 1904, 37, 1463). When boiled with alcoholic potassium hydrosulphide saturated with hydrogen sulphide, *p*-xylylene bromide yields *p*-xylylene hydrosulphide and the monoethyl-ether of *p*-xylylene glycol, b.p. 250°–252°. The former in the presence of hydrogen chloride condenses with aliphatic aldehydes or ketones forming amorphous indefinite products, but with aromatic aldehydes well-crystalline duplo-compounds are formed which are very stable, e.g. duplo-*p*-xylylenebenzylidenemercaptal,



m.p. 248°–249°, is prepared by passing hydrogen chloride into an ice-cold mixture of equal molecular proportions of benzaldehyde and *p*-xylylene hydrosulphide. When oxidised with acid permanganate, the duplo-compound yields the corresponding tetrasulphone (Autenrieth and Beuttel, Ber. 1909, 42, 4346; Kötze and Sevin, Ber. 1900, 33, 729). *p*-Xylylene dibromide, when treated in acetone solution with sodium iodide, yields *p*-xylylene iodide (Finkelstein, Ber. 1910, 43, 1528; Knoll and Co., D. R. P. 230172 of 1908). The di-iodide melts at 175° (F.) or 170° (Grimaux, Zeit. für Chem. 1870, 6, 395). *p*-Xylylene bromide differs in some respects from *o*-xylylene bromide in its action on amines. It does not form ring compounds of the type of dihydroisindole with primary amines, nor does it form ammonium bromides with secondary amines (Manoukian, Ber. 1901, 34, 2082). When treated with fuming nitric acid, *p*-xylylene bromide is converted into terephthalaldehyde, terephthalaldehydic acid, and a compound, $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{O}_4$, needles, m.p. 80° (Löw, Ber. 1885, 18, 2072).

***ω*- ω -Tribromo-*p*-xylene**; by brominating heated *p*-xylene (Atkinson and Thorpe), or cold *p*-xylene in sunlight (Allain-Le Canu, Bull. Soc. chim. 1894, (3) 11, 382; Compt. rend. 1893, 118, 534). Orthorhombic plates, m.p. 116° (A.-Le C.), or m.p. 106° (A. and T.; Löw, Ann. 1885, 231, 363). When hydrolysed with sodium hydroxide the aldehyde-alcohol, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{OH}$, colourless oily liquid, is formed (A.-Le C.).

Symm.- ω -tetrabromo-*p*-xylene, $\text{C}_6\text{H}_4(\text{CHBr})_2$; by passing dry bromine into *p*-xylene heated first at 140°, then at 170°, and finally at 200° (Hönig, Monatsh. 1889, 9, 1150). Glistening monoclinic prisms, m.p. 169°.

***ω*-Hexabromo-*p*-xylene**; in small yield by the direct bromination of *p*-xylene, but better by brominating ω -tetrabromo-*p*-xylene at 170°–180° (Thiele and Balhorn, Ber. 1904, 37, 1463). Needles, m.p. 194°. When heated with nitric acid at 130°–140° terephthalic acid is formed.

2-Bromo-*p*-xylene; by the action of bromine on cold *p*-xylene in the dark (Fittig and Jannasch, Ann. 1869, 151, 283; Jannasch, Ann. 1874, 171, 79; Ber. 1884, 17, 2709; Jacobsen, Ber. 1884, 17, 2379; 1885, 18, 356; Schramm, Ber. 1885, 18, 1276). Tables or leaflets, m.p. 10° (Jannasch), b.p. 199.5°–200.5°; or

m.p. 9-9°, b.p. 205-5°/755 mm. (Jacobsen). On oxidation with chromic acid in acetic acid solution, it yields bromo-*p*-toluic acid. The magnesium derivative condenses with chloral, forming $\beta\beta$ -trichloro- α -xylylethyl alcohol, b.p. 158°/10 mm., which on prolonged boiling with aqueous potassium carbonate is converted into xylylaldehyde (Savariau, Compt. rend. 1908, 146, 297; Carré, *ibid.* 1909, 148, 1108). For the behaviour with the lead salt of aromatic thiophenols, see Bourgeois (Ber. 1895, 28, 2312).

2:5-Dibromo-*p*-xylene; together with 2:6-dibromo-*p*-xylene by brominating *p*-xylene (Blanksma, Chem. Weekblad. 1913, 10, 136); from 5-bromo-*p*-2-xylydine by the Sandmeyer reaction (B.); by brominating *p*-xylene in the presence of iodine (Fittig, Ahrens and Mattheides, Ann. 1867, 147, 26). Leaflets, or monoclinic tables (Miers, Chem. Soc. Trans. 1890, 57, 975), m.p. 75° (Jannasch, Ber. 1877, 10, 1357), b.p. 261° (Jacobsen, Ber. 1885, 18, 358), b.p. 141°/15 mm. or 149-5°/21 mm. (Auwers and Baum, Ber. 1896, 29, 2329). When heated with concentrated sulphuric acid at 215° it yields a small quantity of a liquid isomeride, b.p. 260°-265°, probably impure 2:6-dibromo-*p*-xylene (Koch, Ber. 1890, 23, 2318). When oxidised with chromic acid in acetic acid solution the dibromo-*p*-toluic acid, m.p. 195°, is formed (Schultz, Ber. 1885, 18, 1762).

2:6-Dibromo-*p*-xylene; in small quantity and in an impure condition by brominating *p*-xylene (Jacobsen; Blanksma); from 3:5-dibromo-*p*-2-xylydine (Blanksma). Colourless pearly plates, m.p. 32° (B.).

Tetrabromo-*p*-xylene; together with mono- and dibromo-*p*-toluene and *p*-toluic acid by brominating *p*-xylene in presence of nitric acid (Datta and Chatterjee, J. Amer. Chem. Soc. 1916, 38, 2545); by brominating *p*-xylene (Jacobsen), 1:4-dimethyl-2-ethylbenzene (Bodroux, Bull. Soc. chim. 1898, (3) 19, 888), or hexahydro-*p*-xylene (Zelinsky and Naumow, Ber. 1898, 31, 3208) in presence of aluminium bromide. Long fine needles, m.p. 253°, b.p. about 355° (J.). When heated with potassium permanganate and nitric acid in a sealed tube for 8 hours at 180° it yields tetrabromoterephthalic acid (Rupp, Ber. 1896, 29, 1625).

For iodo-derivatives of *p*-xylene, see Klages and Liocke (J. pr. Chem. 1900, (2) 61, 325); Edinger and Goldberg (Ber. 1900, 33, 2875); Grimaux (Zeit. für Chem. 1870, 6, 395); Ullmann (Ann. 1904, 332, 38); Willgerodt and Plocksties (J. pr. Chem. 1912, (2) 85, 198).

Chlorobromo-*p*-xylene; by brominating chloro-*p*-xylene in presence of iron (Willgerodt and Wolfen, J. pr. Chem. 1889, (2) 39, 403). Pearly laminae, m.p. 66°.

Dichlorobromo-*p*-xylene; needles, m.p. 96° (W. and W.).

Trichlorobromo-*p*-xylene; needles which sublime, m.p. 219° (W. and W.).

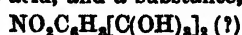
Chlorodibromo-*p*-xylene; by brominating chlorobromo-*p*-xylene in presence of iron. Needles, m.p. 93° (W. and W.).

Dichlorodibromo-*p*-xylene; in small yield by brominating dichloro-*p*-xylene. Needles which sublime, m.p. 226° (W. and W.).

Chlorotribromo-*p*-xylene; by brominating *p*-xylene in presence of iron. Sublimes in needles, m.p. 224° (W. and W.).

***o*-Nitro-*p*-xylene**; similarly to *o*-nitro-*m*-xylene (L.); m.p. 11°-12°; b.p. 150°-151°/85 mm. (slight decomp.); D_4^{20} 1.1234, n_D^{20} 1.58106 at 20° (Konowaloff, J. Russ. Phys. Chem. Soc. 1899, 31, 254).

2-Nitro-*p*-xylene; by the action of fuming nitric acid on ice-cold *p*-xylene (Jannasch, Ann. 1875, 176, 55; Schaumann, Ber. 1878, 11, 1537). Pale yellow liquid, b.p. 238-5°-239°/789 mm.; D_4^{20} 1.132 (Nölting and Forel, Ber. 1885, 18, 2668). When oxidised with potassium ferrieyanide it yields nitro-*p*-toluic acid, nitroterephthalic acid, and a substance,



(Noyes, Amer. Chem. J. 1888, 10, 472). On reduction with zinc dust and water it yields the hydroxylamine (Lumière, Lumière and Seyewitz, Bull. Soc. chim. 1894, (3) 11, 1038; Bamberger and Rising, Ann. 1901, 316, 257; cf. Bamberger, Ann. 1921, 424, 233, 297; Bamberger and Tschirner, Ber. 1900, 33, 955); and on electrolytic reduction in sulphuric acid solution 2-amino-*p*-5-xenol, pale yellow needles, m.p. 238° (decomp.), is formed (Gattermann, Ber. 1894, 27, 1927). 2-Nitro-*p*-xylene cannot be readily sulphated with sulphuric acid (Carslake and Huston, J. Amer. Chem. Soc. 1914, 36, 1244).

β -2:3-Dinitro-*p*-xylene; together with 2:6- and 2:5-dinitro-*p*-xylenes, by nitrating *p*-xylene (Rammer, Bull. Soc. chim. 1868, (2) 9, 434; Fittig, Ann. 1865, 136, 307; 1868, 147, 17; Jannasch, Ann. 1874, 171, 79; Ber. 1881, 14, 1146; 1882, 15, 2304; Nölting, Ber. 1886, 19, 144; Kostanecki, Ber. 1886, 19, 2318; Lellmann, Ann. 1885, 228, 252; Blanksma Chem. Weekblad, 1910, 7, 727). Lustrous, monoclinic prisms, m.p. 93°, $a:b:c = 0.8695:1:0.63818$, $\beta = 81^\circ 14' 52''$ (Barner, Ber. 1882, 15, 2302).

(γ)-2:5-Dinitro-*p*-xylene; in small quantity by nitrating *p*-xylene (L.). Long yellow vitreous needles, m.p. 147°-148°.

2:6-Dinitro-*p*-xylene; by nitrating *p*-xylene; from 3:5-dinitro-*p*-2-xylydine. Long slender needles, m.p. 123-5°-124° (Nölting and Geissmann, Ber. 1886, 19, 144).

***o*-Nitronitroso-*p*-xylene**; by reducing a mixture of *o*- and *m*-dinitro-*p*-xylenes (obtained by direct nitration of *p*-xylene) with hydroxylamine hydrochloride in methyl alcoholic potassium hydroxide solution, extracting unchanged *m*-dinitro-compound with ether, and adding hydrochloric acid to the cooled solution (Meisenheimer and Patzig, Ber. 1906, 39, 2526). Slightly yellow crystals, m.p. 130-5°.

2:3:6-Trinitro-*p*-xylene; by warming *p*-xylene with a mixture of nitric and sulphuric acids (Fittig and Glinzer, Ann. 1865, 136, 307; Nölting and Geissmann, Ber. 1886, 19, 144). Large monoclinic needles, m.p. 137° (F. and G.) or 139°-140° (N. and G.).

Trinitro-*p*-xylene, m.p. 127°, was obtained by Schiff (Ber. 1880, 13, 1407; Gazz. chim. Ital. 1880, 10, 317) by treating hexahydro-*p*-xylene with nitric acid. With hydrazine hydrate it yields 3:5-dinitro-*p*-2-xylylhydrazine, yellow prisms, m.p. 180° (Gina, Gazz. chim. Ital. 1916, 40, ii. 166), and, on reduction with alkali sulphides, is converted into nitro-*p*-xylydine and phonic acid (Fittig, Ahrens and Mattheides,

Ann. 1867, 147, 24; Blankensma, Rec. trav. chim. 1905, 24, 46).

ω-(4)-Chloro-2-nitro-*p*-xylene; together with 3:3'-dinitro-di-*p*-tolylmethane by adding a little more than the theoretical quantity of aluminium chloride to a mixture of *o*-nitro-toluene and *s*-chloromethyl-ether (Stephen, Short and Gladding, Chem. Soc. Trans. 1920, 117, 510). It melts at 45° and has a violent action on the skin, and the vapour attacks the eyes and nose.

Nitro-ω-dichloro-*p*-xylene; by dissolving *p*-xylylene chloride in fuming nitric acid (Grimaux, Zeit. für Chem. 1871, 7, 598). Small plates, m.p. 45°.

2:5-Dichloro-dinitro-*p*-xylene; by nitrating 2:5-dichloro-*p*-xylene with nitric and sulphuric acids (Kluge, Ber. 1885, 18, 2098). Small needles, m.p. 225°.

2-Bromo-5-nitro-*p*-xylene; from 5-nitro-*p*-2-xylydine (Blankensma, Chem. Weekblad, 1913, 10, 136). Colourless crystals, m.p. 70°.

2-Bromo-6-nitro-*p*-xylene; from 6-nitro-*p*-2-xylydine (Blankensma). Pale yellow crystals, m.p. 38°.

2-Bromo-3:5-dinitro-*p*-xylene; by the action of sunlight, or more rapidly by the action of heat, on 3:5-dinitro-*p*-xylene-2-diazoperbromide (Fries and Noll, Ann. 1912, 389, 305). It melts at 117°.

2:5-Dibromo-3-nitro-*p*-xylene; by heating 2:5-dibromo-*p*-xylene with nitric acid and acetic acid on the water-bath until dissolved (Auwers and Baum, Ber. 1896, 29, 2329). It melts at 111°-112° (Fittig, Ann. 1868, 147, 28) or 106°, and boils at 199°/20 mm. (A. and B.).

2:3-Dibromo-5-nitro-*p*-xylene; from 3-bromo-5-nitro-*p*-2-xylydine by the Sandmeyer reaction (Blankensma). Colourless crystals, m.p. 99°.

3:5-Dibromo-2-nitro-*p*-xylene; from 3:5-dibromo-6-nitro-*p*-2-xylydine by the elimination of the amino-group (Blankensma). Colourless crystals, m.p. 83°.

2:6-Dibromo-3:5-dinitro-*p*-xylene; by nitrating 2:6-dibromo-*p*-xylene or 3:5-dibromo-2-nitro-*p*-xylene with nitric and sulphuric acids (Blankensma). Colourless crystals, m.p. 190°.

2:5-Dibromo-3:6-dinitro-*p*-xylene; in small quantity together with 2:5-dibromo-3-nitro-*p*-xylene by nitrating 2:5-dibromo-*p*-xylene (Auwers and Baum). Colourless needles, m.p. 225°.

5-Nitro-2:3-dinitroso-*p*-xylene; by heating 3:5-dinitro-*p*-xylyl-2-azoimide at 105°-130° (Fries and Noll, Ann. 1912, 389, 305). It melts at 81°. It is probable that this compound actually has the constitution of an isooxadiazole oxide and is not a true dinitroso-derivative.

Chlorobromonitro-*p*-xylene; from chlorobromo-*p*-xylene and fuming nitric acid (Willgerodt and Wolfen, J. pr. Chem. 1889, (2) 39, 408). Yellowish needles, m.p. 99.5°.

6-Chloro-3-bromo-2:5-dinitro-*p*-xylene; by heating chlorobromonitro-*p*-xylene with fuming nitric acid (W. and W.). Small crystals, m.p. 245°.

p-Xylene 2-sulphonic acid; from the sulphonyl chloride (Jacobsen, Ber. 1878, 11, 17); by the action of copper powder on a sulphuric acid solution of *p*-xylene-2-diazonium sulphate saturated with sulphur dioxide (Gattermann,

Ber. 1899, 32, 1141); by treating *p*-xylene in carbon disulphide solution with sulphur dioxide in presence of aluminium chloride and hydrogen chloride at 0° (Knoevenagel and Kenner, Ber. 1908, 41, 3315). Flat needles, m.p. 84°-85° (K. and K.; Moschner, Ber. 1901, 34, 1257). When treated in the cold with acetic anhydride, acetic acid and a drop of concentrated sulphuric acid, it yields *p*-xylene 2-sulphinic anhydride, $O[SO \cdot C_6H_4(CH_3)_2]_2$, m.p. 68°-69°. The latter compound decomposes *in vacuo*, forming *p*-xylene 2-sulphonic acid and *p*-xylene disulphoxide, white tables, m.p. 70°-72°; the same products are formed when *p*-xylene sulphonic acid is heated in a sealed tube at 120°-130° (Knoevenagel and Polack, Ber. 1908, 41, 3323). On reduction with zinc dust and sulphuric acid, *p*-xylene 2-sulphinic acid yields the corresponding mercaptan, b.p. 205°-206° (Gattermann, Ber. 1899, 32, 1136).

p-Xylene 2-sulphonic acid; by sulphonating crude xylene (Crafts, Compt. rend. 1891, 114, 1110); by dissolving *p*-xylene in faintly fuming sulphuric acid (Beilstein and Wahlforss, Ann. 1865, 133, 38; Fittig and Glinzer, Ann. 1866, 136, 505; Jacobsen, Ber. 1877, 10, 1009; 1878, 11, 22; Remsen and Emerson, Amer. Chem. J. 1886, 8, 265); by reducing sodium dibromo-*p*-xylene sulphonate with sodium amalgam (Moody and Nicholson, Chem. Soc. Trans. 1890, 58, 974). Large tables or long flat prisms $+2H_2O$ (J.), m.p. 48°, b.p. 149°/0 mm. (Krafft and Wilke, Ber. 1900, 33, 3207). $NaA' + H_2O$ (J.), orthorhombic tables, $a:b:c=1.0767:1:1.4882$ (Miers, Chem. Soc. Trans. 1890, 58, 978); KA' (F. and G.); $KA' + H_2O$; BaA'_2 , irregular crystals; $CuA'_2 + 8H_2O$, pale blue tridinic prisms; $ZnA'_2 + 10H_2O$.

Chloride; large flat prisms, m.p. 24°-26° (J.), b.p. 77°/0 mm. (K. and W.).

Amide; long needles, m.p. 147°-148° (J.; Moschner, Ber. 1901, 34, 1257).

p-Xylene when treated with sulphuryl chloride in presence of aluminium chloride forms *p*-xylene 2-sulphonyl chloride, chloro-*p*-xylene and di-*p*-xylylsulphone (Töhl and Eberhard, Ber. 1893, 26, 2940). *p*-Xylene sulphonic acid is converted into terephthalic acid by fusion with lead peroxide and potassium hydroxide (Graebe and Krafft, Ber. 1906, 39, 2507).

p-Xylene 2:6(?)-disulphonic acid; by warming the monosulphonyl chloride with fuming sulphuric acid (Holmes, Amer. Chem. J. 1891, 13, 372; Pfannenstilk, J. pr. Chem. 1892, (2) 46, 152). Needles. $BaA'' + 3H_2O$; $CaA'' + 4H_2O$; $MgA'' + 7H_2O$; $PbA'' + 3H_2O$; $Ag_2A'' + H_2O$; all of these salts are very hygroscopic (H.).

Chloride; white radiating tufts, m.p. 72°-74° (H.), or 74°-75° (P.).

Amide; microscopic plates, m.p. 294°-295° (decomp.) (H.), or 250° (P.).

Chloro-*p*-xylene sulphonic acid; from chloro-*p*-xylene and fuming sulphuric acid (Kluge, Ber. 1888, 18, 2099). Crystals. $NaA' + H_2O$, prisms; $BaA'_2 + H_2O$, needles.

2-Bromo-*p*-xylene 5-sulphonic acid; from *p*-2-xylydine 5-sulphonic acid by the Sandmeyer reaction (Nölting and Kohn, Bull. Soc. Ind. Mulhouse, 1888, 58, 636; Ber. 1890, 19, 137). It is probably identical with the compound obtained by Jacobsen (Ber. 1896, 17, 2979) by sulphonating bromo-*p*-xylene. $BaA'_2 + 2H_2O$

(N. and K.); BaA' , thin six-sided plates or small prisms; $\text{NaA}' + \text{H}_2\text{O}$, long thin prisms or rhombic six-sided plates (J.).

Chloride; small prisms, m.p. $77^\circ\text{--}78^\circ$ (N. and K.).

Amide; small white scales, m.p. $200^\circ\text{--}201^\circ$ (N. and K.), or flat prisms, m.p. 206° (J.).

3:6-Dibromo-*p*-xylene 2-sulphonic acid; by sulphonating 3:6-dibromo-*p*-xylene with fuming sulphuric acid (20 p.c. SO_3) at 80° (Moody and Nicholson, Chem. Soc. Trans. 1890 57, 974). Glistening silky needles, m.p. 151° (decomp.). $\text{NaA}' + \text{H}_2\text{O}$, microscopic needles BaA' , scales or flat needles.

Chloride; flat needles, m.p. $78^\circ\text{--}79^\circ$.

Amide; thin pearly plates or thin rhombic plates, m.p. 198° .

3-Nitro-*p*-xylene 2-sulphonic acid; together with the 6-nitro-derivative and small quantities of the 5-nitro-derivative by nitrating *p*-xylene 2-sulphonic acid; the products are separated preferably by fractional crystallisation of the sulphonyl chlorides (Carslake and Huston, J. Amer. Chem. Soc. 1914, 36, 1244; 1915, 37 2119). Long deliquescent plates, m.p. $143^\circ\text{--}145^\circ$.

Chloride; m.p. $109.5^\circ\text{--}110.5^\circ$, is also formed together with 6-nitro-*p*-xylene 2-sulphonyl chloride by nitrating *p*-xylene 2-sulphonyl chloride.

Amide; m.p. $191^\circ\text{--}192^\circ$; *anilide*, m. $181.5^\circ\text{--}182.5^\circ$.

Phenyl-ester; m.p. $83^\circ\text{--}83.5^\circ$ (C. and H.).

5-Nitro-*p*-xylene 2-sulphonic acid; see above very hygroscopic needle-like plates $+ \text{H}_2\text{O}$ which lose H_2O at 108° and then melt at $138^\circ\text{--}140^\circ$.

Chloride; m.p. $74.5^\circ\text{--}75.5^\circ$, is also obtained together with 6-nitro-*p*-xylene 2-sulphonyl chloride by the action of chlorosulphonic acid on 2-nitro-*p*-xylene.

Amide; m.p. $197^\circ\text{--}198^\circ$; *anilide*, m.p. $130.5^\circ\text{--}131^\circ$.

Phenyl-ester; m.p. $120^\circ\text{--}120.5^\circ$ (C. and H.).

6-Nitro-*p*-xylene 2-sulphonic acid; see above plates $+ \text{H}_2\text{O}$, which darken at 128° and do not melt at 200° .

Chloride; m.p. $60^\circ\text{--}61^\circ$.

Amide; m.p. $172^\circ\text{--}173^\circ$; *anilide*, m. $133^\circ\text{--}144^\circ$.

Phenyl-ester; m.p. $117^\circ\text{--}118^\circ$.

Xylidines. (Aminoxylenes, or Aminodimethylbenzenes.) Theory predicts the existence of six isomeric aminodimethylbenzenes, and all are known. They are obtained by the reduction of the corresponding nitro-compounds with iron and hydrochloric acid, or with iron powder and acetic acid, or, in the case of the commercial products, with iron turnings and hydrochloric acid. Commercial xylidine contains *o*-3-xylidine, *o*-4-xylidine, *m*-2-xylidine, *m*-4-xylidine, and *p*-2-xylidine. The chief constituents are *m*-4-xylidine and *p*-2-xylidine. The percentage of the former may be estimated by converting the bases into the hydrochlorides or acetates, as these salts of *m*-4-xylidine are insoluble in water. When glacial acetic acid is used as precipitant, equal quantities of the acid and base give the best results. More accurate results are obtained, however, by converting the acetate into the bromide. *m*-4-Xylidine takes up 1 atom of bromine, and although *m*-2-xylidine behaves in a similar manner, its salts, particularly the hydrochloride, are readily soluble in water. The other bases form dibromides with bromine (Vaubel, Zeitsch. anal. Chem. 1897, 36, 285).

larly the hydrochloride, are readily soluble in water. The other bases form dibromides with bromine (Vaubel, Zeitsch. anal. Chem. 1897, 36, 285).

p-Xylidine may be obtained from commercial xylidine by gradually adding the latter to fuming sulphuric acid (15–20 p.c. SO_3) in such proportions that exactly 1 mol. xylidine is used with each mol. of sulphuric anhydride. The mixture is heated for some time on the water-bath, cooled, and then treated with water, when the sparingly soluble *m*-xylidine sulphonic acid is precipitated. The free acids contained in the mother-liquor are converted into their sodium salts; the sodium salt of *p*-xylidine sulphonic acid separates first, that of the *m*-xylidine sulphonic acid being very soluble (Witt, Nölting and Forel, Bull. Soc. Ind. Mulhouse, 1888, 53, 630; Ber. 1885, 18, 2664; Witt, Dingl. poly. J. 260, 95). *p*-Xylidine may also be separated from its isomerides by means of the benzylidene derivative, which is converted into the free base subsequently by hydrolysis (Limpach, Eng. Pat. 11822 of 1886; Fr. Pat. 178616; D. R. P. 39947 of 1886; Bayer & Co., D. R. P. 71969 of 1893). *m*-2-Xylidine may be obtained from commercial xylidine by converting the bases into the sulphates, allowing the solution of the salts to crystallise, and fractionating the mixture of bases obtained from the mother-liquor from the last crop of crystals. The portion distilling at $212^\circ\text{--}216^\circ$ is acetylated, and the mixture of acetyl-derivatives is boiled for a few hours with 4 times its weight of 25 p.c. sulphuric acid. On cooling, the greater part of the aceto-*m*-2-xylidide separates unchanged, the remainder being extracted from the previously diluted mother-liquor by means of ether. The acetyl-derivative is then hydrolysed by heating at 150° with concentrated hydrochloric acid, or at 200° with 3 times its weight of 70–75 p.c. sulphuric acid. *m*-2-Xylidine may be obtained also from commercial xylidine by heating the mixture of bases, obtained from the mother-liquor from the sulphates (see above), for 24 hours with an equal weight of glacial acetic acid, and distilling the product. The portion distilling below 300° is then treated with acetic anhydride, and the acetyl-derivatives boiled with 25 p.c. sulphuric acid and isolated as above (Nölting and Pick, Ber. 1888, 21, 3150). The *p*- and *m*-xylidines may also be separated by means of benzaldehyde, with which the *p*-isomeride yields di-*p*-amino-di-*p*-xylyl-phenyl-methane, m.p. 208° (Schultz, J. pr. Chem. 1907, (2) 76, 331). For use in the preparation of colouring matters, Limpach (Eng. Pat. 6890 of 1888; J. Soc. Chem. Ind. 1889, 8, 281) described the following method for separating the xylidines from the commercial product; 121 grms. of commercial xylidine are treated with 30 grms. of 100 p.c. acetic acid, and kept for 24 hours. Crystals separate, which consist of pure *m*-4-xylidine acetate. The mother-liquors are treated with hydrochloric acid, and after keeping for 3–4 days, about 20 p.c. of *p*-xylidine separates as hydrochloride. A modification of this process for effecting a complete separation of all the isomerides in commercial xylidine, making use of the method for isolating *m*-4-xylidine as acetate, of *p*-xylidine as hydrochloride (Limpach, Eng. Pat.

11822 of 1886; Fr. Pat. 178616; D. R. P. 39947 of 1886), and of *m*-2-xylydine as formo-*m*-2-xylydide (Limpach, Ber. 1899, 32, 1008), has been described by Hodgkinson and Limpach (Chem. Soc. Trans. 1900, 77, 65). 300 grms. of commercial pure xylydine are treated with slightly more than the necessary amount of glacial acetic acid, or 80 p.c. acetic acid, required to convert the *m*-4-xylydine into its acetate. The amount of acetic acid required can be ascertained approximately by preliminary experiments with a test sample. After keeping for 24 hours the separation of *m*-4-xylydine acetate is practically complete, the yield of the base being 40–42 p.c. of the original xylydine. The crude product is basified with sodium hydroxide and purified by conversion into its formyl-derivative, followed by hydrolysis. To the filtrate and mother-liquors, which contain a considerable amount of *p*-xylydine and smaller quantities of *o*-3-xylydine, *o*-4-xylydine, and *m*-2-xylydine, concentrated hydrochloric acid is added until the whole dissolves. On cooling, practically pure *p*-xylydine hydrochloride separates, the yield of the base being about 30 p.c. of the original xylydine. The residue, containing the two *o*- and the *m*-isomerides, is concentrated in a retort until semi-solid, and when heated gently, *m*-2-xylydine hydrochloride sublimes in silky needle-shaped crystals. The yield of the base, obtained by this method, is 2·7 p.c. of the total xylydine. Another method of obtaining this isomeride when larger quantities are used, is to distil about 20 p.c. of the contents of the retort by heating rapidly; the distillate then solidifies very quickly, and may be purified by conversion into its formyl-derivative. The black residue in the retort, from which *m*-2-xylydine hydrochloride has been sublimed, consists of the hydrochlorides of *o*-3- and *o*-4-xylydine. It is dissolved in water, basified, the bases separated and steam distilled. The distillate, containing 9–11 p.c. of *o*-3-xylydine and 11–14 p.c. of *o*-4-xylydine, is treated with formic acid, and the formyl-derivatives are separated by fractional crystallisation, the *o*-3-isomeride crystallising fairly readily, the *o*-4-isomeride only with difficulty.

When the vapours of the xylydines and methyl alcohol vapour are passed over aluminium oxide at 360°–380°, a mixture of the mono- and dimethyl-derivatives is obtained. Mixtures of α -naphthol or α -naphthylamine and xylydine may be used as a flotation agent, the latter mixture acting as a collector and a frother (Consolidated Copper Mines Co., Chem. Met. Eng. 1919, 21, 418; Robie, Eng. and Min. J. 1919, 108, 730).

***o*-3-Xylydine**, (*o*)-*o*-xylydine, *c*-*o*-xylydine, or β -amino-*o*-xylene; from commercial xylydine (Hodgkinson and Limpach, Chem. Soc. Trans. 1900, 77, 65); by reducing 3-nitro-*o*-xylene with iron filings and acetic acid (Nölting and Forel, Ber. 1885, 18, 2671; Wroblewsky, *ibid.* 2904); by treating 4:5-dibromo-*o*-3-xylydine with sodium amalgam in the cold (Töhl, *ibid.* 2562). A xylydine (acetyl-derivative, m.p. 134°) was obtained by Müller (Ber. 1887, 20, 1039) by heating *o*-4-xylenol with ammonium bromide and zinc-ammonium bromide at 300°, this unexpected result being explained by Müller as due to isomerisation of the *o*-4-xylydine first formed to *o*-3-xylydine. Liquid, b.p. 223°/739

mm., D₄²⁰ 0·991 (N. and F.); b.p. 223·5°/728 mm. (Ullmann, Ber. 1898, 31, 1698); absorption spectrum (Purvis, Chem. Soc. Trans. 1910, 97, 1546). When oxidised with chromic acid mixture, it yields *o*-xyloquinone (N. and F.), whilst on oxidation with lead peroxide it yields azoxylene, m.p. 111°, aminodixylylamine (4-amino-2:3:2':3'-tetramethyldiphenylamine), m.p. 74°–75°, and xyloquinonexylyldi-imine, m.p. 67·5°–68·5° (Goldschmidt, Ber. 1920, 53, 28). By the interaction of *o*-3-xylydine and phthalyl chloride in ethereal solution, *o*-3-xylylphthalimide is obtained together with a yellow substance consisting probably of *aa*-*o*-3-xylylphthalimide and *a*-*o*-3-xylylphthalimide (Kuhara and Comatsu, Mem. Coll. Sci. Eng. Kyōto, 1910, 2, 365). B'HCl+H₂O, large glistening plates (Nölting and Pick, Ber. 1888, 21, 3153), m.p. 254°, b.p. 256°/728 mm., or 258°/760 mm. (Ullmann); B'HNO₃, needles; B'H₂SO₄, large leafy crystals (N. and P.).

Formyl-derivative; m.p. 100°–102° (Hodgkinson and Limpach).

Acetyl-derivative; long fine needles, m.p. 131° (Töhl; Wroblewsky; Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352), 132° (H. and L.), or 134° (N. and F.).

4:5-Dibromo-*o*-3-xylydine; from 3-nitro-4:5-dibromo-*o*-xylene by reduction with iron and acetic acid (Töhl, Ber. 1885, 18, 2561; Crossley and Smith, Chem. Soc. Trans. 1913, 103, 989). Needles, volatile with steam, m.p. 103°. It does not possess basic properties, and on treatment with sodium amalgam it is converted into *o*-3-xylydine.

4:6-Dibromo-*o*-3-xylydine; by brominating *o*-3-xylydine in glacial acetic acid solution (Jaeger and Blanksma, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153; Rec. trav. chim. 1906, 25, 352). It melts at 56°.

4:5-Dichloro-6-nitro-*o*-3-xylydine; by reducing 3:6-dinitro-4:5-dichloro-*o*-xylene (Claus, &c., J. pr. Chem. 1891, (2) 43, 563). Yellow needles, volatile with steam, m.p. 54°.

The nitro-derivatives of *o*-3-xylydine may be obtained either by nitrating aceto-*o*-3-xylydide, or by the direct nitration of the base at low temperatures in presence of sulphuric acid. In the former case, the separation of the products may be effected by steam distillation, although the process is very tedious, the relative proportions being 30 p.c. of 4-nitro-*o*-3-xylydine, 13 p.c. of 5-nitro-*o*-3-xylydine, and 55 p.c. of 6-nitro-*o*-3-xylydine. The yield obtained by direct nitration of the amine varies, the amount of 5-nitro-*o*-xylydine increasing with the amount of sulphuric acid used. Using 20 parts of sulphuric acid, the yields are 25 p.c. of 4-nitro-*o*-3-xylydine, 45 p.c. of 5-nitro-*o*-3-xylydine, and 30 p.c. of 6-nitro-*o*-3-xylydine (Nölting, Braun and Thesmar, Ber. 1901, 34, 2245).

4-Nitro-*o*-3-xylydine; together with the 5-nitro- and 6-nitro-derivatives by nitrating *o*-3-xylydine sulphate with sulphuric acid and nitric acid at –10°, or, as the acetyl-compounds by a similar nitration of aceto-*o*-3-xylydide (Nölting, Braun and Thesmar; Nölting and Stöcklin, Ber. 1891, 24, 567). Brick-red lozenge-shaped crystals with feebly basic properties.

Acetyl-derivative; colourless needles, m.p. 160°

Benzoyl-derivative; white crystals, m.p. 177°–178° (N., B. and T.).

5-Nitro-o-3-xylylidine; light yellow needles, m.p. 111°–112°. It is more strongly basic than the preceding compound.

Acetyl-derivative; white needles, m.p. 230°–231°.

Benzoyl-derivative; crystals, m.p. 227°–228° (N., B. and T.).

6-Nitro-o-3-xylylidine; brownish-yellow prisms, m.p. 114°.

Acetyl-derivative; faintly yellow needles, m.p. 149°–150°.

Benzoyl-derivative; yellowish crystals, m.p. 208°–209° (N., B. and T.).

4:5-Dinitro-o-3-xylylidine; by heating the acetyl derivative to 90° for 5 minutes with 10 times its weight of sulphuric acid (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345). Orange needles, m.p. 143°.

Acetyl-derivative; by nitrating 5-nitro-aceto-o-3-xylylidine with fuming nitric acid and keeping the mixture at 8°–10° for 1½–2 hours (C. and M.). Colourless needles, m.p. 225°.

5:6-Dinitro-o-3-xylylidine; by hydrolysing the acetyl-derivative with 10 times its weight of sulphuric acid at 110°–115° for 20 minutes (C. and M.). Deep yellow needles, m.p. 172°.

Acetyl-derivative; by nitrating 5-nitro-aceto-o-3-xylylidine with fuming nitric acid and sulphuric acid. White plates, m.p. 180°.

4:6-Dinitro-o-3-xylylidine; by treating 3:4:6-trinitro-o-xylene with alcoholic ammonia (C. and M.; Crossley and Pratt, Chem. Soc. Trans. 1913, 103, 982). Golden-yellow needles, m.p. 161°.

Diacetyl-derivative; fern-like aggregates, m.p. 139°.

o-3-Xylylidine 4-sulphonic acid; by reducing 3-nitro-o-xylene 4-sulphonic acid with ferrous sulphate (Simonsen, Chem. Soc. Trans. 1913, 103, 1144). Octahedral prisms, which blacken but do not melt at 300°. BaA'_2 , rectangular prisms which become pink on exposure to air.

o-3-Xylylidine 5-sulphonic acid; by reducing 3-nitro-o-xylene 5-sulphonic acid with ferrous sulphate (the yield is poor with stannous chloride, owing to the formation of chlorinated products); together with *o-3-xylylidine 6-sulphonic acid*, by sulphonating *o-3-xylylidine* for 2 hours at 160° and then for 1 hour at 180° (S.). Slender needles + 1 (?) H_2O . BaA'_2 , is difficult to crystallise.

o-3-Xylylidine 6-sulphonic acid; bunches of sheaf-like needles, which do not darken at 305°. BaA'_2 , glistening octahedral pyramids, which rapidly effloresce in the air (S.).

Methyl-o-3-xylylidine; by hydrolysing acetyl-methyl-o-3-xylylidine with boiling diluted sulphuric acid for 15 hours (Menton, Ann. 1891, 263, 316). The product, purified by means of the nitroso-derivative, is an oil, b.p. 222°–223°. B'HCl , colourless needles; $\text{B'H}_2\text{SO}_4$; $\text{B}'_2\text{H}_2\text{PtCl}_6$.

Acetyl-derivative; by heating a xylene solution of *o-3-aceto-xylylidine* at 140° with rather more than the theoretical quantity of sodium, and carefully warming the sodium compound produced with methyl iodide (M.). Well-defined crystals, m.p. 75°, volatile with steam. B'HCl , colourless needles; $\text{B'H}_2\text{SO}_4$; $\text{B}'_2\text{H}_2\text{PtCl}_6$.

6-Nitroso-derivative; by treating the nitro-

samine (obtained when the hydrochloride of the base is treated with sodium nitrite in ice-cold aqueous solution) with alcoholic hydrochloric acid. Green needles, m.p. 160°–161°.

When heated with aniline and aniline hydrochloride, the nitroso-derivative yields a red induline (M.).

Ethyl-o-3-xylylidine; obtained from ethyl-aceto-o-3-xylylidine as above (M.). Oil, b.p. 227°–228°. B'HCl , crystals; $\text{B}'_2\text{H}_2\text{PtCl}_6$.

Acetyl-derivative; yellow oil, b.p. about 268°.

p-Nitroso-derivative; green needles, m.p. 123°–124°; hydrochloride, slender yellow needles.

Dimethyl-o-3-xylylidine; together with trimethyl-o-3-xylylidine ammonium iodide by heating *o-3-xylylidine* hydrochloride with the theoretical quantity of methyl alcohol at 180°–190° for 10 hours, and boiling the mixture of methyl- and dimethyl-o-xylylidines formed with methyl iodide for 2–3 hours; the product is treated with soda, and the dimethyl-o-3-xylylidine is distilled with steam (M.). Oil, b.p. 199°–200°. B'HCl , slender needles; $\text{B}'_2\text{H}_2\text{PtCl}_6$, defined needles.

The following alkylamino- and arylamino-derivatives of 4:6-dinitro-o-xylene have been obtained from 3:4:6-trinitro-o-xylene by Crossley and Pratt (Chem. Soc. Trans. 1913, 103, 982): *3-methylamino*-, orange needles, m.p. 90°–91°; *3-dimethylamino*-, orange needles, m.p. 91°–92°; *3-ethylamino*-, stout orange needles, m.p. 75°–76°; *3-anilino*-, bright red plates, m.p. 137°; *3-p-toluidino*-, orange-red plates, m.p. 111°; *3-o-anisidino*-, brick-red needles, m.p. 126°–127°; *3-p-anisidino*-, garnet-coloured flat needles, m.p. 118°; *3-benzylamino*-, orange prisms, m.p. 59°; *3-piperidino*-, orange plates, m.p. 98°.

(a) *o-4-Xylylidine*, *i-o-xylylidine*; from commercial xylylidine (Hodgkinson and Limpach, Chem. Soc. Trans. 1900, 77, 65); by reducing 4-nitro-o-xylene with tin and hydrochloric acid (Jacobsen, Ber. 1884, 17, 160); by heating *m*-toluidine hydrochloride with methyl alcohol at 250° (Limpach, Ber. 1888, 21, 646); by reducing ω (2)-chloro-4-nitro-o-xylene with tin and hydrochloric acid (Stephen, Short and Gladding, Chem. Soc. Trans. 1920, 117, 510); by heating *o*-xylene for several hours with hydroxylamine hydrochloride and aluminium chloride (Graebe, Ber. 1901, 34, 1778). Vitreous rhombic tables, or large monoclinic crystals, m.p. 49°, b.p. 226°, D_{20}^{25} 1.0755 (J.); b.p. 224°/728 mm. (Ullmann, Ber. 1898, 31, 1698); m.p. 50° (Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352), or m.p. 52° (Hodgkinson and Limpach), not coloured on exposure to air and light. It gives no colour with bleaching powder, and its solutions colour pine-wood yellow. On heating the hydrochloride with methyl alcohol at 300°–320°, it yields pseudocumidine (Nöling and Forel, Ber. 1885, 18, 2680). When oxidised together with diamino-diphenylamine a safranine is formed (Nietzki, Ber. 1886, 19, 3163). $\text{B'HCl} + \text{H}_2\text{O}$, long thin prisms (J.), m.p. 266°, b.p. 264°/728 mm., or 266°/760 mm. (Ullmann); B'HNO_3 ; $\text{B}'_2\text{H}_2\text{SO}_4$ (Nöling and Pick, Ber. 1888, 21, 3153).

Formyl-derivative; m.p. 52°.

Acetyl-derivative; m.p. 99°.

5-Chloro-o-4-xylylidine; glistening leaflets.

which sublime, m.p. 86° (Claus, J. pr. Chem.

Acetyl-derivative; colourless slender prisms, m.p. 154°, is formed by heating the oxime of 5-chloro-o-xylyl-4-methyl ketone with sulphuric acid (Claus).

3:5-Dichloro-o-4-xylidine; by the hydrolysis of its acetyl-derivative, obtained by dichlorinating o-4-acetoxylidide (Crossley, Chem. Soc. Trans. 1904, 85, 264). Long glistening silky needles, m.p. 44.5°.

6-Bromo-o-4-xylidine; by reducing 3-bromo-5-nitro-o-xylene with stannous chloride (Crossley and Bartlett, Chem. Soc. Trans. 1913, 103, 1297). Silky needles, m.p. 82°.

Acetyl-derivative; small transparent plates, m.p. 205°-206°; *diacetyl-derivative*, four-sided plates, m.p. 109° (C. and B.).

3:5-Dibromo-o-4-xylidine; by brominating o-4-xylidine in glacial acetic acid solution (Jaeger and Blanksma, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153; Rec. trav. chim. 1906, 25, 352). It melts at 63°.

3:6-Dibromo-o-4-xylidine; by successive bromination and hydrolysis of aceto-o-4-xylidide. Crystals, m.p. 65° (J. and B.).

o-4-Xylidine on nitration yields three mono-nitro-derivatives, the relative proportions when the nitration is carried out in presence of sulphuric acid being 47 p.c. of 5-nitro-o-4-xylidine, 31 p.c. of 3-nitro-o-4-xylidine, and 13 p.c. of 6-nitro-o-4-xylidine (Nölting, Braun and Thesmar).

3-Nitro-o-4-xylidine; together with the 5-nitro- and 6-nitro-derivatives by nitrating o-4-xylidine with nitric acid and sulphuric acid at -15° (Nölting, Braun and Thesmar, Ber. 1901, 34, 2248; cf. Nölting and Stöcklin, *ibid.* 1891, 24, 564). Scarlet-red prisms, m.p. 65°-66°. Readily volatile with steam and more strongly basic than the 5-nitro-derivative.

Acetyl-derivative; small white needles, m.p. 115°-116°, is also formed by reducing 3:4-dinitro-o-xylene with stannous chloride and heating the product for 2 hours with acetyl chloride (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345); *benzoyl-derivative*, small white needles, m.p. 199°-200°.

5-Nitro-o-4-xylidine; brownish-red prisms, m.p. 139°-140°; is also obtained by heating 5-nitro-o-4-xylol with ammonia and ammonium chloride for 20 hours at 140°-150° (Diepolder, Ber. 1909, 42, 2916); its salts are decomposed by water.

Acetyl-derivative; small light yellow needles, m.p. 117°; *benzoyl-derivative*, light yellow silky needles, m.p. 149°-150° (N., B. and T.).

6-Nitro-o-4-xylidine; long lustrous orange-coloured plates, m.p. 74°-75°, less volatile with steam than the 3- and 5-nitro-derivatives.

Acetyl-derivative; by nitrating aceto-o-4-xylidide with nitric acid (D 1.42) and sulphuric acid (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345) or by acetylating the amine. Small white needles, m.p. 209°-210°; *benzoyl-derivative*, small white needles, m.p. 223°-224°.

3:5-Dinitro-o-4-xylidine; by the action of alcoholic ammonia on 3:4:5-trinitro-o-xylene (Crossley and Morrell, Chem. Soc. Trans. 1911, 99, 2345; Crossley and Pratt, *ibid.* 1913, 103, 982). Orange-red needles, m.p. 143° (C. and B.).

Acetyl-derivative; by nitrating 3-nitro-aceto-o-4-xylidide with a mixture of nitric and sulphuric acids at -2° (C. and M.), or by nitrating aceto-o-4-xylidide with fuming nitric acid at -5° (C. and M.). Transparent needles, m.p. 223°.

5:6-Dinitro-o-4-xylidine; by hydrolysing the acetyl-derivative with 10 times its weight of concentrated sulphuric acid for 10 minutes at 110° (C. and M.). Deep orange-red needles, m.p. 212°.

Acetyl-derivative; by nitrating aceto-o-4-xylidide with nitric acid (D 1.5) and sulphuric acid; by the further nitration of 6-nitro-aceto-o-4-xylidide with fuming nitric acid (C. and M.). Fine white needles, m.p. 173°.

o-4-Xylidine 5-sulphonic acid; by reducing 4-nitro-o-xylene 5-sulphonic acid with alkaline ferrous sulphate; together with o-4-xylidine 6-sulphonic acid by sulphonating o-4-xylidine, or *s*-dixylylcarbamide (Simonsen, Chem. Soc. Trans. 1913, 103, 1144). Tablets, which blacken at 280°, but do not decompose at 300°. $\text{BaA}'_2 + 8\text{H}_2\text{O}$, rectangular plates or spangles.

o-4-Xylidine 6-sulphonic acid; see above. Plates $+2\text{H}_2\text{O}$ (?), which do not readily redden on exposure to air. It darkens at 283°, and melts at 294° with decomposition. $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, large orthorhombic (?) plates, which become pink (S.). The same (?) acid is obtained by heating dixylylcarbamide with sulphuric acid (D 1.71) at 150°-160° (Cazeneuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 21).

Dimethyl-o-4-xylidine; by heating a toluene solution of o-4-xylidine with dimethyl sulphate for 3 hours on the water-bath (Bielecki and Koleniew, Anzeiger Akad. Wiss. Krakau, 1908, 296); by distilling the quaternary ammonium hydroxide (E. Fischer and Windaus, Ber. 1900, 33, 351). It boils at 232° (F. and W.), or at 225°-227° (B. and K.). The ammonium iodide forms prisms, decomposing at 235°-237°. The following alkylamino- and arylamino-derivatives of 3:5-dinitro-o-xylene have been prepared by the action of ammonia and various amines on 3:4:5-trinitro-o-xylene (Crossley and Pratt, Chem. Soc. Trans. 1913, 103, 972): 4-methylamino-, stout scarlet plates, m.p. 143°; 4-di-methylamino-, orange-red needles, m.p. 103°-104°; 4-ethylamino-, orange-red needles, m.p. 115°; 4-anilino-, orange-red needles, m.p. 134°; 4-p-toluidino-, fine orange needles, m.p. 133°; 4-o-anisidino-, stout crimson-lake needles, m.p. 138°-139°; 4-p-anisidino-, bright crimson needles, m.p. 131°; 4-benzylamino-, orange plates, m.p. 128.5°.

The following diamines are prepared by reducing the corresponding nitro-o-3- and o-4-xylidines (Nölting, Braun and Thesmar, Ber. 1901, 34, 2242; Nölting and Thesmar, *ibid.* 1902, 35, 628).

3:4-Diamino-o-xylene; white quadratin plates, m.p. 89°.

Diacetyl-derivative; small white needles, m.p. 196°-197°.

3:5-Diamino-o-xylene; small white needles, m.p. 68°-67°.

Diacetyl-derivative; small white needles, m.p. 240°-241°.

3:6-Diamino-o-xylene; thick pale yellow needles, m.p. 116°, is obtained also by reducing the azo-dye obtained from o-3-xylidine and

diazobenzene sulphonio acid with tin and hydrochloric acid.

Diacetyl-derivative; small white needles, m.p. 275°–276°.

4:5-Dichloro-derivative; needles which sublime, m.p. 176° (Claus and Berkefeld, J. pr. Chem. 1891, (2) 43, 583). The dichloro-diamine on oxidation with chromic acid yields 4:5-dichloro-*o*-xylo-3:6-quinone, m.p. 159°, which sublimes in thin yellow leaflets (C. and B.).

4:5-Diamino-o-xylene; white plates, m.p. 125°–126° (anhydrous).

Diacetyl-derivative; m.p. 227°–228°.

A table differentiating the diamines by their behaviour with ferric chloride, potassium dichromate, sodium nitrite, and bleaching powder is given by Nölting and Thesmar (*l.c.*).

m-2-Xylidine, *v-m-xylidine*, *c-m-xylidine*, or *β-xylidine*; by distilling 2-amino-mesitylenic acid with lime (Schmitz, Ann. 1878, 193, 179); from commercial xylidine (Nölting and Pick, Ber. 1888, 21, 3150; cf. Wroblewsky, Ber. 1879, 12, 1226; Ann. 1881, 207, 91; Noyes, Amer. Chem. J. 1898, 20, 789; Hodgkinson and Limpach, Chem. Soc. Trans. 1900, 77, 65; Winkelhausen, D. R. P. 251334 of 1911); by reducing 2-nitro-*m*-xylene (Grevink, Ber. 1884, 17, 2430; Nölting and Förel, Ber. 1885, 18, 2668; Bull. Soc. chim. 1884, (2) 42, 332, 338; Miolatti and Lotti, Gazz. chim. ital. 1897, 27, i. 293; Busch, Ber. 1899, 32, 1008). Liquid, b.p. 214°/739 mm. (N. and F.); b.p. 211°–212° (B.); b.p. 216°/735 mm., D_{15}^{20} 0.980 (H. and L.). Absorption spectrum (Purvis, Chem. Soc. Trans. 1910, 97, 1546). $B'HCl + \frac{1}{2}H_2O$, needles which sublime; $B'HN O_3$, needles; $B'H_2SO_4 + 2\frac{1}{2}H_2O$ (N. and P.).

Formyl-derivative; very long needles, m.p. 164°, or 176°–177° when heated rapidly (H. and L.); *acetyl-derivative*, needles, m.p. 174° (G.), or m.p. 177° (H. and L.); *benzoyl-derivative*, silky needles, m.p. 164° (Friedländer and Brand, Monath. 1898, 19, 627), or m.p. 159°–160° (B.); *benzylidene-derivative*, yellow oil (B.); *m-nitro-benzylidene-derivative*, yellow crystals, m.p. 105°; *o-nitro-benzylidene-derivative*, reddish-brown crystals; *o-hydroxy-benzylidene-derivative*, yellow oil (B.). When oxidised, *m-2-xylidine* is converted into *m*-xyloquinone (N. and F.). The hydrochloride when heated with methyl alcohol at 300°–320° yields mesidine. The base condenses with formaldehyde in presence of hydrochloric acid, forming diaminodixylylmethane, m.p. 126°, and with *p*-nitro-benzaldehyde forming *p*-nitro-diaminophenyldixylylmethane, yellow prisms, m.p. 136° (F. and B.). By the Sandmeyer reaction *m-2-xylidine* yields 2-cyano-*m*-xylene, white prisms which sublime, m.p. 89° (N.). Acetyl-*m-2-xylidyl-nitrosamine* is obtained by the action of nitrous acid on aceto-*m-2-xylidide* and forms yellow plates, m.p. 62°–63°, which are converted into 7-methylindazole, m.p. 138°, and acetic acid by boiling with benzene (Jacobson and Huber, Ber. 1908, 41, 660). Aceto-*m-2-xylidide* is oxidised by potassium permanganate in presence of magnesium sulphate to 2-acetylaminophthalic acid (Nölting and Gachot, Ber. 1906, 39, 73).

4:6-Dichloro-m-2-xylidine (?); from the corresponding nitro-dichloro-xylene by reduction with stannous chloride, hydrochloric acid, and alcohol. Colourless needles which soon

become coloured, m.p. 85° (Claus and Runschke, J. pr. Chem. 1890, (2) 42, 110). B', H_2PtCl_6 , brown powder.

4-Bromo-m-2-xylidine; by reducing 4-bromo-2-nitro-*m*-xylene (Nölting, Braun and Thesmar, Ber. 1901, 34, 2242). Lustrous colourless needles, m.p. 21.5°, b.p. 146°–147°/15 mm. (N., B. and T.; cf. E. Fischer and Windaus, Ber. 1900, 33, 1967).

Acetyl-derivative; small needles, m.p. 136°, preferably prepared indirectly from 4-nitroaceto-*m-2-xylidide*, by reduction and replacement of the amino-group by bromine (N., B. and T.).

5-Bromo-m-2-xylidine; by brominating *m-2-xylidine* in glacial acetic acid (N., B. and T.); by brominating *m-2-xylidine* in presence of a large excess of hydrochloric acid or hydrobromic acid and treating the N-halogen derivative with hydrochloric acid (F. and W.). Prisms or lot white needles, m.p. 49°–50° (F. and W.), m.p. 50°–51° (N., B. and T.).

Acetyl-derivative; small white needles, m.p. 193°–194° (N., B. and T.), or 197° (corr.) (F. and W.). *m-2-Aceto-m-xylidide* on bromination yields a mixture of 4- and 5-bromo-derivatives.

4:5-Dibromo-m-2-xylidine; by warming a mixture of 4-bromo-*m-2-xylidine* with bromine in presence of hydrobromic acid (Jaeger and Blankema, Rec. trav. chim. 1906, 25, 352; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153). Crystals, m.p. 51°.

4:6-Dibromo-m-2-xylidine; by reducing 4:6-dibromo-2-nitro-*m*-xylene with iron and acetic acid (Auwers and Traun, Ber. 1899, 32, 3309); from *m*-xylene by bromination, nitration, reduction, and diazotisation (J. and B.). Fine felted needles, m.p. 99°–100° (A. and T.), or m.p. 120° (J. and B.).

4:5:6-Tribromo-m-2-xylidine; by brominating 4:6-dibromo-*m-2-xylidine* in acetic acid solution (J. and B.). Colourless crystals, m.p. 197°.

4-Nitro-m-2-xylidine; by nitrating *m-2-xylidine* with a mixture of nitric and sulphuric acids at 0° in presence of a little urea (Nölting and Stöcklin, Ber. 1891, 24, 564). Sulphur-coloured needles, m.p. 81°–82° (N. and S.).

Acetyl-derivative; from the nitroamine; by nitrating *m-2-acetoxylidide* dissolved in 5 parts of sulphuric acid with 1 mol. of nitric acid (97–98 p.c.) (N. and S.). Long white needles, m.p. 170° (N. and S.), or 167°–168° (N., B. and T.).

5-Nitro-m-2-xylidine; in low yield by heating 2:5-dinitro-*m*-xylene with methyl alcoholic ammonia for 32 hours at 200° (Ibbotson and Kenner, Chem. Soc. Trans. 1923, 123, 1260). Orange-yellow needles, m.p. 158°.

Acetyl-derivative; m.p. 178°.

4:6-Dinitro-m-2-xylidine; by the hydrolysis of the acetyl-derivative obtained by nitrating aceto-*m-2-xylidide* with 2 parts of nitric acid and 10 parts of sulphuric acid at 0° (N. and S.). Yellow needles, m.p. 177° (N. and S.), or small yellow leaflets, m.p. 174°–175° (N. and T.).

Acetyl-derivative; white needles, m.p. 225°–226° (N. and S.), or 226°–228° (decomp.) (Nölting and Thesmar, Ber. 1902, 35, 628).

Methyl-m-2-xylidine; by the action of methyl iodide on *m-2-xylidine* (Friedländer and Brand, Monath. 1898, 19, 627). Colourless

oil with an odour of camphor, volatile with steam, b.p. 207°. It does not react with aldehydes, nitrous acid, or diazonium compounds. $B_2H_3PtCl_6$, long yellow needles.

Acetyl-derivative; tables, m.p. 94°–95°, volatile with steam.

Dimethyl-m-2-xylydine; by the action of excess of methyl iodide and sodium hydroxide on *m-2-xylydine* for 5 hours at 130° under pressure (F. and B.). Oil, b.p. 195°–196° (F. and B.); E. Fischer and Windaus, Ber. 1900, 33, 345), with similar properties to the preceding compound. $B_2H_3PtCl_6$, yellow needles.

Ethyl-m-2-xylydine; colourless liquid of camphoraceous odour, b.p. 217°–218° (F. and B.). $B_2H_3PtCl_6$, prisms.

Diethyl-m-2-xylydine; colourless oil of camphoraceous odour, volatile with steam, b.p. 220°–221° (F. and B.). $B_2H_3PtCl_6$, small needles.

m-4-Xylydine, as-*m-xylydine*, *i-m-xylydine*, or α -xylydine; by treating *m-xylene* with hydroxylamine hydrochloride in presence of aluminium chloride (Graebe, Ber. 1901, 34, 1778); by reducing 4-nitro-*m-xylene* with iron and acetic acid (Deumelandt, Ann. 1867, 144, 273; Zeit. für Chem. 1866, 2, 21; Grevingk, Ber. 1884, 17, 2430; Tawildarow, Zeit. für Chem. 1870, 6, 418; Ber. 1869, 2, 553; Wallach, Ann. 1890, 258, 331; Wroblewsky, Ann. 1878, 192, 215; 1881, 207, 91); by heating aniline hydrochloride, *o*- and *p*-toluidine hydrochlorides with methyl alcohol at 250°–300° (Hofmann, Ber. 1876, 9, 1295; Limpach, Ber. 1888, 21, 640); by distilling (4:3:1:5)-amino-mesitylenic acid with lime (Schmitz, Ann. 1878, 193, 177); by heating *m-4-xylenol* with zinc ammonium bromide and ammonium bromide (Müller, Ber. 1887, 20, 1041); by the hydrolysis of its sulphonic acid with hydrochloric acid (Limpach, Ber. 1887, 20, 871); from commercial xylydine (Hodgkinson and Limpach, Chem. Soc. Trans. 1900, 77, 65; M. L. B., D. R. P. 87615 of 1895). Liquid, b.p. 215.8°–216°/728 mm. (Ullmann), b.p. 212°, D^{20}_D 0.9184 (H.), b.p. 216°, D^{18}_D 0.985 (T.). $BHCl$, monoclinic prisms (S.), tables or leaflets + $\frac{1}{2}H_2O$ (Städel and Hölz, Ber. 1885, 18, 2920), m.p. 235°, b.p. 253.1°/728 mm., or 255.1°/768 mm. (Ullmann, Ber. 1898, 31, 1699); $BHBr$, tables or columns (Städel, Ber. 1883, 16, 28; 1885, 18, 2920), or trimetric crystals (Bertram, Jahresberichte, 1882, 386); $BHNO_3$, rhombic tables; $B_2H_3SO_4 + 4\frac{1}{2}H_2O$, cubes (S. and H.; Nölting and Pick, Bull. Soc. chim. 1888, (2), 50, 606); $B_2H_3PO_4$ (Lewy, Ber. 1886, 19, 2728), colourless needles, m.p. 172° (Lemoult, Compt. rend. 1906, 142, 1193); $B_2H_3Br_2$ (Fries, Ber. 1904, 37, 2338; Ann. 1906, 346, 128); $B_2H_3C_2O_4$, m.p. 167° (Anselmino, Ber. Deut. pharm. Ges. 15, 422); telluribromide, small glistening plates (Guthier, &c., J. pr. Chem. 1912, (2) 86, 150); B_2ZnCl_4 (Lachovitch, Monatsch. 1888, 9, 514); $B_2HgH_2(SO_4)_2 + H_2O$; $B_2Cu_2H_2(SO_4)_2$ (Deniges, Compt. rend. 1890, 112, 870); $B_2H_3ZnCl_4$ (Tombeck, Ann. Chim. Phys. 1900, (7) 21, 438); $B_2H_3ZnBr_4$; $B_2H_3CdCl_4$; $B_2H_3CdBr_4$; $B_2H_3ZnI_4$; $B_2H_3CdI_4$; B_2ZnBr_4 (Tombeck, Ann. Chim. Phys. 1900, (7) 21, 408); B_2ZnI_4 ; $B_2Zn(NO_3)_4$; B_2CdCl_4 ; B_2CdBr_4 ; B_2CdI_4 ; $B_2Cd(NO_3)_4$; B_2CdSO_4 ; B_2AgNO_3 ; $B_2Ag_2SO_4$; see also Leeds (Jahresberichte,

1882, 504). $B_2C_2H_3SO_4H$, needles, m.p. 129.5° (Hälsig, J. pr. Chem. 1897, (2) 56, 218). $B_2C_2H_3(NO_3)_4$, reddish-brown crystals, m.p. 96°–98° (Nölting and Sommerhoff, Ber. 1906, 39, 76); $B_2C_2H_3(CH_3)(NO_2)_2$, red crystals, m.p. 43°–45°; $B_2C_2H_3OH$, m.p. 16° (Kremann, Monatsch. 1906, 27, 91). *Formyl-derivative*, needles or leaflets, m.p. 113°–114° (Hodgkinson and Limpach; Gasiorowski and Merz, Ber. 1885, 18, 1011); or m.p. 111° (Gudemann, Ber. 1888, 21, 2549); *acetyl-derivative* (Auwers, J. pr. Chem. 1881, 23, 456), m.p. 129°–130° (Nölting and Forel, Ber. 1885, 18, 2677; Städel and Hölz, or m.p. 127°–128° (Willgerodt and Schmierer, *ibid.* 1904, 38, 1472; Töhl, Ber. 1885, 18, 359; Hofmann, Ber. 1876, 9, 1297; Wroblewsky, Ann. 1881, 207, 91), or 120° (Graebe); *diacetyl-derivative*, crystals, m.p. 60° (Wallach, Ann. 1890, 258, 330); *phenyl-derivative*, m.p. 157°–158° (S. and H.); *benzoyl-derivative*, needles, m.p. 192° (Hübner, Ann. 1881, 208, 318), or 187°–189° (Gudemann, Ber. 1888, 21, 2549); *benzylidene-derivative*, oil, b.p. above 300° (Michaelis, Ann. 1893, 274, 200).

When *m-4-xylydine* is heated with potassium ethyl oxalate at 180°–190°, oxalxylydic acid, $C_8H_8NHCOCOOH$, needles + H_2O , m.p. 128°–129°, is obtained. On heating, this acid forms oxalxylydide, flat needles, m.p. 210° (Mauthner and Suida, Monatsch. 1888, 9, 736). *m-4-Xylydine* forms a carbamate, m.p. 57°, a cyanate, b.p. 205°, and a cyanurate, m.p. 162° (Frentzel, Centralblatt, 1888, 1361). The *acetyl-derivative* of *m-4-xylydine*, when heated with phosphorus pentasulphide, is converted into thioaceto-*m-4-xylydide*, m.p. 94°–95° (Jacobsen and Ney, Ber. 1889, 22, 904; Gudemann, Ber. 1888, 21, 2551). When treated with paraldehyde in presence of hydrochloric acid, *m-4-xylydine* forms dimethylquinaldine, m.p. 146°, b.p. 260°/719 mm., readily volatile with steam (Panajotow, Ber. 1887, 20, 32). Diamino-dimethylstilbene sulphide is obtained by heating *m-4-xylydine* with $\frac{1}{2}$ of its weight of sulphur at 185°–195°, until the evolution of hydrogen sulphide ceases (Anschütz and Schultz, Ber. 1889, 22, 580).

m-4-Xylydine may be converted by the Sandmeyer reaction into 4-iodo-*m-xylene*, which on treatment with concentrated sulphuric acid and keeping for about 5 weeks yields a mixture of 4-iodo-*m-xylene* 6-sulphonic acid and a diiodo-*m-xylene* (Hammerlich, Ber. 1890, 23, 1634). *m-4-Xylydine* forms the nitrile, $C_8H_7(CH_3)_2CN$, m.p. 23°–24°, which on treatment with hydroxylamine for 5 to 6 hours, at 80°–85°, is converted into xylenylamidoxime, colourless needles, m.p. 178° (Oppenheimer, Ber. 1889, 22, 2242). Aceto-*m-4-xylydide*, when heated with an equal weight of sodium ethoxide in the absence of air at 250°–300°, followed by addition of water and distillation with steam, yields 2:5-dimethyl-indole, m.p. 114°, whilst the free base on treatment with succinic anhydride yields 2:4-xylylsuccinamic acid, m.p. 164° (Salway, Chem. Soc. Trans. 1913, 103, 1988; Raschen, Ann. 1887, 239, 227).

With phosphorus pentachloride *m-4-xylydine* forms the chloride, $PCl(NH-C_8H_7)_2$, m.p. 264° (decomp.); the corresponding nitrate, $P(NH-C_8H_7)_2NO_3$, forms silky needles, m.p. 246°–248° (Lemoult, Compt. rend. 1904, 139,

185). *m*-4-Xylidine nitrite is obtained by treating *m*-4-xylidine hydrochloride in concentrated aqueous solution with alkaline sodium nitrite (Wallach, Ann. 1907, 353, 318). When acetaldehyde is added to a solution of *m*-4-xylidine in dilute hydrochloric acid and the mixture is kept for 24 hours, condensation occurs, and a mixture of 2-isomeric substances, $C_8H_9(CH_3)_2NHCH(CH_3)CH_2CHO$, is eventually obtained (Miller, Plöchl and Mozdzyński, Ber. 1896, 29, 1462). The derivatives and relationship of these substances have been described and re-examined by Edwards, Garrod and Jones (Chem. Soc. Trans. 1912, 101, 1376). With iodine monochloride, *m*-4-xylidine yields 5-iodo-*m*-4-xylidine, m.p. 65°, and when 2 mols. of iodine chloride are used the iodo-derivative is accompanied by a small quantity of 3:5:3':5'-tetramethyl-2:2'-diaminodiphenyl, m.p. 180° (Kerschbaum, Ber. 1895, 28, 2798). By heating 1 part of *m*-4-xylidine with 4 parts of sulphur and 1 part of aniline at 200°–240°, an isomeric derivative of dehydrothio-*p*-toluidine is obtained (Green and Jansen, Eng. Pat. 4448 of 1895). When *m*-4-xylidine is kept in contact with acetylbenziminio-ethylether and the acetyl-group is then hydrolysed, *m*-4-xylidylbenzamine, m.p. 106°, is formed (Wheeler and Walden, Amer. Chem. J. 1898, 20, 568). Treatment of *m*-4-xylidine with chloroacetic acid in ethereal solution yields *α*-*m*-xylidylglycine, m.p. 133° (Ehrlich, Ber. 1883, 16, 204). *m*-4-Xylidine hydrochloride is converted into mesidine by heating with methyl alcohol at 250°–300° (Limpach, Ber. 1888, 21, 640, 643). *m*-4-Xylidine, heated with a mixture of ethylene dibromide and sufficient sodium carbonate to neutralise the hydrogen bromide evolved, is converted into di-*m*-xylidylethylenediamine, feathery needles, m.p. 74°–75° (Senior and Goodwin, Chem. Soc. Trans. 1901, 79, 254). *as*-*m*-4-Xylidylphthalimide, yellow needles, m.p. 142°–143°, *m*-4-xylidylphthalimide, silky needles, m.p. 202°–203°, and *s*-*m*-4 xylidylphthalimide, m.p. 154°, are formed by the interaction of phthalyl chloride and *m*-4-xylidine in ethereal solution. The first named substance is converted by mineral acids or alkalis into *s*-*m*-xylidylphthalimide (Kuhara and Komatsu, Mem. Coll. Sci. Eng. Kyōto, 1910, 2, 365).

5-Chloro-m-4-xylidine; by the hydrolysis of its acetyl-derivative (Orton and King, Chem. Soc. Trans. 1911, 99, 1185). Feathery needles, volatile with steam, m.p. 37°–38° (O. and K.), or 40°–41° (Bamberger and Reber, Ber. 1913, 46, 800).

Acetyl-derivative; by treating aceto-*m*-4-xylidine in glacial acetic acid solution with 1 equivalent of acetylchloroamino-2:4-chlorobenzene in acetic acid and $\frac{1}{10}$ gram molecular proportion of hydrochloric acid for 70 hours in the dark. The mixture is then diluted to 50 p.c. acetic acid, and kept for 3 days, when the major portion of the 2:4-dichloroacetanilide separates. Finally the mother liquor is diluted to 5 p.c. acetic acid, and extracted with chloroform (O. and K.). Short prisms, m.p. 196°–5°–197°–5°.

6-Chloro-m-4-xylidine; by reducing 6-nitro-4-chloro-*m*-xylene with tin and hydrochloric acid (Bamberger and Reber, Ber. 1913, 46, 787); by the action of concentrated hydro-

chloric acid on *m*-xylidyl-4-hydroxylamine (Cadgène, Dissertation, Zürich, 1903, 61). Leaflets, m.p. 98°–99°, readily volatile with steam.

Acetyl-derivative; silky needles, m.p. 158°–5° (B. and K.).

Chloro-m-4-xylidine; together with *m*-4-xylidine by reducing 4-nitro-*m*-xylene with tin and hydrochloric acid (Tawildarow, Zeit. für Chem. 1870, 6, 419). Crystals, m.p. 89°.

2:5:6-*Trichloro-m-4-xylidine*; by treating aceto-*m*-4-xylidide with nitric acid (D 1398) and hydrochloric acid (D 119) and then hydrolysing the acetyl-group (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20). Crystals, m.p. 203°.

Acetyl-derivative; white needles, m.p. 192°.

2-*Bromo-m-4-xylidine*; by reducing 2-bromo-4-nitro-*m*-xylene (Nölting, Braun and Thesmar, Ber. 1901, 34, 2242). Colourless silky needles, m.p. 47°–48°.

Acetyl-derivative; small colourless needles, m.p. 151°–152° (N., B. and T.; Fries, Ann. 1906, 346, 128).

p-*Nitrobenzylidene derivative*; small yellow needles, m.p. 182°–183°.

5-*Bromo-m-4-xylidine*; by brominating *m*-4-xylidine in acetic acid solution (N., B. and T.; cf. Vaubel, J. pr. Chem. 1896, (2) 53, 549); by reducing 5-bromo-4-nitro-*m*-xylene (N., B. and T.); from 4-nitro-*m*-5-xylidine by the Sandmeyer reaction, followed by reduction (N., B. and T.); by brominating *m*-4-xylidine in presence of a large excess of cold hydrochloric acid or hydrobromic acid and treating the yellowish-red crystalline mass with warm hydrochloric acid (E. Fischer and Windaus, Ber. 1900, 33, 1967; Fries, Ber. 1904, 37, 2338; Ann. 1906, 346, 128). Prisms, m.p. 45° [V.], or 46°–47° (F. and W.), or colourless silky needles, m.p. 47°–48° (N., B. and T.).

Acetyl-derivative; by acetylating the base. Prisms or needles, m.p. 193° [V.], or 196°–197° (F. and W.). When aceto-*m*-4-xylidide is brominated, however, an isomeric bromoacetyl-*m*-4-xylidide, m.p. 95°–96°, is obtained [V.]; *diacetyl-derivative*, prisms, m.p. 59°.

p-*Nitrobenzylidene-derivative*; yellow needles, m.p. 130°.

6-*Bromo-m-4-xylidine*; by reducing 6-nitro-4-bromo-*m*-xylene (N., B. and T.; Bamberger and Reber, Ber. 1913, 46, 787); as the main product of the bromination of *m*-4-xylidine in presence of concentrated sulphuric acid (Fries). White plates, volatile with steam, m.p. 99°–100° (N., B. and T.), or m.p. 96° (Jaeger and Blankens, Rec. trav. chim. 1907, 25, 352; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153; Genz, Ber. 1870, 3, 225).

Acetyl-derivative; plates, m.p. 168°–169° (N., B. and T.); *diacetyl-derivative*, plates, m.p. 70° (Fries, Ann. 1906, 346, 128).

p-*Nitrobenzylidene derivative*; yellow needles, m.p. 130° (N., B. and T.).

2:6-*Dibromo-m-4-xylidine*; by the hydrolysis of the acetyl-derivative (J. and B.). Crystals, m.p. 65°.

Acetyl-derivative; together with a mono-bromo-aceto-*m*-4-xylidide by brominating aceto-*m*-4-xylidide (J. and B.).

5:6-*Dibromo-m-4-xylidine*; from 6-bromo-*m*-4-xylidine by the action of bromine in presence

of hydrochloric acid (J. and B.), rather than from 5-bromo-*m*-4-xyldine (Fries, Ann. 1906, 346, 128). Needles, m.p. 38° (J. and B.), or m.p. 40° (F.).

Acetyl-derivative; needles, m.p. 192° (F.); *diacetyl-derivative*, prisms, m.p. 183° (F.).

2:5:6-*Tribromo-m-4-xyldine*; by the hydrolysis of the acetyl-derivative, m.p. 246°–248°, obtained by boiling aceto-*m*-4-xyldide with nitric acid (D 1398) and hydrobromic acid (D 148) (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20).

Methyl-m-4-xyldine; by heating *m*-4-xyldine hydrochloride with methyl alcohol, for 7 hours at 170°–180°, treating the crude product with sodium nitrite and hydrochloric acid, and reducing the nitrosoamine with tin and hydrochloric acid (Pinnow and Oesterreich, Ber. 1898, 31, 2926). Oil, b.p. 220.5°–221.5°/760 mm.

N-Nitroso-derivative; an uncrystallisable oil.

Acetyl-derivative; fine white needles and thick prisms, m.p. 65° (P. and O.).

Dimethyl-m-4-xyldine; by heating *m*-4-xyldine with dimethyl sulphate at 200° (Bielecki and Koleniew, Anzeiger Akad. Wiss. Krakau, 1908, 296); by heating *m*-4-xyldine hydrobromide with methyl alcohol (Baur and Städel, Ber. 1883, 16, 32); by distilling the quaternary hydroxide (E. Fischer and Windaus, Ber. 1900, 33, 345). Oil, b.p. 203° (F. and W.), or 203°–205° (B. and S.); *methiodide*, m.p. 183° (decomp.); *methochloride* is hygroscopic (F. and W.).

5-Bromo-dimethyl-*m*-4-xyldine; oil, b.p. 246°–247°/759 mm. (E. Fischer and Windaus, Ber. 1900, 33, 1967). $B'H_2PtCl_6$, yellowish-red lanceolate crystals.

2-Nitro-*m*-4-xyldine; by reducing 2:4-dinitro-*m*-xylene with hydrogen sulphide in alcoholic ammoniacal solution; in small quantity by treating *m*-4-xyldine with a mixture of nitric and sulphuric acids (Grevingk, Ber. 1884, 17, 2425, 2428; Nölting, Braun and Thesmar, Ber. 1901, 34, 2242). Golden-yellow needles, m.p. 78° (G.), or 81°–82° (N., B. and T.).

Acetyl-derivative; white needles, m.p. 149° (G.), or 147° (Blanksma, Rec. trav. chim. 1909, 28, 92); *benzoyl-derivative*, white silky needles, m.p. 236° (Errera and Maltese, Gazz. chim. ital. 1903, 33, ii. 277).

5-Nitro-*m*-4-xyldine; by nitrating aceto-*m*-4-xyldide and hydrolysing the product (Hofmann, Ber. 1876, 9, 1292; Wroblewsky, Ann. 1881, 207, 91; Nölting and Collin, Ber. 1884, 17, 261; Töhl, Ber. 1885, 18, 359; Nölting and Forel, Ber. 1885, 18, 2068; Gabriel and Stelzner, Ber. 1896, 29, 303; Willgerodt and Schmierer, Ber. 1905, 38, 1472; Blanksma, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 170; Rec. trav. chim. 1906, 25, 165); by heating 5:6-dinitro-*m*-xylene with alcoholic ammonia for 3 hours at 180° (Blanksma), or with methyl alcoholic ammonia for 14 hours at 160° (Ibbotson and Kenner, Chem. Soc. Trans. 1923, 123, 1260). Long red needles, m.p. 67°–68° (I. and K.), 69° (H.), or 76° (W.; N. and F.; B.; G. and S.).

Acetyl-derivative; yellowish needles, pale yellow octahedra or colourless needles, m.p. 171° (I. and K.), 172°–173° (H.; T.; W. and S.), or 180° (W.; B.).

5-Nitro-*m*-4-xylylcarbimide forms microscopic yellow needles, m.p. 71°–72° (Vittenet, Bull. Soc. chim. 1899, (3) 21, 586, 948, 952). 5-Nitro-*m*-4-xyldine on treatment with sodium nitrite and dilute sulphuric acid is converted into 1:3-nitromethyl-indazole (G. and S.), but when diazotised and the solution treated with concentrated potassium hydroxide, potassium-5-nitro-*m*-xyleneisodiazooxide, pale yellow leaflets, is formed. This is oxidised with difficulty by potassium ferricyanide to 5-nitro-*m*-4-xylylnitramine, long vitreous yellow needles, m.p. 90°–91°, and 5-nitro-*m*-xylene (Bamberger and von Goldberger, Ber. 1920, 53, 2321).

6-Nitro-*m*-4-xyldine; by hydrolysing 6-nitro-*m*-4-xyldine 5-sulphonic acid with boiling hydrochloric acid (Jungbahn, Ber. 1902, 35, 3747); by the partial reduction of 4:6-dinitro-*m*-xylene with alcoholic ammonium sulphide (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 18; Morgan, Micklethwait and Couzens, Chem. Soc. Trans. 1906, 89, 1289; Morgan and Micklethwait, *ibid.* 1907, 91, 360; Blanksma, Rec. trav. chim. 1909, 28, 92); together with 2-nitro-*m*-4-xyldine by nitrating *m*-4-xyldine with nitric and sulphuric acids (Nölting and Collin, Ber. 1884, 17, 261; Pearman, Chem. Soc. Trans. 1921, 119, 717). Orange-red needles, m.p. 123° (M., M. and C.).

Acetyl-derivative; monoclinic plates (Errera and Maltese, Gazz. chim. ital. 1903, 33, ii. 277), m.p. 160° (B.), or m.p. 159°–160° (Pearman); *diacetyl-derivative*, anorthic elongated colourless plates, m.p. 115°, converted into the monoacetyl-derivative, m.p. 161°, by boiling with dilute alcohol (Ahrens, Ann. 1892, 271, 15; E. and M.); *benzoyl-derivative*, white silky needles, m.p. 200° (E. and M.); *benzenesulphonyl-derivative*, colourless prismatic crystals, m.p. 148.5°, converted by methylation into benzenesulphonylmethyl-6-nitro-*m*-4-xyldide, m.p. 185° (M., M. and C.); *toluene-p-sulphonyl-derivative*, m.p. 192° (M. and M.); 6-nitro-*m*-4-xylylcarbimide, b.p. 212°–214°/97 mm., m.p. about 0° (Vittenet); the dinitro-dixylylcarbimide forms microscopic needles, which sublime (V.).

2:5-Dinitro-*m*-4-xyldine; by nitrating aceto-*m*-4-xyldide with nitric acid and sulphuric acid and keeping the mixture for 6–8 hours (Klages, Ber. 1896, 29, 310), or by nitrating with nitric acid [D 152] (Blanksma, Rec. trav. chim. 1909, 28, 92), followed by hydrolysis. Colourless needles, m.p. 115°, which deflagrate when heated (K.).

Acetyl-derivative? colourless needles, m.p. 226° (K.), or 233° (B.).

2:6-Dinitro-*m*-4-xyldine; by reducing 2:4:6-trinitro-*m*-xylene with ammonium sulphide (Miolati and Lotti, Gazz. chim. ital. 1897, 27, i. 296; Ibbotson and Kenner, Chem. Soc. Trans. 1923, 123, 1260; cf. Maltese, Gazz. chim. ital. 1909, 39, i. 517). Orange-yellow needles or dark-red prisms, m.p. 145°, or amber-coloured elongated rectangular prisms, m.p. 193° (I. and K.); *acetyl-derivative*, transparent lozenge-shaped crystals, m.p. 176° (I. and K.); *benzoyl-derivative*, by benzoylating the amine, also by nitrating 2-nitro-4-benzoylamino-*m*-xylene. Shining lamellae, m.p. 244° (M.), or colourless prismatic needles, m.p. 212° (I. and K.). The products described by Maltese appear to be of doubtful orientation.

5:6-Dinitro-*m*-4-xylidine; by nitrating 5-nitro-aceto-*m*-4-xylidide at the ordinary temperature with nitric acid and sulphuric acid (Blanksma, *Rec. trav. chim.* 1906, 25, 165; *Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 70), or by nitrating 6-nitro-aceto-*m*-4-xylidide with nitric acid (D 1.52), or with a mixture of nitric and sulphuric acids, followed by hydrolysis (Blanksma, *Rec. trav. chim.* 1909, 23, 92). Yellow crystals, m.p. 170°.

Acetyl-derivative; yellow crystals, m.p. 217°.

5-Bromo-6-nitro-*m*-4-xylidine; by brominating 6-nitro-*m*-4-xylidine (Nölting, Braun and Thesmar, *Ber.* 1901, 34, 2242). Large prisms, m.p. 66°–67°.

5-Nitromethyl-*m*-4-xylidine; by boiling the nitrosamine with aniline and hydrochloric acid in alcoholic solution for 14 hours (Pinnow and Oesterreich, *Ber.* 1898, 31, 2926). Long carmine-red plates with a green reflex, m.p. 58°.

Nitrosamine; by nitrating the xylylmethyl-nitrosamine with nitric acid (D 1.4) at low temperatures (P. and O.). Yellowish crystalline powder, m.p. 63°.

6-Nitro-4-methylamino-*m*-xylene; *toluene-*p*-sulphonyl-derivative*, colourless prismatic crystals, m.p. 135°–136°, obtained by treating toluene-*p*-sulphonyl-6-nitro-*m*-4-xylidine with methyl iodide and alcoholic soda (Morgan and Micklethwait); *benzene-sulphonyl derivative*, colourless prisms, m.p. 184°–185° (Morgan, Micklethwait and Couzens, *Chem. Soc. Trans.* 1906, 89, 1289).

6-Nitro-4-dimethylamino-*m*-xylene; by heating a mixture of the hydrobromide of 6-nitro-*m*-4-xylidine and methyl alcohol for 5 hours at 160° (Morgan and Micklethwait, *Chem. Soc. Trans.* 1907, 91, 360). It forms a picrate which melts with violent decomposition at 170°–173°.

***m*-4-Xylidine 6-sulphonic acid**; by heating *m*-xylene 4-sulphonamic acid at 220°–230° for a short time; in low yield together with the 6-sulphonic acid as main product by adding *m*-xylidine to boiling chlorosulphonic acid; by heating the acid sulphate of *m*-xylidine at 210°–230° for 2½–3 hours under reduced pressure, or heating the sulphate similarly with four times its weight of *m*-xylidine (Junghahn, *Ber.* 1902, 35, 3747); by heating *m*-xylidine sulphate at 160° and then at 220° while a current of carbon dioxide or air is passed through the mass (Junghahn, *Chem. Ind.* 1903, 26, 57); by heating *m*-4-xylidine with 1 mol. of 100 p.c. sulphuric acid at 185°–195° for 6 hours (Armstrong and Wilson, *Chem. Soc. Proc.* 1900, 17, 229). Anhydrous rhombic plates. The sulphonic group is removed when the acid is heated with concentrated hydrochloric acid for 1½ hours at 150°–155° (J.). KA', anhydrous white leaflets; NaA', leaflets; BaA', +2H₂O, quadratic tables; PbA', anhydrous white needles; AgA', anhydrous white needles (J.).

Potassium acetyl-*m*-4-xylidide 5-sulphonate; spindle-shaped needles, by acetylating potassium *m*-4-xylidine 5-sulphonate (A. and W.).

***m*-4-Xylidine 6-sulphonic acid**; by sulphonating aceto-*m*-4-xylidide at 140° with 1½ times its weight of 20 p.c. fuming sulphuric acid and boiling the solution after the addition of water (Moody, *Chem. Soc. Proc.* 1891, 7, 189); by sulphonating *m*-4-xylidine with slightly fuming sulphuric acid at 140°–150° (Jacobsen and Ledderboge, *Ber.* 1883, 16, 193; cf. Deume-

landt, *Zeit. für Chem.* 1866, 2, 22; Limpriht, *Ber.* 1885, 18, 2172); by reducing 4-nitro-*m*-xylene 6-sulphonic acid with ammonium sulphide (J. and L.); by the nitration and subsequent reduction of *m*-xylene 4-sulphonic acid, or by sulphonating *m*-4-xylidine (Nölting and Kohn, *Ber.* 1886, 19, 137); by heating symm.-di-*m*-xylyl carbamide with sulphuric acid (D 1.711) at 150°–160° (Cazeneuve and Moreau, *Bull. Soc. chim.* 1898, (3) 19, 21). Long flat needles. NaA' + H₂O, large transparent rhombic plates; KA', large transparent rhombic plates; BaA' + H₂O, aggregates of microscopic needles (J. and L.), or +2H₂O (Sartig, *Ann.* 1885, 230, 333; Nölting and Kohn). When treated with nitric acid the sulphonic acid does not yield a nitroamine but forms 2-nitro-4-diazo-*m*-xylene 6-sulphonic acid, needles, which explode on heating (Zincke and Maué, *Ann.* 1905, 339, 202).

Acetyl-derivative; by treating aceto-*m*-4-xylidide with 3 times its weight of fuming sulphuric acid and keeping at the ordinary temperature until dissolved (Junghahn, *Ber.* 1900, 33, 1364).

6-Nitro-*m*-4-xylidine 5-sulphonic acid; needles + 1½H₂O (Junghahn, *Ber.* 1902, 35, 3747). KA', glistening golden-yellow needles + H₂O, or pale yellow needles when anhydrous. The free acid yields 6-nitro-*m*-4-xylidine when boiled with hydrochloric acid.

5-(?)Bromo-*m*-4-xylidine 6-sulphonic acid; by brominating the sulphonic acid in alkaline solution, followed by acidification, or by the action of bromine or hydrobromic acid on a solution in glacial acetic acid. No dibromoderivative could be obtained, as attempted further bromination eliminated the sulphonic group (Nölting and Kohn, *Ber.* 1886, 19, 137).

Nitro-*m*-4-xylidine 6-sulphonic acid; by nitrating *m*-4-xylidine 6-sulphonic acid (Sartig, *Ann.* 1885, 230, 333; Limpriht, *Ber.* 1885, 18, 2172). KA' + 1½H₂O, large rhombic plates; BaA' + 1½H₂O, yellow rhombic plates; PbA' + H₂O, yellow glistening needles.

***m*-5-Xylidine, or *s*-*m*-xylidine**; by reducing 5-nitro-*m*-xylene (Wroblewski, *Ann.* 1881, 207, 95; Töhl, *Ber.* 1885, 18, 362; Nölting and Forel, *Ber.* 1885, 18, 2678; Noyes, *Amer. Chem. J.* 1888, 20, 789; Willgerodt and Schmierer, *Ber.* 1906, 38, 1472); from mesitylene and from *m*-4-xylidine (Haller, Adams and Wherry, *J. Amer. Chem. Soc.* 1920, 42, 840). Liquid, b.p. 220°–221°, D₂₀ 0.9035, or b.p. 220°/739 mm., D₂₀ 0.972 (N. and F.). B'HCl, long needles; B'HNO₃, long needles; B'H₂SO₄ + H₂O; B'H₂PO₄, needles (Raikow and Scharbanow, *Chem. Zeit.* 1901, 25, 244); B'H₂PO₄, crystals (R. and S.).

Formyl-derivative, prisms, m.p. 76.5° (Limpach, *Ber.* 1888, 21, 643). **Acetyl-derivative**; large flat needles, m.p. 144.5° (W.), or 138° (Töhl, *Ber.* 1885, 18, 362), or 140.5° (Nölting and Forel, *ibid.* 2678), or m.p. 139.6°–140.2°, n_D 1.45, n_F 1.69 (H., A. and W.).

***m*-5-Xylidine** when heated with methyl alcohol at 250°–300° yields isocumidine (Limpach; Nölting and Forel), and forms *m*-xyloquinone when oxidised (Nölting and Forel, *Bull. Soc. chim.* 1884, 42, 332).

4-Chloro-*m*-5-xylidine; together with a little dichloro-*m*-5-xylidine by reducing 4-chloro-5-nitro-*m*-xylene with tin and hydrochloric acid

Klages, Ber. 1896, 29, 310). Oil, b.p. 251°, solidifying on cooling. It combines with the carbon dioxide of the air, and forms a *benzoyl-derivative*, m.p. 218°.

Dichloro-m-5-xylidine (see above). Colourless needles, m.p. 72°, b.p. 265°–266°; *benzoyl-derivative*, m.p. 158° (K.).

2:4:6-Tribromo-*m-5-xylidine*; by brominating *m-5-xylidine* in glacial acetic acid solution (Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153). Colourless prisms, m.p. 195°.

2-Nitro-*m-5-xylidine*; together with the 4-nitro-isomerido by nitrating a sulphuric acid solution of *m-5-xylidine* with nitric and sulphuric acids (Ibbotson and Kenner, Chem. Soc. Trans. 1923, 123, 1260). Orange rectangular prisms, m.p. 132°. *Acetyl-derivative*; prisms, m.p. 163°.

4-Nitro-*m-5-xylidine*; in small quantity by heating 4:5-dinitro-*m-xylene* with methyl alcoholic ammonia for 14 hours at 160° (Ibbotson and Kenner); by nitrating a solution of *m-5-xylidine* in sulphuric acid with a mixture of nitric and sulphuric acids (Nölting and Forel, Ber. 1885, 18, 2668; Ibbotson and Kenner). It melts at 56° (I. and K.), or 54° (N. and F.). *Acetyl-derivative*, m.p. 114° (I. and K.).

2:6-Dinitro-*m-5-xylidine*; by the action of alcoholic ammonia on 2:5:6-trinitro-*m-xylene* (Blanksma, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). It melts at 94°.

4:6-Dinitro-*m-5-xylidine*; by partial reduction of 4:5:6-trinitro-*m-xylene* (Blanksma, Rec. trav. chim. 1909, 28, 92), or by the action of alcoholic ammonia on the corresponding trinitro-*xylene* at 110° (Blanksma, Rec. trav. chim. 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). Yellow crystals, m.p. 101°.

2:4:6-Trinitro-*m-5-xylidine*; by treating 2:4:6-trinitro-5-chloro-*m-xylene* with alcoholic ammonia at 130° (Klages and Knoevenagel, Ber. 1895, 28, 2044). Yellowish-brown needles, which sublime, m.p. 206°. *Phenylamino-derivative*, long yellow needles, m.p. 175° (K. and K.).

4-Chloro-2:6-dinitro-*m-5-xylidine*; by heating 4-chloro-2:5:6-trinitro-*m-xylene* with alcoholic ammonia for 2 hours on the water-bath (Blanksma). Yellow crystals, m.p. 186°.

2-Bromo-4:6-dinitro-*m-5-xylidine*; by the action of ammonia at 150° on 2:5-dibromo-4:6-dinitro-*m-xylene* (Blanksma); by the action of bromine on 4:6-dinitro-*m-5-xylidine* in glacial acetic acid solution (Blanksma). Yellow crystals, m.p. 183°.

4-Bromo-2:6-dinitro-*m-5-xylidine*; by brominating 2:6-dinitro-*m-5-xylidine* (Blanksma); by the action of alcoholic ammonia on 4-bromo-2:5:6-trinitro-*m-xylene* or 4:5-dibromo-2:6-dinitro-*m-xylene* (Blanksma). It melts at 186°.

Dimethyl-m-5-xylidine; liquid, b.p. 226.5°–227.5° (Nölting, Ber. 1891, 24, 563; cf. Limpach, Ber. 1888, 21, 643). The trimethylammonium iodide forms white needles (N.).

2-Nitroso-*derivative*, greenish-yellow needles or green prisms, m.p. 104° (Pechmann and Nold, Ber. 1896, 31, 557).

2:6-Dinitromethyl-*m-5-xylidine*; by the

action of methylamine on 2:5:6-trinitro-*m-xylene* (Blanksma, Rec. trav. chim. 1902, 21, 327; 1906, 25, 165; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 70). Yellow crystals, m.p. 27°. When nitrated with nitric acid (D 1.52) it yields 2:4:6-trinitro-*m-xylidyl-5-methylnitramine*, m.p. 181° (B.).

4:6-Dinitromethyl-*m-5-xylidine*; by the action of methylamine on 4:5:6-trinitro-*m-xylene* (B.). Yellow crystals, m.p. 85°. When nitrated with nitric acid (D 1.52) it yields 2:4:6-trinitro-*m-xylidyl-5-methylnitramine*, m.p. 81° (B.).

2:4:6-Trinitromethyl-*m-5-xylidine*; by the action of methylamine on trinitro-*m-xylidylmethyl ether* (B.). Yellow crystals, m.p. 164°.

2:4:6-Trinitroethyl-*m-5-xylidine*, crystals, m.p. 122° (B.).

2-Bromo-4:6-dinitromethyl-*m-5-xylidine*; by brominating 4:6-dinitromethyl-*m-5-xylidine*, or by the action of methylamine at 170° on 2:5-dibromo-4:6-dinitro-*m-xylene* (B.). Long yellowish-red needles, m.p. 146°. When nitrated it yields 2-bromo-4:6-dinitro-*m-xylidyl-5-methylnitramine*, m.p. 103° (B.).

4-Bromo-2:6-dinitromethyl-*m-5-xylidine*; by the action of methylamine on 4-bromo-2:5:6-trinitro-*m-xylene* or 4:5-dibromo-2:6-dinitro-*m-xylene* (B.); by brominating 2:6-dinitromethyl-*m-5-xylidine* in glacial acetic acid (B.). It melts at 175°–176°, and on nitration yields the *nitramine*, m.p. 152° (B.).

2-Nitrosoethyl-*m-5-xylidine*; by ethylating *m-5-xylidine* with ethyl bromide, treating the product with nitrous acid, heating the nitrosoamine with alcoholic hydrochloric acid and basifying the yellow hydrochloride with ammonia (O. Fischer and Cammerloher, Ber. 1901, 34, 948). It forms steel-blue needles, m.p. 138°.

2:4-Diamino-*m-xylene*; by reducing 2:4-dinitro-*m-xylene* with tin and hydrochloric acid (Grevingk, Ber. 1884, 17, 2427; Nölting and Thesmar, Ber. 1902, 35, 628), or with iron and dilute hydrochloric acid (Morgan, Chem. Soc. Trans. 1902, 81, 86); by reducing β -dinitro-mesitylenic acid with tin and hydrochloric acid (Bamberger and Demuth, Ber. 1901, 34, 27). White needles, m.p. 65°–66° (N. and T.), or 64° (G.).

Di-formyl-derivative; colourless needles, m.p. 219°–220° (M.); *diacetyl-derivative*, felted needles, m.p. above 260° (M.); *dibenzoyl-derivative*, felted needles, m.p. 232° (M.), or m.p. 226°–5–227.5° (B. and D.).

6-Nitro-2:4-diamino-*m-xylene*; by reducing 4:6-dinitro-*m-2-xylidine* with ammonium sulphide (N. and T.). Long slender orange-coloured needles, m.p. 151°–152°.

2:5-Diamino-*m-xylene*; in a similar manner to the 2:4-diamino-*m-xylene* (N. and T.); by reducing 2-nitro-*m-5-xylidine* with stannous chloride (Ibbotson and Kenner, Chem. Soc. Trans. 1923, 123, 1260); by coupling *m-xylidine* with diazobenzene-*m-sulphonic acid* and reducing the product (N. and T.). Pearly plates, m.p. 103°–104° (N. and T.), or 101° (I. and K.).

Benzoyl-derivative; m.p. 234° (Klages, Ber. 1896, 29, 310).

4-Chloro-2:5-diamino-*m-xylene*; by reducing 4-chloro-2:5-dinitro-*m-xylene* with tin and

hydrochloric acid in alcoholic solution (Klages). Oil, volatile with steam, b.p. 280°–281°.

Benzoyl-derivative, m.p. 164°.

4 : 6-Dichloro-2 : 5-diamino-m-xylene; by reducing a suspension of 2 : 5-dinitro-4 : 6-dichloro-m-xylene in alcohol with stannous chloride (Claus and Runschke, J. pr. Chem. 1890, (2) 42, 110). White prisms or needles when pure, m.p. 176°. B'HCl, needles; B',H₂PtCl₆, yellowish-red scales, decomposing about 230°.

4 : 5-Diamino-m-xylene; by reducing 2 : 4-dibromo-5 : 6-dinitro-m-xylene with tin and hydrochloric acid (Jacobsen, Ber. 1888, 21, 2821); by reducing 5-nitro-m-4-xylydine with tin and hydrochloric acid (Hofmann, Ber. 1876, 9, 1292; N. and T.); by reducing aminoazo-m-xylene with tin and hydrochloric acid (Nölting and Forel, Ber. 1883, 18, 2683). Leaflets, flat needles, or rhombic plates, m.p. 77°–78° (N. and T.), m.p. 78·5° (J.), or m.p. 74°–75° (H.).

2 : 4-(or 4 : 5-) Diamino-m-xylene 6-sulphonic acid; by boiling 2-(or 5-) nitro-m-4-xylydine 6-sulphonic acid with a mixture of stannous chloride and hydrochloric acid (Sartig, Ann. 1885, 230, 333; Limpricht, Ber. 1885, 18, 2172). Prisms. The aqueous solution is coloured wine-red by ferric chloride. KA' + H₂O, slender prisms; BaA', + 3H₂O, microscopic tables; PbA₂, prisms; B'HCl + H₂O, prisms.

4-Methyl-4 : 5-diamino-m-xylene; by reducing 5-nitromethyl-m-4-xylydine with tin and hydrochloric acid (Pinnow and Oesterreich, Ber. 1898, 31, 2926). Oil, b.p. 260°–262°. B'HCl, m.p. 225°.

Nitrosoamine, white plates, m.p. 81°; picrate, light yellow prisms, m.p. 128°; acetyl-derivative, white plates, m.p. 135°; phenylthiocarbamide, prisms, m.p. 132°–132·5°.

4-Acetomethylamino-5-acetamino-m-xylene; needles, m.p. 195°–196° (P. and O.).

4 : 5-Dimethylamino-m-xylene; by reducing 1 : 3 : 4 : 6-tetramethylhydrobenzimidazole-2-ol with sodium and alcohol (O. Fischer and Römer, J. pr. Chem. 1906, (2) 73, 419). Oil, b.p. 245°–250°/730 mm. Dihydrochloride, white flat prisms.

4 : 6-Diamino-m-xylene; by reducing 4 : 6-dinitro-m-xylene with tin and hydrochloric acid (Luhmann, Ann. 1867, 144, 275; Fittig, Ahrens and Matthesides, Ann. 1868, 147, 15; Grevingk, Ber. 1884, 17, 2422), or with iron and dilute hydrochloric acid (Morgan, Chem. Soc. Trans. 1902, 81, 86); by reducing 6-nitro-m-4-xylydine (Witt, Ber. 1888, 21, 2418; Nölting and Thesmar, Ber. 1902, 35, 628); by reducing a dinitro-mesitylenic acid with tin and hydrochloric acid (Bamberger and Demuth, Ber. 1901, 34, 30). Long pale yellow needles, m.p. 104°–105° (N. and T.; M.), or 105°–105·5° (B. and D.).

Diformyl-derivative; flat silky needles, m.p. 182°–183° (M.); *diacetyl-derivative*, silky needles, m.p. above 260° (M.); *dibenzoyl-derivative*, small lustrous plates, m.p. 252°–253° (M.), or 258°–259° (corr.) (B. and D.); *4-acetyl-derivative*, needles, m.p. 164°–166° (Pearman, Chem. Soc. Trans. 1921, 119, 717); *4-benzene-sulphonyl-derivative*, colourless leaflets, m.p. 167° (Morgan, Micklethwait and Couzens, Chem. Soc. Trans. 1906, 89, 1289); *s-dibenzenesulphonyl-derivative*, prismatic needles, m.p. 176° (Morgan and Clayton, *ibid.* 1906, 89, 1054); *di-p-toluene-*

sulphonyl-derivative, small white needles, m.p. 221°–222° (Pearman).

Bromo-diamino-m-xylene; by the action of bromine water on diamino-m-xylene (Hofmann, Zeit. für Chem. 1865, 1, 555). Needles.

2-Nitro-4 : 6-diamino-m-xylene; together with a monoamine by treating 2 : 4 : 6-trinitro-m-xylene with alcoholic ammonium sulphide (Bussenius and Eisenstuck, Ann. 1860, 113, 159; Fittig and Velguth, Ann. 1868, 148, 6; Miolati and Lotti, Gazz. chim. ital. 1897, 27, i. 293). Long ruby-red prisms which sublime, m.p. 212°–213°.

4 : 6-Diamino-m-xylene 5-sulphonic acid; by reducing 6-nitro-m-4-xylydine 5-sulphonic acid with stannous chloride and hydrochloric acid. Long needles. KA', yellow pillars; BaA', + H₂O, quadratic tables (Junghahn, Ber. 1902, 35, 3747).

4-Methyl-4 : 6-diamino-m-xylene; by hydrolysing 4-toluene-p-sulphonyl-4-methyl-4 : 6-diaminoxylene hydrochloride with hydrochloric acid at 120°–130° in sealed tubes (Morgan and Micklethwait, Chem. Soc. Trans. 1907, 91, 360). Colourless plates from benzene, m.p. 57°, b.p. 166°–167°/10 mm.; very sensitive to oxidising agents.

Toluene-p-sulphonyl-derivative; by reducing toluene-p-sulphonyl-6-nitro-4-methylamino-m-xylene with iron and dilute acetic acid.

Hydrochloride, almost colourless prisms, m.p. 225°; *acetyl-derivative*, colourless felted needles, m.p. 176° (M. and M.); *benzene-sulphonyl-derivative*, oil; *hydrochloride*, leaflets, m.p. about 160° (Morgan, Micklethwait and Couzens.).

4-Dimethyl-4 : 6-diamino-m-xylene; by reducing 4-dimethylamino-6-nitro-m-xylene with tin and hydrochloric acid (M. and M.). Colourless oil, b.p. 149°–150°/21 mm., which is coloured red by exposure to air.

Benzoyl-derivative; colourless glistening plates, m.p. 123°; *benzene-sulphonyl-derivative*, colourless needles, m.p. 112°–113° (M. and M.).

s-Dimethyl-4 : 6-diamino-m-xylene; by hydrolysing 5-dibenzene-sulphonyldimethyl-4 : 6-diamino-m-xylene with concentrated hydrochloric acid in a sealed tube at 160° for 5 hours. Colourless plates, m.p. 100°–101° (Morgan and Clayton, Chem. Soc. Trans. 1906, 89, 1054).

Dinitrosoamine; pale yellow rectangular plates, m.p. 76°–77°; *s-dibenzene-sulphonyl-derivative*; by boiling *s-dibenzene-sulphonyl-4 : 6-diamino-m-xylene* with alcoholic sodium hydroxide and methyl iodide for 6 hours (M. and C.). Colourless crystals, m.p. 196°–197°.

Trimethyl-4 : 6-diamino-m-xylene; by hydrolysing benzene-sulphonyl-trimethyl-4 : 6-diamino-m-xylene with hydrochloric acid in a sealed tube at 130°–150° for 4 hours (M. and M.). Colourless crystals, m.p. 40°–42°, b.p. 145°/15 mm.

Benzene-sulphonyl-derivative; by heating benzene-sulphonyl-4-dimethyl-4 : 6-diamino-m-xylene with methyl iodide and alcoholic potassium hydroxide for 9 hours under a reflux (M. and M.). Lustrous colourless needles, m.p. 122°–123°.

Mononitrosoamine; almost colourless crystals, m.p. 45° (M. and M.).

4 : 6-Tetramethyldiamino-m-xylene; by heating 4 : 6-diamino-m-xylene hydrochloride or hydrobromide with excess of methyl alcohol in

a sealed tube at 180° (Morgan, Chem. Soc. Trans. 1902, 81, 650). Pale brownish-yellow oil, b.p. 124°–125°/12 mm.; D_{15}^{20} 0.9434. $B'H_2PtCl_6$, orange-yellow acicular prisms, m.p. above 200°.

Picrate; transparent yellow rhombic prisms, m.p. 193°–195°, or 202°–203°, according to the rate of heating.

p-Xylidine, *p-2-xylidine*, or *2-amino-1:4-xylene*; from commercial xylidine (Nölting, Witt and Forel, Bull. Soc. Ind. Mulhouse, 1888, 58, 630; Ber. 1885, 18, 2664; Witt, D. R. P. 34854 of 1885; Limpach, Eng. Pat. 11822 of 1886; Fr. Pat. 178616; D. R. P. 39947 of 1886; Hodgkinson and Limpach, Chem. Soc. Trans. 1900, 77, 65; Bayer and Co., D. R. P. 71969 of 1893; Schultz and Peteny, J. pr. Chem. 1907, 76, 331; Bornstein and Kleemann, D. R. P. 56322 of 1890); by reducing 2-nitro-*p*-xylene with iron and acetic acid (Schaumann, Ber. 1878, 11, 1537); together with methyl-*p*-xylidine by reducing di-1:4:2-xylene-methylenedihydroxylamine with aluminium amalgam in ethereal solution (Bamberger and Destraz, Ber. 1902, 35, 1874; see also Wroblewsky, Ann. 1881, 207, 91; Ber. 1879, 12, 1226; Jacobsen, Ber. 1884, 17, 159). Colourless liquid, b.p. 213°–5°/762 mm., which on prolonged cooling crystallises in large colourless tablets, m.p. 15°–5° (Michael, Ber. 1893, 26, 39); b.p. 215°/739 mm.; D_{15}^{20} 0.981 (N., W. and F.). or b.p. 217°–1° (U.). $B'HCl$, m.p. 228°, b.p. 245°–4°/728 mm., or b.p. 247°–4°/760 mm (Ullman, Ber. 1898, 31, 1699); $B'HCl + xH_2O$, plates (S.); $B'HNO_3$, plates or flat needles (N., W. and F.); $B'HNO_3$, plates or needles (N., W. and F.; S.); $B'_2H_2SO_4$, small plates (N., W. and F.); $B'_2H_2C_2O_4$, pink prisms, converted on heating to 125°–130° into oxal-*p*-xylidide, slender colourless needles, which sublime at 125° without melting (S.); *telluribromide*, small brownish-red laths (Gutbier, Flury and Ewald, J. pr. Chem. 1912, (2) 86, 150); $B'_2H_2PO_4$, needles (Rackow and Scharbanow, Chem. Zeit. 1901, 25, 244).

Formyl-derivative; long colourless needles, m.p. 111°–112°, coloured red on keeping (Pfug, Ann. 1889, 255, 168), or m.p. 116°–117° (Hodgkinson and Limpach); *acetyl-derivative*, glistening needles, m.p. 139° (N., W. and F.; Schaumann); *benzoyl-derivative*, needles, m.p. 140° (P.); *benzylidene-derivative*, yellowish plates, m.p. 102°–103° (Bayer & Co., D. R. P. 71969 of 1893), or 101°–102° (P.); *benzyl-derivative*, light yellow oil, b.p. 320°–325° (*hydrochloride*, colourless needles) (P.); *m-nitrobenzylidene-derivative*, yellow needles, m.p. 126° (P.); *p-nitroso-derivative*, green needles, m.p. 169° (P.); *p-xyllyphthalamide*, silky needles, m.p. 209°–210°, *s-p-xyllyphthalimide*, slender needles, m.p. 147°–148°, and *as-p-xyllyphthalimide*, amber needles, m.p. 178°–181°, are obtained by the action of phthaloylchloride on *p*-xylidine in ethereal solution at low temperatures (Kuhara and Komatsu, Mem. Coll. Sci. Eng. Kyōto, 1910, 2, 365). When *p*-xylidine is heated with finely powdered arsenic acid and the product is distilled, 4-amino-2:5-xyllyphthalic acid, m.p. 215° (when anhydrous), is formed. The therapeutic germicidal action of this compound is analogous to that of *p*-amino phenylarsenic acid (M. L. B., Eng. Pat. 14937 of

908; U.S. Pat. 913940; D. R. P. 219210 of 1907). When *p*-xylidine is condensed with benzaldehyde in presence of alcoholic hydrochloric acid, phenyl-di-*p*-amino-di-*p*-xylidimethane, m.p. 208°, is formed (Schultz and Peteny, J. pr. Chem. 1907, (2) 76, 331). *p*-Xylidine can be converted by the Sandmeyer reaction into *p*-xylene-2-nitrile, yellow oil, b.p. 223°–226°/730 mm., slowly volatile with steam (Schmid, Decker and Hock, Ber. 1906, 39, 933). By heating *p*-xylidine with sulphur at 200° a thio-base, $C_{10}H_{12}N_2S$, long yellowish needles, m.p. 144°, is formed (Anschtütz and Schultz, Ber. 1889, 22, 580).

5-Chloro-p-2-xylidine; together with *p*-xylidine by reducing nitro-*p*-xylene with tin and hydrochloric acid (Jannasch, Ann. 1875, 176, 177; Kluge, Ber. 1885, 18, 2098); by heating di-*p*-xylidyl-O-methylenedihydroxylamine with hydrochloric acid (Bamberger and Baum, Ber. 1900, 33, 941). Plates, m.p. 91° (B. and B.), or 92°–93° (J.; K.); $B'HCl + 2H_2O$, long needles (J.); $B'HNO_3$, large rhombohedral tables (J.); $B'_2H_2SO_4 + 2H_2O$, small needles (J.); $B'_2H_2C_2O_4$, rhombic tables (J.).

Acetyl-derivative; colourless needles, m.p. 171° (J.; K.).

Bromo-p-2-xylidine; by brominating formyl-*p*-xylidine in glacial acetic acid solution, followed by hydrolysis with alcohol and hydrochloric acid (D 1:19) for 6 hours under a reflux (E. Fischer and Windaus, Ber. 1900, 33, 1975). Needles, m.p. 96° (corr.). *Acetyl-derivative*, large prisms, m.p. 148° (150° corr.).

5-Bromo-p-2-xylidine; by reducing 2-bromo-5-nitro-*p*-xylene with iron powder and sulphuric acid (Blanksma, Chem. Weekblad, 1913, 10, 136). Colourless crystals, m.p. 96°.

Acetyl-derivative; from the bromo-xylidine, or by brominating aceto-*p-2*-xylidide in glacial acetic acid solution (B.). Colourless crystals, m.p. 180°.

3:5-Dibromo-p-2-xylidine, by brominating *p*-xylidine or *p-2*-xylidine 5-sulphonic acid (Nölting and Kohn, Ber. 1886, 19, 137; Blanksma, l.c.; Jaeger and Blanksma, Rec. trav. chim. 1906, 25, 352; Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 153). Needles, m.p. 65° (N. and K.; B.).

Acetyl-derivative; colourless crystals, m.p. 192°.

3:6-Dibromo-p-2-xylidine; by reducing 2:5-dibromo-3-nitro-*p*-xylene with iron powder and acetic acid (Auwers and Baum, Ber. 1896, 29, 2344). Needles, m.p. 91°–92°.

5-Nitro-p-2-xylidine; by nitrating *p*-xylidine with nitric acid and an excess of sulphuric acid (Nölting, Witt and Forel, Ber. 1885, 18, 2667); by reducing 2:5-dinitro-*p*-xylene with alcoholic ammonium sulphide (Kostanecki, Ber. 1886, 19, 2318; Blanksma, Chem. Weekblad, 1913, 10, 136). It melts at 142° (B.).

Acetyl-derivative; long needles, m.p. 166° (N., W. and F.). A *nitroacetyl-p-xylidide*, slightly yellow irregular crystals, m.p. 192°, is obtained by nitrating aceto-*p-2*-xylidide (Schaumann, Ber. 1878, 11, 1537).

6-Nitro-p-2-xylidine; by reducing 2:6-dinitro-*p*-xylene with hydrogen sulphide in ammoniacal solution (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 22; Kostanecki). Long yellow needles, m.p. 96°. $B'HCl$, long needles,

Acetyl-derivative; small needles, m.p. 180° (K.).

3:5-Dinitro-*p*-2-*xylylidine*; by prolonged boiling of 2:3:5-trinitro-*p*-xylene with alcoholic ammonia (Nölting and Geissmann, Ber. 1886, 19, 144). Yellow needles, m.p. 202°–203°.

3:5-Dinitro-*p*-*xylyl*-2-nitramine; by adding *p*-xylylidine sulphonic acid to nitric acid at –5° (Zincke and Ellenberger, Ann. 1905, 339, 202). Colourless needles, m.p. 130° (decomp.). When boiled with phenol it yields 3:5-dinitro-*p*-2-*xylylidine*.

3-Bromo-5-nitro-*p*-2-*xylylidine*; by brominating 5-nitro-*p*-2-*xylylidine* in glacial acetic acid solution (Blanksma, Chem. Weekblad, 1913, 10, 136). Pale yellow crystals, m.p. 125°.

Acetyl-derivative; colourless crystals, m.p. 208°.

3:5-Dibromo-6-nitro-*p*-2-*xylylidine*; by brominating 6-nitro-*p*-2-*xylylidine* (B.); by hydrolysing the acetyl-compound obtained by nitrating 3:5-dibromo-aceto-*p*-2-*xylylidine* (B.). Yellow crystals, m.p. 176°.

Acetyl-derivative; colourless crystals, m.p. 256°.

p-2-*Xylylidine* 5-sulphonic acid; by heating *p*-2-*xylylidine* sulphate at 160°, then at 220°, and at the same time passing a current of carbon dioxide or air through the mass (Junghahn, Chem. Ind. 26, 57); by sulphonating *p*-*xylylidine* at 230° for 5–6 hours with sulphuric acid (D 184) (Nölting, Witt and Forel, Ber. 1885, 18, 2664; Bull. Soc. Ind. Mulhouse, 1888, 58, 630; Nölting and Kohn, Ber. 1886, 19, 137). It forms prismatic plates or needles, which begin to char at 230° but do not melt at 300° (Carslake and Huston, J. Amer. Chem. Soc. 1914, 36, 1244). NaA', pearly plates; BaA', +7H₂O, leaflets. This acid on treatment with bromine yields 3:5-dibromo-*p*-2-*xylylidine*. The dry distillation of sodium *p*-2-*xylylidine* 5-sulphonate yields *p*-*xylylidine*, whilst on oxidation with chromic acid *p*-xyloquinone is obtained (N. and K.).

Acetyl-derivative; by heating aceto-*p*-2-*xylylidine* for a long time with fuming sulphuric acid (20 p.c. SO₃) at a temperature which does not exceed 40° (Junghahn, Ber. 1900, 33, 1364). Long greyish-white needles +2H₂O.

Acetyl-sulphonyl-derivative; by the action of chlorosulphonic acid on aceto *p*-*xylylidine* at 80° for one hour. Colourless needles, m.p. 160°; *sulphonanilide*, m.p. 213°–214°. On treatment with zinc dust in acetic-hydrochloric acid solution the acetyl sulphonyl-derivative is converted into 2:2'-diacetyl-*p*-*xylyl* 5:5'-disulphide, long needles, m.p. 284°–285° (Johnson and Smiles, Chem. Soc. Trans. 1923, 123, 2384).

Aceto-*p*-2-*xylylidine* 5-sulphinic acid; by reducing the acetyl-sulphonyl-derivative of *p*-2-*xylylidine* 6-sulphonic acid with aqueous sodium sulphite. Colourless needles, m.p. about 125° (decomp.) (Johnson and Smiles).

p-2-*Xylylidine* 6-sulphonic acid (see also Caze-neuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 24); together with the above 5-sulphonic acid by the successive nitration and reduction of *p*-xylene sulphonic acid with ammonium sulphide (Nölting and Kohn, l.c.; Bull. Soc. Ind. Mulhouse, 1888, 58, 636). It crystallises in needles and yields a monobromo-derivative when treated with bromine. It is not oxidised to *p*-xyloquinone by chromic acid.

BaA', +7H₂O (Carslake and Huston).

3-(or 5-)Bromo-*p*-2-*xylylidine* 6-sulphonic acid; by brominating *p*-2-*xylylidine* 6-sulphonic acid (N. and K.). Small white leaflets, KA'. With excess of bromine a substance, yellow needles, m.p. 106°–107°, which appears to be a brominated quinone, is obtained.

Methyl-p-2-*xylylidine*; together with *p*-2-*xylylidine* by reducing di-1:4:2-xylenemethyl-enedihydroxylamine with aluminium amalgam in ethereal solution (Bamberger and Destraz, Ber. 1902, 35, 1874); by boiling formyl-*p*-2-*xylylidine* with potassium hydroxide and methyl iodide in methyl alcoholic solution and treating the product with concentrated hydrochloric acid (Pflug, Ann. 1889, 255, 168). Yellowish oil, b.p. 225°–227°/735 mm.; D 0.962.

Nitrosoamine; yellow oil.

p-Nitroso-derivative; green needles with a blue reflex, m.p. 164° (P.; B. and D.).

3:5-Dinitromethyl-*p*-2-*xylylidine*; by heating 2:3:5-trinitro-*p*-xylene with methylamine in a sealed tube in alcoholic solution (Blanksma, Rec. trav. chim. 1905, 24, 46). Slender orange crystals, m.p. 175°. On nitration it yields a nitroamine, m.p. 94°.

3:5-Dinitroethyl-*p*-2-*xylylidine* (Blanksma). It melts at 133°, and on nitration yields a nitroamine, m.p. 36°.

Dimethyl-p-2-*xylylidine*; by heating *p*-*xylylidine* with dimethyl sulphate for 1 hour at 145°. Oil, b.p. 205° (Bielecki and Koleniew, Anzeiger Akad. Wiss. Krakau, 1908, 296); *methiodide*, prisms, m.p. 219°–222° (corr.), or 215°–218° (uncorr.) (E. Fischer and Windaus, Ber. 1900, 33, 345).

5-Bromodimethyl-*p*-2-*xylylidine* *methiodide*; leaflets, decomposing about 188° (uncorr.), or 191° (corr.) (E. Fischer and Windaus, *ibid.* 1970).

Some *xylylidine* derivatives of doubtful orientation have been described by Genz (Ber. 1869, 2, 686; 1870, 3, 225); Hübner (Ann. 1881, 208, 321); Lippmann and Strecker (Ber. 1879, 12, 82); Bussenius and Eisenstuck (Ann. 1860, 113, 165; cf. Ann. 1865, 133, 45; 1867, 144, 277; 1868, 147, 24); Krell (Ber. 1872, 5, 879); Hofmann (Ber. 1872, 5, 712); Seemann (Ber. 1873, 6, 446); Girard and Vogt (Bull. Soc. chim. 1872, (2) 18, 69); Wallach (Ann. 1874, 173, 283).

2:3-Diamino-*p*-xylene; by reducing the corresponding dinitro-*p*-xylene or nitro-*p*-*xylylidine* (Lellmann, Ann. 1885, 228, 251; Nölting and Geissmann, Ber. 1886, 19, 145; Nölting and Thesmar, Ber. 1902, 35, 628). It sublimes in needles, m.p. 75°. It gives a cherry-red coloration with ferric chloride, and with sodium nitrite in acetic acid solution a yellow solution and then a white precipitate is formed. The hydrochloride is coloured a deep red by ferric chloride.

2:5-Diamino-*p*-xylene; by reducing xylene-azoxylidine with tin and hydrochloric acid (Nietzki, Ber. 1880, 13, 470; Nölting and Forel, Ber. 1885, 18, 2685); by reducing 5-nitro-*p*-2-*xylylidine* (Nölting, Witt and Forel, Bull. Soc. Ind. Mulhouse, 1888, 58, 630; Ber. 1885, 18, 2666; Nölting and Thesmar, Ber. 1902, 35, 628; von Kostanecki, Ber. 1886, 19, 2318; Marchwald, Ber. 1890, 23, 1021); by reducing *p*-xyloquinone dioxime with tin and hydrochloric

acid (Sutkowski, Ber. 1887, 20, 979). Pale yellow or colourless needles, which sublime, m.p. 149°–150° (N. and T.; N.), or leaflets, m.p. 142° (decomp.) (S.). It yields xyloquinone, m.p. 123°, on oxidation. $B''2HCl$, leaflets; $B'H_2SO_4$, crystalline mass.

2:6-Diamino-p-xylene; by reducing 6-nitro-*p*-2-xylydine sulphonic acid with tin and hydrochloric acid (Blanksma, Rec. trav. chim. 1905, (2) 24, 320); by reducing the corresponding dinitro-compound (Lellmann, Ann. 1885, 228, 252; Nölting and Geissmann, Ber. 1886, 19, 145; Nölting and Thesmar, Ber. 1902, 35, 628). It sublimes in needles, m.p. 101.5°–102.5° (L.; N. and G.), or long yellowish prisms, m.p. 102°–103° (N. and T.). No coloration is produced by ferric chloride or potassium dichromate in neutral solution, but in warm sulphuric acid solution these oxidising agents produce a cherry-red coloration and a quinone odour.

5-Nitro-2:3-diamino-p-xylene; by reducing 3:5-dinitro-*p*-xylyl-2-azoimidé with alcoholic sodium sulphide (Fries and Noll, Ann. 1912, 389, 305). Red needles, m.p. 169°. When boiled with formic acid it yields 6-nitro-4:7-dimethylbenziminazole, m.p. 221°, and with sodium nitrite and hydrochloric acid in boiling alcoholic solution 5-nitro-4:7-dimethyl-1:2:3-benzotriazole, m.p. above 300°, is formed (F. and N.).

2-Methyl-2:5-diamino-p-xylene; by reducing 5-nitroso-*p*-2-methylxylydine with tin and hydrochloric acid (Pflug, Ann. 1889, 255, 168). Almost colourless needles, m.p. 83°.

F. M. R. and J. S. H. D.

XYLOSE v. CARBOHYDRATES. Ling and Nanji have slightly modified Hudson and Hardinge's method of extraction from maize cobs, whereby the yields of xylose have the correct specific rotatory power and melting-point, the yield was uniformly 10–12 p.c. of the cobs used (Chem. Soc. Trans. 1923, 123, 620).

Y

“Y” ALLOY. An alloy consisting of 4 p.c. copper, 2 p.c. nickel, 1.5 p.c. magnesium, and the rest aluminium. Has a tensile strength of about 20 tons per sq. in. and an elongation of 5–6 p.c. after suitable heat treatment. Rods of this alloy will stand 12,000,000 reversals of a maximum fibre stress of 7 tons per sq. in. The most satisfactory heat treatment of the cast rods consists in plunging them into a salt bath at $520 \pm 5^\circ$, maintaining them at the same temperature for 6 hours, then quenching them in boiling water. Temperatures above 525° cause the formation of blisters on the surface of the rods, but if these are turned off the rods have a satisfactory tensile strength (Rosenhain, Archbutt and Wells, Inst. Metals, March 1923; J. Soc. Chem. Ind. 1923, 358 A.).

YARA-YARA (*Nerolin*). Trade name for β -naphthyl methyl ester.

YATREN (*Griserin novum*). Trade name for iodo-hydroxyquinoline sulphonic acid, mixed with acid sodium carbonate.

YEAST v. FERMENTATION.

Yeast incubated in oxygenated water shows a diminished carbohydrate content and an increase in fat. Propyl, butyl, and isoamyl alcohols inhibit this conversion, whilst the sodium salts of formic, propionic, and butyric acids, glycol, glycerol, and acetone, in 0.1 M-solution, behave like water. Incubation in 0.5 p.c. solutions of ethyl alcohol, or of the sodium salts of acetic, lactic, and pyruvic acids gives the same results as 0.5 p.p. solutions of dextrose; in the first two cases increase of the total carbohydrate of the yeast-cell is observed. In the presence of dextrose, laevulose, and sucrose the yeast-cell stores both carbohydrate and fat. Maltose is exceptional in producing a greater carbohydrate and lesser fat storage than the other sugars investigated. It is suggested that maltose is assimilated as such by the yeast-cell. Continuous oxygenation during incubation greatly increases the amount of fat produced, but has little or no effect on the carbohydrate. In oxygenated solutions, added phosphate reduces the amount of carbohydrate stored and increases

the fat formation. Phosphate is taken up by the cell in proportion to the sugar concentration of the solution; more phosphate is taken up from oxygenated than from non-oxygenated solutions. It is suggested that the formation of hexose phosphate is the first stage in the conversion of carbohydrate into fat (I. S. MacLean and D. Hoffer, Bio-Chem. J. 1923, 17, 220; Chem. Soc. Abstr. 1924, 126, i. 352).

Influence of Nitrates on Yeast.—According to Fernbach and Nicolau (Ann. Brass. Dist. 22, 305, 321) fermentation experiments were carried out in nutrient solutions containing sucrose and mineral salts. Flasks containing the solution with increasing quantities of potassium nitrate were seeded with yeast from a mineral nutrient solution in quantities close to the limiting concentration (A. J. Brown), in order to suppress any complications arising from the multiplication of the yeast. After several days 'forcing' the alcohol was determined. A favourable effect was observed with additions of 5 and 10 grms. KNO_3 per litre both when the nitrogen in the nutrient solution was in the form of ammonium salts and when present only as nitrates. In the former case the effect was more marked at the beginning of fermentation, in the second the effect was more marked and persisted to the end of fermentation. It is concluded that the presence of potassium nitrate as the only source of nitrogen permits the yeast to carry through the fermentation completely. The value of nitric nitrogen cannot, however, be compared with that of nitrogen in other forms. Determination of the alcohol formed after $\frac{1}{3}$ of the sugar originally present had been fermented showed that the presence of nitrate does not modify the physiological properties of yeast from the point of view of alcohol formation. The nitrate acts simply as an accelerator to the zymase. Potassium nitrate appears to have no sensible effect on the other enzymes of yeast, though quantities greater than 40 p.c. have a retarding effect on the proteolytic enzymes. The authors confirm Fernbach and Lanzenberg's experiments, show-

ing that potassium nitrate has a harmful effect on the multiplication of yeast, and they further show that yeast is incapable of building up its cells from nitric nitrogen (*J. Soc. Chem. Ind.* 1924, 43, B. 610).

For the action of ultra-violet rays on yeast, see Fernbach (*Ann. Brass. et Dist.* 1923, 22, 97-100), who has discussed the results of the work of Romolo and Remi de Fazi. The mechanism of the ultra-violet rays is comparable to the effect of antiseptics. Industrial yeast is a mixture of cells of different ages and resisting powers. The rays destroy the weaker cells and activate the vigorous. The rays are not to be considered a means of revivifying all degenerate yeast, for the vitality of even the strongest cells of such a yeast is lowered, and as such is very sensitive to attack by the rays and an undesirable result is produced. This explains the unfavourable results obtained by several experimenters (*cf.* also H. Lüers and H. Christoph (*Zentr. Bakt. u. Parasit.* 1923, ii, 59, 8-13)).

For an account of the varieties of yeast from Saxi, see Takahashi, Yukawa, Eda, Yamamoto (*J. of the College of Agric. Imp. Univ. of Tokyo*, 1922, 7, 2).

For the dietary properties of yeast, see Nelson, Heller, and Fulmer (*J. Biol. Chem.* 1923, 57, 415-424).

Fermentation of Dextrose by Dried Yeast.—The rate of fermentation of dextrose by yeast dried by various methods has been measured by determining the rate of production of carbon dioxide. With such dried yeasts there usually occurs a more or less marked period of induction. Increase of the concentration of the yeast decreases this period. If the yeast is first of all incubated with sugar solution the induction period disappears. After being ground up in a mortar, dried yeast ferments sugar more slowly. Determination of the sugar at intervals during the fermentation by dried yeast shows that a certain disappearance of the carbohydrate takes place, amounting to from 20-50 p.c. of the sugar used, which cannot be accounted for by the carbon dioxide produced (*H. Sobotka, Zeitsch. physiol. Chem.* 1924, 134, 1-21; 1925, 145, 91; *Chem. Soc. Abstr.* 1924, i, 802; 1925, i, 865).

Effect of Nitrogenous Nutrition on the Activity of Brewer's Yeast.—Fermentation with brewer's yeast is most active and produces the maximum amount of ethyl alcohol and acid at 15° in a bouillon containing 0.1 p.c. of ammonium hydrogen carbonate (*I. Bay, Compt. rend. Soc. Biol.* 1923, 89, 1044-1045; *Chem. Zentr.* 1924, i, 680; *Chem. Soc. Abstr.* 1924, i, 802-803).

Role of the Reaction of the Medium in Selective Fermentation.—The fermentation of sugar solutions by 8 types of yeast has been studied, and in each case it has been found that levulose is at first attacked more readily than dextrose, until a point is reached, varying with the yeast employed and not occurring in the case of Sauternes yeast, at which the relative rate of attack is reversed. It was found possible to modify the course of the fermentation in other cases than that of the Sauternes yeast by decreasing the acidity of the solution (*Fernbach and Schiller, Compt. rend.* 1924, 178, 2196; *Chem. Soc. Abstr.* 1924, 126, i. 917).

Influence of Alkaloids of the Atropine, Cocaine, and Morphine Groups on Yeast Invertase.

—According to P. Rona, C. van Eweyk, and M. Tennenbaum (*Biochem. Zeitsch.* 1924, 144, 490), a series of alkaloids of the above groups have been found to possess an inhibiting influence on the action of yeast invertase. Although the intensity of the inhibition varies with the various alkaloids, the general inactivating influence proceeds logarithmically according to the concentration of the alkaloid present. The inhibition is reversible, and is influenced by the hydrogen-ion concentration of the medium. No connection exists between the optical configuration and the inhibitory power of *dl*-atropine and *l*-hyoscyamine; *l*-cocaine and *dl*-cocaine; and *l*-ecgonine and *d*-ecgonine. In none of these three cases was there any difference between the inhibitory power of the isomers. Tropine inhibits much less markedly than atropine, whilst tropic acid does not inhibit at all; nor does an equimolecular mixture of tropine and tropic acid have a greater inhibiting effect than tropine alone, *d*- and *l*-ecgonine do not inhibit, but, on the other hand, the chemically-related cocaine does. The substitution of the hydrogen of morphine by the methyl group (codeine) produced no apparent change in inhibitory power, but substitution by ethoxyl (dionine) produced a small though definite change (*Chem. Soc. Abstr.* 1924, 126, i. 468).

The effect of pyridine and nicotine respectively on the fermentative activity of yeast has been studied by M. Y. Otero (*Anal. Assoc. Quim. Argentina*, 1923, 11, 62), using 25 c.c. of a culture solution containing dextrose, to which 1 c.c. of yeast suspension and varying amounts of nicotine or pyridine were added. Increased activity was observed after the addition of as little as 0.05 mg. in the case of pyridine and 0.00005 mg. in the case of nicotine. No proportionality was observed between the change in activity and the amount of pyridine or nicotine added (*J. Soc. Chem. Ind.* 1923, 42, 1192 A).

Co-enzyme of Yeast.—The concentration, purification, and characterisation of co-enzyme are described by Euler and Myrbäck. A method has been devised for determining co-enzyme, based on the measurement of the carbon dioxide evolved with zymase and dextrose under standard conditions at $p_H = 6.2-6.6$. The fermentative power of dried yeast preparations is increased by the addition of co-enzyme and also by the addition of washed inactive yeast free from the co-enzyme. The rate of fermentation therefore depends on the relative quantities of zymase and co-enzyme, and it is assumed that the two together form a dissociable compound which constitutes the active enzyme. By the addition of either zymase or co-enzyme the dissociation of this active compound is suppressed, resulting in an increase in the activity of the mixture. The results on the thermostability of co-enzyme are similar to those arrived at by Tholin. Co-enzyme is decomposed rapidly in solutions more alkaline than $p_H 10$, shows maximum stability at $p_H 7$, and is still active in 0.5N hydrochloric acid ($p_H 0.6$). Contrary to the view hitherto accepted, it was found that lead acetate is capable of

precipitating the co-enzyme to a greater or less extent, according to the p_H of the solution. The co-enzyme is not affected by hydrogen sulphide, but is inactivated by traces of lead. When lead acetate was added to yeast juice containing the co-enzyme at p_H 6, the free phosphate and the hexosephosphate were precipitated and the co-enzyme was found mainly in the filtrate. When the latter was brought to p_H 8.3–10.0 the co-enzyme was almost completely precipitated. It could be recovered from the lead precipitate by suitable means, and such fractional precipitation may be employed for purification. It can also be purified in a solution free from phosphate, by adsorption on alumina, which is almost quantitative at p_H 10, whilst in acid solutions no adsorption occurs. The alumine adsorbate is strongly active and the co-enzyme is not eluted therefrom by water or very dilute acids, although it can be readily eluted quantitatively with 1 p.c. phosphate solution at p_H 6.3 (H. von Euler and K. Myrbäck, *Zeitsch. physiol. Chem.* 1924, 136, 107; *Chem. Soc. Abstr.* 1924, 126, i. 918).

YEAST FAT. Pressed yeast when treated with alcohol, light petroleum, or ether yields, on evaporation of the solvent, a brown liquid from which crystals of a sterol separate on standing, and from which lipins are precipitated by acetone. The crude yeast fat has a high but variable iodine value, ranging from 121 to 175.5, dependent chiefly on the amount of sterol present. The saponification value is low and shows wide variation from the same cause (138–199). The unsaponifiable matter present ranges from 25 to 45 p.c. According to I. S. MacLean and E. M. Thomas (*Bio-chem. J.* 14, 1920, 483, which contains a full bibliography), the fat contains palmitic, lauric, oleic, and linoleic acids, and an acid having the melting-point of arachidic acid. The pentadecic acid of Hinsberg and Roos (*Zeitsch. physiol. Chem.* 38, 1; 42, 189) is a mixture of palmitic and lauric acids, and their dodecenoic acid is possibly a mixture of lauric with oleic and linoleic acids.

The sterol present in yeast appears to be identical with the ergosterol isolated from ergot by Tanret. It exists partly in the free state and partly as fatty acid esters, and may constitute 20 p.c. of the total yeast fat. It is probably identical with the mycosterol isolated by Ikeguchi (*J. Biol. Chem.* 40, 1919, 175) from certain fungi, and is characteristic of the group of the cryptogams, as cholesterol is of the animal and phytosterol of the higher plant kingdom.

YEAST GUM v. GUMS.

YEAST JUICE, which has been boiled for 8 hours and so freed from co-enzyme, has a marked effect in increasing the activity of zymase in various yeasts. This effect is not due to a buffering action. It is ascribed to a 'zymase protector' (correlated with Euler's vitamin biocatalyst B. II.) which is also shown to have an anti-proteolytic action running parallel with the zymase-activating properties. It is suggested that the latter is due to protection of the enzyme—probably of a protein nature—from the proteolytic action of the endo-tryptase present in the yeast. This 'protective juice' also contains an activator for the zymase co-enzyme, and shows an anti-lipolytic

action again running parallel to the activating properties, and suggesting direct correlation or identity of the substances concerned. It was found that 'post war' yeasts grown in worts containing a high percentage of rice or maize show a lessened stability to maceration processes as compared with 'pre-war' yeasts (H. Haehn and H. Schifferdecker, *Biochem. Zeitsch.* 1923, 138, 209–268; *J. Soc. Chem. Ind.* 1923, 42, 850 A.).

YEAST, PRESSED OR BAKER'S. *Physical character.*—Pressed yeast, formerly called 'German' yeast, reaches the baker in the form of a very stiff creamy paste, which, on drying, readily crumbles to a coarse powder.

It should possess a bright creamy colour, an odour resembling that of sweet apples, a sharp, bitter but not unpleasant taste, and should not be sticky to the touch. Microscopically examined it should consist only of healthy oval or round cells, many of which should be budding. Chains of upwards of eight or even ten cells are not uncommonly seen. There should be no 'foreign' type of organism present, such as rods, sarcina forms, or moulds. A good sample of yeast will also be free from dead or disintegrating cells.

Pressed yeast after being kept for 5 to 10 days (depending on the weather) commences to deteriorate by drying and cracking into small pieces, which become exceedingly hard and develop a bad odour. The autodigestion and liquefaction of brewery yeast is not observed in distiller's pressed yeast.

Treatment of Yeast for Preservation of Vitality.—According to the Distillers' Company, Ltd., Edinburgh, and E. A. Meyer, Bristol (Eng. Pat. No. 204164, Sept. 27, 1923), pressed yeast is mixed with about one-sixth of its weight of cocoa butter or other fatty substance, which melts at a temperature sufficiently low to prevent damage to the yeast. The mixture is then dried at the ordinary or a slightly elevated temperature and the coating of fat around the cells is claimed to prevent deterioration of the yeast without further treatment (*J. Inst. Brewing Abstr.* 1924, 30, 243).

Before the war about 50 p.c. of the yeast used in the United Kingdom was imported from the Continent—mainly from Holland.

The several stages of the manufacture usually consist of:

- (i) Milling, steaming, malting or other preparation of the raw material;
- (ii) Admixture (mashing) of the raw or prepared material with water;
- (iii) Separation of the extracted raw material, leaving an aqueous extract technically called 'wash,' this extract being a nutrient liquid well suited to the vigorous reproduction of yeast;
- (iv) The admixture of seed yeast with the wash;
- (v) The collection of yeast from the fermented wash;
- (vi) The purification and pressing of the yeast.

In 1796 yeast was first pressed in bags with the aid of a press, much resembling the household linen press, whilst in 1860 iron-framed presses were first introduced. In 1878 a great discovery was made by Graham, who noticed

the increased rate of fermentation and benefit to the yeast of a gentle stream of air blown through the fermenting wash.

In Great Britain very little progress was made in the manufacture of yeast until after the repeal of the malt tax in 1880, whereby the distiller was enabled to make greatly advantageous changes in his method of mashing.

One of the first attempts to make a yeast specifically for baking purposes was made in the Midlands in 1888, when a process was used in which molasses were inverted by boiling with acid, the neutralised product being diluted and used as liquor to mash a mixture of malt-culms and bran. Drainage was effected through the usual false bottom; the unboiled wash diluted to about 1040°, and fermented by a bottom yeast. The outcrop was collected and pressed in small bags for distribution to the baker. This early process illustrates the general conduct of operations in a yeast distillery, the requirements being simple, namely, a liquid well suited to the rapid and healthy reproduction of the yeast organism. To push reproduction to its furthestmost limits without injury to the yeast cell is, briefly, the yeast manufacturer's object.

Brewer's yeast is unsuited to the present day requirements of bread making, mainly by reason of its poor keeping qualities, comparative slowness in fermentation, and the slightly bitter flavour and darker colour which it imparts to the loaf.

There are to be found in the botanical world numerous storehouses and reserves of sacchariferous material which are well suited to the yeast maker's requirements. The use of some of the materials mentioned below is still in the experimental state, but a closer examination into their suitability for yeast-making should prove profitable, particularly in view of the world shortage of cereals, which is bound to adversely affect the conduct of the yeast manufacturer's business for many years to come.

In addition to barley, wheat, rye, oats, and maize, both malted and unmalted, there are also used buckwheat, potatoes, beet, and cane molasses, tapioca, sago, rice, malt coombs, bran, locust beans, cotton seed, artichokes, dates, and many varieties of beans and seeds capable of yielding either sugar or nitrogenous food stuff, or both, after suitable treatment.

Tapioca and sago have already proved most satisfactory substitutes for the more costly maize, whilst Sudan dhurra, date, and sand locust beans are plentiful and relatively cheap.

Barley is malted much as in brewery maltings, except that the condition of flooring must conduce to the greatest possible production of diastase, followed by such kiln heats as will not cripple the enzyme. It is not difficult by the use of an excess of warm dry air to produce a tender friable malt high in diastatic power. Such malts contain from 12 to 15 p.c. of moisture. Small heavy barleys are usually chosen, and preferably those yielding a large percentage of soluble uncoagulable albuminoids, such, for example, as Danubian and Russian. In Scotland a large proportion of home grown barley is used.

Green malt, that is, unkilned malt, is not infrequently used. Such malt at the end of the withering stage is passed through a machine containing rollers and mixers converting it

(with the aid of a little water) into 'malt milk,' which may be mashed along with the other materials as described below. Wheat, oats, and rye may be used either malted or unmalted. Maize may be used in the form of grits, but usually a meal from the entire corn is employed. The maize meal is sometimes simply mixed with the malt, &c., in the course of mashing, or it may be subjected to treatment in the mash tun before adding the bulk of the malt and the other ingredients, or, as is most usual, separate converters may be employed.

A form of converter, much commoner on the Continent than in this country, consists of a long inverted cone, provided with a dome-shaped cover, and designed to withstand considerable pressure. The maize, either entire or cracked into three or four pieces, is introduced, and after a preliminary soaking and steaming is subjected to considerable steam pressure which completely loosens up the whole texture. This accomplished, steam is turned into the space beneath the dome cover, and a comminuting or grid valve opened at the apex of the cone. The gelatinised mass is blown violently through this valve, thus completing its disintegration.

Open converters, consisting only of a wooden vessel provided with a powerful rake, are also used. In this case the maize must be ground to a fine meal, gelatinised and liquified by malt, as in brewery working. Potatoes are commonly used on the Continent. They are washed, sliced, and converted into a pulp. Beet and artichokes are treated similarly. Malt coombs and bran are of use as providing valuable assimilable nitrogenous food stuff for the yeast, whilst their value in assisting drainage of the mash must not be overlooked.

The methods employed in individual European yeast distilleries vary so widely that it will be better to give a more or less detailed account of two of the commoner methods rather than attempt a general description intended to cover all the methods in use. A preliminary process common to most methods is the making of 'bub.' It is well-known that one explanation of the fact that micro-organisms living in a medium favourable to their development will cease reproduction long before the available food supply is exhausted is to be found in the fact that their excretory products or the by-products of their vital processes are poisonous to them and exert an inhibitory effect on their development.

Now the distiller in fermenting an unboiled, and consequently unsterilised, wash at temperatures above 80°F. is likely to be faced with an enormous development of the organisms producing lactic and butyric acids. The butyric organism in particular is undesirable, on account of the characteristic odour and taste of rancid butter which accompanies its growth. Undue development of such disease organisms not only reduces the vigour and keeping properties of the yeast, but results also in great loss of alcohol. The development of these deadly organisms may be prevented if there is already present in the wash a small amount of lactic acid. Very small amounts of lactic acid suffice to prevent the growth of both the lactic and butyric organisms. To produce the acid, a small portion, say 5 p.c. of the total raw material,

is mashed at a suitable temperature in a small vessel, known as a bub tun, and after a suitable saccharifying period the mash is cooled to 120°F., which is about the optimum temperature for the lactic organism, and the whole allowed to become sour. The souring may be produced by adding a pure culture of the lactic organism or by adding a few gallons of bub reserved from a previous operation. After a further stand this sour mash, now known as bub, is added to the main mash which would itself rapidly become sour. Previous to separating the wash from the grains the mash would require to be raised to say 160°F., in order to kill the acid producing bacterium. Instead of acidifying the whole mash, a rough extract from the bub may be added after sterilisation to the fermenting tun or wash back prior to fermentation. Some distillers make a practice of keeping the acidified main mash at a temperature of 125°F. for many hours, it being thought that lactic acid has a peptonising or digestive action on some of the insoluble albuminoids, thereby converting them into readily assimilable yeast food. It is improbable that any such peptic action takes place, and the benefit to be derived from the introduction of the lactic organism lies in the security it affords against unrestrained multiplication of acid-producing organisms in the fermenting tun. It has been suggested that a like degree of protection may be obtained by the use of commercial lactic acid, thus obviating the dangers attendant on the encouragement of bacterial growths on distillery premises and also in effecting a great saving of time. Commercial lactic acid has, however, proved a failure, although the suitability of certain mineral acids has been demonstrated.

In yeast making, a water comparable in many respects with that from the London clay is generally regarded as most suitable. The yeast manufacturer strives to obtain the greatest possible extract from his materials, and to that end a soft extractive water is decidedly an advantage, whilst the presence in considerable quantities of the chlorides of calcium and sodium undoubtedly contributes to the fermentability of the wash and so to the yield of yeast obtained.

Waters containing nitrates, nitrites, and other salts known to exert a harmful influence on yeast, would naturally be rigorously excluded. The biological purity of the water should claim the yeast manufacturers' attention, since that complete sterilisation afforded to the brewer in his copper is not available to the distiller. A thorough boiling with subsequent sedimentation is as far as most yeast manufacturers go in the matter of liquor treatment.

The Main Mashing Operation.

Distillery mash-tuns are remarkable for their great size. They are usually of cast iron, and some may possess a false bottom whilst others have no false bottoms, filtration being effected by the aid of filter presses; or both these means of filtration may be employed in conjunction. In some cases coarse sieves only are found. An extremely powerful rake or rouser is necessary.

The two methods of yeast manufacture to

be described are known respectively as the Vienna process and the air-yeast process. The grist, or raw material, which has been finely ground, may consist of from 15 to 25 p.c. of malt, 50 to 80 p.c. of maize treated separately, and about 20 p.c. of either barley, oats, rye, and wheat, or a mixture of any or all of these cereals. Equal proportions of malt, maize, and rye form a not uncommon mixture. An American yeast factory uses 30 p.c. barley malt and 35 p.c. each of maize and rye. The ground malt together with the finely ground raw cereals which should be kiln dried is mashed with water of such a temperature as to give a final or mixture heat of 125° to 130°F. The maize 'conversion' may now be run in at such a temperature as to raise the whole mash to perhaps 135°-140°F. The rakes would be running the whole operation. Steam or hot water may now be injected, raising the mash to 150°F. The total quantity of water used would be at the rate of 35 to 40 gallons per 100 lbs. of grist or raw material. A suitable 'standing on' completes the operation. The addition of 'bub' at some convenient stage has already been referred to.

The methods up to this point would probably not differ greatly in either of the two processes mentioned, namely 'Vienna,' and 'air-yeast,' but from this point there is a pronounced divergence, inasmuch as with the Vienna process the actual mash itself, cooled, and perhaps slightly diluted, is fermented. The entire mash is transferred to fermenting vessels, and sufficient yeast to ensure an early and vigorous fermentation is added. The yeasty heads push their way through the grains, and are skimmed off by hand. Such skimmings are then passed through sieves of fine bolting silk, which separate the yeast from the grains, the yeasty washings being collected in settling tanks. The course of the fermentation is described below. The yield of yeast from this process is small, as, apart from other considerations, some 15-20 p.c. of the yeast produced escapes the sieving and passes to waste with the grains. The Vienna process results in high spirit yields but the yeast is often weak.

In the 'air-yeast' method the mash after standing a few hours is passed to filter presses; which effect the complete separation of the 'grains' from the liquid extract or wash. The wash is collected in wood or wrought-iron vessels usually fitted with tempering coils, and provided with a star-shaped arrangement of perforated iron or copper pipes lying on the bottom through which air can be forced.

The specific gravity of the wash before fermentation varies from 1030° to 1040°. A pitching temperature of say 75°-78°F. is aimed at and yeast added in sufficient quantity to ensure a very active fermentation immediately setting in. Throughout the whole course of fermentation, except in certain special cases, a current of air is blown through the wash, giving the tun the appearance of being gently on the boil. Aëration is of greatest importance during collection of the wash, that is to say, during the periods immediately anterior to and subsequent to the addition of the seed yeast. Aëration throughout the whole course of fermentation effects the removal of the large quantities of CO₂ produced, thus leaving an

fettered the reproductive capacity of the yeast organism, whilst the passage of a strong air current also effects both mechanically and by volatilisation the removal of some of the alcohol. Possibly also yeast metabolism is assisted by the presence of an ample supply of oxygen. Undoubtedly the very complete mechanical intermixture of yeast and wash ensured by the passage of the air current increases the amount and the rate of attenuation.

Two typical fermentations are given below :—

No. 1, 28 hours			No. 2, 10 hours		
Time	Sp gr	T°	Time	Sp gr	T°
Midnight .	38	76	Midnight .	30.0	79
6 a.m. .	32	78	1 a.m. .	29.0	80
Noon .	20	82	2 .. .	27.0	82
6 p.m. .	10	84	3 .. .	23.0	84
Midnight .	4	86	6 .. .	14.5	86
4 a.m. .	2	86	7 .. .	10.0	86
			9 .. .	3.5	86
			10 .. .	1.5	86

No. 1 was a top fermentation in which a portion of the yeast was removed by means of mechanical skimmers, and No. 2 represents a bottom yeast without removal during fermentation. In the air process the separation of the yeast from the wash is variously effected but commonly by means of centrifugal separators, which produce a thick creamy yeast suitable for pressing into cakes by means of a yeast press. The cakes are broken up and packed into the well-known 7 and 14 lb. jute bags.

Yield of Yeast.

The weight of pressed yeast produced is usually referred to the weight of the grist, and a yield of 20–22 p.c. of pressed yeast is expected in most British distilleries. Continental manufacturers claim to have obtained a yield of 50 p.c.

A yield of 35 p.c. is not difficult to obtain, but the quality of the yeast is poor. The American yeast factory already referred to produces only 12½ p.c. of yeast using the Vienna process, whilst a certain Continental yeast factory produces 20 p.c. of yeast by the Vienna process, and 35 p.c. by the aëration method. It used to be common to add a proportion of potato starch to the yeast before pressing, probably with a view to increasing its dryness and consequent keeping property, but the practice is discontinued. Pressed yeast packed in bags leaves the factory containing about 70 p.c. of moisture.

Both 'top' and 'bottom' yeasts are employed, the characters of the particular races found suitable, being preserved by the aid of pure culture apparatus. The absence of any effective sterilisation during wash preparation renders it difficult to preserve a pure yeast for any such lengthy periods as are common in well conducted breweries, and frequent replacements of the pitching yeast are necessary. The method of pure culture follows closely the principles and practice as laid down by Hansen and his co-workers. Valuable by-products resulting

from the manufacture of pressed yeast are alcohol and grains. The alcohol is recovered from the fermented wash, after removal of the yeast, by distillation. Many types of distilling apparatus are in use, the usual type in Great Britain being the Coffey still, in which raw steam is blown through the wash, thereby effecting the removal of the alcohol. The resulting mixture of steam and alcohol vapour is fractionally condensed.

The differences between Vienna and air-yeast methods occasion some modification in the type of still used, as, in the Vienna process, it is not usual to separate the grains from the fermented wash before recovering the alcohol. In the air-yeast process the liquid passed to the still is practically free from suspended matter—certainly no particles of grain are present sufficiently large to block the passage of the wash through the perforated copper plates used in the Coffey still.

In the Vienna process a yield of 6½ gallons of 90 p.c. alcohol per cwt. of grist may be obtained, whilst in air-yeast distilleries the yield per cwt. probably will not exceed 5½ gallons of 90 p.c. alcohol.

Yields of yeast and spirit are roughly inversely proportionate, as the following figures, giving two examples of the two common methods, will show :—

Method	Vienna		Air process	
Yeast, per cent. .	12.5	20.0	22.0	35.0
Spirit, galls. per cwt. of proof spirit .	6.0	6.8	5.8	4.0

The spent grains resulting from the manufacture are usually dried, when they may be sold for cattle food, or they may be mixed with sludge from the fermenting vessels, sweetened with molasses and pressed into cakes.

In some distilleries also the large quantity of carbonic acid gas produced is collected and compressed into steel tubes for use commercially.

For methods of detecting the presence of brewer's yeast in pressed yeast, see Vautier, Ann. Chim. anal. 1919, 1, 345; J. Soc. Chem. Ind. 1920, 38 A.

YEASTS FERMENTS OF, YEAST-FAT, v. FERMENTATION.

YELLOW, ACID, v. AZO-COLOURING MATTERS; also NAPHTHALENE.

YELLOW, ANILINE v. AZO-COLOURING MATTERS.

YELLOW, BRILLIANT, v. AZO-COLOURING MATTERS; also NAPHTHALENE.

YELLOW, BUTTER, v. AZO-COLOURING MATTERS.

YELLOW, CAMPOBELLO, v. NAPHTHALENE.

YELLOW CEDAR. The *Rhodospheera rhodanthema* (Engl.) or yellow cedar, a tree growing to the height of 70 or 80 ft., is indigenous to the northern part of New South Wales.

The colouring matter of this dyewood is *fisetin*, which is readily isolated by the method described in connection with Young Fustic (Perkin, Chem. Soc. Trans. 1897, 71, 1194).

A second substance $C_{20}H_{20}O_{11}$, colourless

needles, m.p. 215°–217°, is also present in small amount, and may be identical with *fustin*, the glucoside of *fisetin* (Schmid, Ber. 1886, 19, 1755).

The shades given by the yellow cedar are slightly weaker and differ considerably from those given by young fustic (*Rhus Cotinus*), although both contain the same colouring matter. Employing mordanted woollen cloth, the following distinctions are observed—

	Chromium	Aluminium	Tin	Iron
Young fustic .	Reddish brown	Orange	Orange yellow	Brown olive
Yellow cedar .	Yellowish brown	Brownish yellow	Golden yellow	Olive yellow

and these may be due to varying amounts of a brown extractive matter, which is contained in both plants. A. G. P.

YELLOW, CHROME, v. CHROMIUM.

YELLOW, CITRON, v. CHROMIUM.

YELLOW, COLOGNE, v. CHROMIUM.

YELLOW, CROCEIN, v. NAPHTHALENE.

YELLOW, FAST, v. AZO-COLOURING MATTERS.

YELLOW, GOLDEN, *Martius yellow*, v. NAPHTHALENE.

YELLOW, HESSIAN, v. AZO-COLOURING MATTERS.

YELLOW, IMPERIAL, v. AURANTIA.

YELLOW, KING'S, v. ARSENIC; also PIGMENTS.

YELLOW, LEIPSIC, v. CHROMIUM.

YELLOW, LEMON, v. CHROMIUM.

YELLOW, MANCHESTER, v. NAPHTHALENE.

YELLOW, MARTIUS, v. NAPHTHALENE.

YELLOW, METANIL, v. AZO-COLOURING MATTERS.

YELLOW, NAPHTHALENE, v. NAPHTHALENE.

YELLOW, NAPHTHOL, v. NAPHTHALENE.

YELLOW, NEW, v. NAPHTHALENE.

YELLOW, ORANGE, v. AZO-COLOURING MATTERS.

YELLOW, PARIS. *Lead chromate* v. CHROMIUM.

YELLOW, RESORCIN, v. AZO-COLOURING MATTERS.

YELLOW, SALICYLIC, v. SALICYLIC ACID.

YELLOW, SUN, v. AZO-COLOURING MATTERS; also STILBENE.

YELLOW, TURNER'S, v. PIGMENTS.

YELLOW ULTRAMARINE. *Citron yellow*, *Lemon yellow*, *Barium chromate*, v. CHROMIUM; also PIGMENTS.

YELLOW WALLFLOWER (*Cheiranthus cheiri*). The purplish-brown petals of the common garden wallflower are comparatively rich in colouring matter, though the shade given by these on alumina mordant possesses a greenish-olive-yellow tint, and is of a less pure character than that given by the variety known as 'Cloth of Gold.' A boiling aqueous extract of these latter flowers on treatment with sulphuric acid gradually deposits a yellow precipitate, and this is most readily purified by pouring the concentrated alcoholic solution into much ether. The main impurity is thus precipitated, whereas the colouring matter remains dissolved in the ether. By fractional crystallisation from alcohol two colouring matters can be isolated from this extract: (a) *amaranthine* soluble in water, and (b) *guercetin*. The existence of isorhamnetin was first demonstrated by an examination of these flowers (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1566). A. G. P.

YELLOW WOOD v. OLD FUSTIC.

YENITE, v. ILVAITE.

YEW (*Taxus*; *If commun*, Fr.; *Eibe*, Ger.). It has long been known that the leaves and berries of the common yew, *Taxus baccata* (Linn.), (Bentl. and Trim. 253), possess powerful toxic properties. Yew is a reputed emmenagogue, and it has been used for the purpose of procuring criminal abortion, but its efficiency is more than doubtful, and its employment often leads to fatal consequences (cf. Redwood, Pharm. J. [iii.] 8, 361). The contraction of the uterus is probably reflex, as a result of the irritation of the intestine by the essential oil (Meyer and Gottlieb, Experimentelle Pharmakologie, 1914, 213). The first thing to do in cases of poisoning is to empty the stomach; milk may then be given to allay irritation, and such stimulants as alcohol or ammonia employed. Yew is seldom used in medicine.

Chevallier and Lassaigne (J. Pharm. Chim. 1818, 4, 558), Peretti (*ibid.* 1828, 14, 537), Lucas (Arch. Pharm. [ii.] 85, 145), and others have examined yew chemically, but no definite compound was isolated till the discovery of an alkaloid *taxine* by Marmé in 1876 (Chem. Zentr. 1876, 166). Taxine was further studied by Amato and Capparelli (Gazz. chim. ital. 10, 349), who also obtained a non-nitrogenous crystalline compound *milossin*, and a *volatile oil* which distils with steam, and has the odour of fennel. The chemical reactions of taxine obtained by Marmé's process have been examined by Hilger and Brande (Ber. 1890, 23, 464). Taxine is prepared by exhausting yew leaves or seeds with alcohol or ether. The residue, after distilling off the alcohol or ether, is extracted with acidified water, and from the clear aqueous solution alkalis precipitate the base in white flakes, which, when washed and dried over sulphuric acid, assume the appearance of a white crystalline powder. The leaves, when dry, contain 0.7–1.4 p.c. of alkaloid, the seeds less. Leaves which have been preserved without preliminary drying yield very much less alkaloid. The preliminary extractions of the leaves with alcohol or ether may be dispensed with; they can be treated directly with a weak solution of an acid. Thorpe and Stubbs (Chem. Soc. Trans. 1902, 81, 874) have investigated the conditions under which taxine can be extracted. They find that it undergoes change with extreme ease during the process of extraction, thus accounting for the difference in the description of its properties by earlier investigators. The method of extraction giving the best results was found to be treatment with dilute sulphuric acid (1 p.c.) in the cold. Taxine, so obtained, consists of very fine glistening particles or a white amorphous powder. It does not crystallise. It is odourless, but possesses a very bitter taste. It is very slightly soluble in water, is soluble in dilute acids, alcohol, ether, benzene, or chloroform, and insoluble in light petroleum. At 82° taxine practically melts, undergoing at the same time some decomposition. Analysis gives

proposed by Hilger and Brande. Taxine gives reactions characteristic of the alkaloids when treated with the usual reagents, and also combines with acids to form definite salts, which have, however, not been obtained crystalline. From the residue, insoluble in very dilute acids, after the removal of the taxine, alcohol and animal charcoal extract milossin. Its purification is tedious and difficult. It crystallises in stellate groups of needles, which melt at 86° – 87° , and which are insoluble in water, but soluble in boiling alcohol (Amato and Caparelli).

A glucoside, *taxicatin*, has been found in the leaves of the yew by Bourquelot (J. Pharm. Chim. [vi.] 1906, 23, 369). Taxicatin $C_{18}H_{22}O_7$, crystallises from alcohol in colourless needles, m.p. 169° – 170° (corr.); the crystals obtained from aqueous solutions contain $2H_2O$. It is hydrolysed by emulsin or by 2 p.c. sulphuric acid into dextrose and a substance readily soluble in ether or chloroform (Lefebvre, *ibid.* [vi.] 1907, 26, 241).

The twigs of *Taxus baccata* were found to contain invertin and emulgin (Lefebvre), and raffinose and sucrose have been isolated from the leaves and twigs (Hérissey and Lefebvre, *ibid.* [vi.] 1907, 26, 56).

The leaves of yew have been further examined by Winterstein and Iatrides (Zeitsch. physiol. Chem. 1921, 117, 240). With colloidal platinum taxine takes up four atoms of hydrogen; it also takes up four bromine atoms. Acid hydrolysis yields cinnamic and acetic acids and an amorphous substance reducing Fehling's solution. Taxine forms a methiodide $C_{27}H_{51}O_{10}N \cdot CH_3I$ and a tri- or tetra-acetyl derivative. Similar results were obtained by Kondo and Amano (J. Pharm. Soc. Japan, 1922, No. 490, 1074; Chem. Soc. Abstr. 1923, i, 361; J. Soc. Chem. Ind. 1923, 290 A.). An alcoholic extract, treated with ammonia yielded a precipitate of taxine, as a white amorphous powder, $C_{27}H_{51}NO_{10}$, sintering at 82° and melting at 105° – 111° ; $[\alpha]_D^{18} = +32^{\circ} 20'$, and 35° for 5 and 10 p.c. alcoholic solutions respectively. By warming with 5 p.c. sulphuric acid, the alkaloid was partly decomposed, a compound reducing Fehling's solution being produced which was, however, not a sugar. On warming with alcoholic potash taxine was decomposed into formic and acetic acids, an amorphous acid of m.p. 94° – 95° , and mol. wt. 215, a crystalline acid (perhaps cinnamic acid), m.p. 133° , and a compound $C_{22}H_{33}NO_4$, m.p. 105° – 110° , insoluble in dilute sulphuric acid. By brominating in glacial acetic acid, the alkaloid gave a tetrabromide $C_{27}H_{41}NO_{10}Br_4$, yellow amorphous powder, while in dilute sulphuric acid a tribromide $C_{27}H_{41}NO_{10}Br_3$, or $C_{27}H_{41}NO_{10}Br_2 \cdot HBr$, light yellow amorphous powder, was produced.

The amount of taxine present in the Irish yew, *Taxus baccata*, var. *fastigiata*, has been investigated by Mons (Sci. Proc. Roy. Dubl. Soc. 12, 92). The results seem to indicate that the Irish yew contains much more taxine than the common yew.

G. B.

YLANG-YLANG : OILS, ESSENTIAL.

The ylang-ylang and cananga oil are obtained from the *cananga odorata*, but the blossoms of the *cananga latifolia* are also used for distillation. These two oils are the most valuable perfumes

of the tropics, but there is an essential difference between them, and their quality varies according to the land of their origin, probably on account of the more or less primitive distillation methods and the greater or smaller care observed in the collection of the blossoms. On the island of Réunion a full-grown cananga tree bears 10 to 15 kilograms of blossoms, and in rare cases 40 to 50 kilograms. This means a blossom harvest of about 2,000 kilograms per hectare. The trees bloom in January, and the best yield of oil is obtained in May and June, or later. Gathered just before the anthesis, the blossoms are subjected to distillation in as fresh a state as possible. The best ylang-ylang oil is furnished by the first fractions, while the rest of the distillate consists of cananga oil. In the Bantam districts of Java this inferior oil is obtained from the crushed blossoms which are distilled with water, but without sufficient cooling. The yield varies between 1.5 and 2.5 p.c., while the first fractions, which represent a prime distillate, only amount to 1 p.c. The clear, amber-coloured ylang-ylang oil is very sensitive to the influence of light and oxygen, and its composition is highly complicated. So far, the presence of the following substances in the oil has been definitely established: Benzoic and acetic acids (the formic acid sometimes found seems to be an impurity), linalool, geraniol, paracresol, methyl ether, cadinene, a pinene, a phenol, saffrol, isosafrol, nerol, farnesol, eugenol and isoeugenol, eugenic acid methyl ester, benzyl acetate and benzoate, anthranilic and salicylic acid methyl esters, and a sesquiterpene alcohol. The cananga oil is richer in sesquiterpenes, but poorer in esters, and the javanese varieties contain nerol and farnesol. About 2,000 kilograms of Manila-ylang were exported in 1920 from the Philippine Islands. The first ylang oil was distilled on the island of Luzon in the 'sixties of the last century (Deutsche Parfümerie-Zeitung, through Amer. Perf. and Ess. Oil Rev. February, 1924, 629; Pharm. J. 1924, 112, 334).

YOGHURT. A preparation of sour milk made in Bulgaria and Turkey by the action of the *Bacillus bulgaricus* and other micro-organisms, giving rise to a mixture of dextro-rotatory and lævo-rotatory lactic acid, the former predominating.

YOHIMBINE (=Quebrachine) $C_{21}H_{23}O_2N_2$ occurs along with other alkaloids in yohimbe bark of *Corynanthe yohimbe*, K. Schum = *Pausinystalia yohimbe* (K. Schum) Pierre, N. O. Rubiaceae, which occurs in the Cameroons and other parts of West Africa. False yohimbe bark of *C. macroceras*, K. Schum = *P. macroceras* (K. Schum), Pierre contains very little yohimbine, but a considerable quantity of other alkaloids. Yohimbine is further present in *P. Trillesii*, Pierre. These species are related to the genus *Cinchona* of the same order. For an account of the anatomical characters of true and false barks, with illustrations, see Small and Adams (Pharm. J. 1922, 108, 282, 311), who also give an account of the literature. Yohimbe bark is used by the natives as an aphrodisiac, and the alkaloid yohimbine, patented by Spiegel in 1896 (Chem. Zeit. 1896, 20, 970; 1897, 21, 833; 1899, 23, 59, 81; Ber. 1903, 36, 169; 1904, 37, 1759; 1905, 38, 2825), is now used for

the same purpose, chiefly in veterinary medicine. Spiegel considers that yohimbine has the composition $C_{21}H_{26}O_2N_2$, but a detailed study by Fourneau and Fiore (Bull. Soc. chim. 1911 [iv.] 9, 1037), and by Fourneau and Page (Bull. Sci. Pharmacol. 1914, 21, 7) have established the formula $C_{21}H_{26}O_2N_2$ and the identity of yohimbine with quebrachine, isolated from the bark of *Aspidosperma Quebracho-blanco*, Schlecht. by Hesse, in 1882. This identity was confirmed by Ewins (J. Chem. Soc. 1914, 105, 2738), so that, except for practical reasons, the name yohimbine should not be retained. The formula $C_{21}H_{26}O_2N_2$ is also supported by Miss Field (J. Chem. Soc. 1923, 123, 3003). Spiegel (Ber. 1915, 48, 2077) maintains that this formula belongs to another alkaloid, *mesoyohimbine*, m.p. 247°, also present in the bark.

Yohimbine crystallises in needles, m.p. 234° (Spiegel), 247°–248° (Fourneau and Page). The melting-point varies considerably with the rate of heating. Yohimbine sublimes at 210°–220°/8 mm., and has $[\alpha]_D^{20} +56.0^\circ$ in alcohol. The hydrochloride $C_{21}H_{26}O_2N_2 \cdot HCl$ has m.p. 302°–303°, $[\alpha]_D^{20} +106.4^\circ$ in water; the sulphate $(C_{21}H_{26}O_2N_2)_2 \cdot 8H_2O$, m.p. 281°–282° (anhydrous), and $[\alpha]_D^{20} +100^\circ$ in water. The hydrochloride and particularly the nitrate are sparingly soluble in water. The colourless solution of the alkaloid in concentrated sulphuric acid becomes violet and then green on stirring in a crystal of potassium dichromate. Yohimbine is a monacid tertiary base, and the monomethyl ester of a hydroxy acid derived from indole (and quinoline?). Hydrolysis with alkali yields *yohimbic acid* $C_{20}H_{24}O_4N_2$, an amphoteric substance, soluble in hot water, m.p. 257°–260°, on the composition of which all authors agree. It can be re-esterified with methyl alcohol and hydrogen chloride to yohimbine (e.g. Field, l.c.), and with other alcohols to homologues of yohimbine. Two oxygen atoms of yohimbine are therefore present in a carboxyl group; the third is in a hydroxyl, which is esterified when yohimbine is dissolved in cold concentrated sulphuric acid (Barger and Field, J. Chem. Soc. 1915, 107, 1025; 1923, 123, 1038). When the solution is poured on ice *yohimbine sulphuric ester* separates, which, crystallised from 1400 parts of boiling water, forms needles, m.p. 292°–295°. This characteristic derivative is also formed from quebrachine (Ewins). When it is warmed with dilute sodium hydroxide, *apoyohimbine* separates $C_{21}H_{24}O_2N_2$, m.p. 251°–252°, $[\alpha]_D = +40^\circ$; this unsaturated base has a very sparingly soluble hydrochloride (1 : 1300 in water at room temperature), and can be reduced catalytically to *deoxy-yohimbine*



(Barger and Field).

For the determination of yohimbine in the bark, see Schomer, Pharm. Zentralh. 1922, 63, 385; for the physiological action, Oberwarth, Virchow's Archiv. 1898, 153, 292; F. Müller, Arch. f. Anat. Physiol., Physiol. Abt. 1906, 391; Gunn, Quart. J. exp. Physiol. 1908, 1, 111; Tait, ibid. 1910, 3, 185; Rumry, J. Pharm. exp. Ther., Proc. 1918, 11, 172). G. B.

VOL. VII.—7.

YOUNG FUSTIC. Young fustic consists of the wood of the stem and larger branches of the *Rhus cotinus* (Linn.), a small tree which is a native of Southern Europe and the West India Islands. It is a hard compact yellow wood, and is usually imported in small bundles or faggots. Within the last few years young fustic has almost disappeared from the market, not only on account of the artificial colouring matters, but because the shades it yields lack permanence, and the percentage of colouring matter it contains is small. The leaves of the *R. cotinus* constitute Venetian sumach, a tanning material which is employed to some extent in Italy and Southern Europe.

Fisetin $C_{15}H_{10}O_6$, the colouring matter of young fustic, was first isolated by Chevreul (Leçons de Chimie appliquée à la Teinture, A. ii. 150), who gave it the name 'Fustin.' Bolley (Schweiz. polyt. Zeitschr. 1864, 9, 22) considered that it was identical with quercetin, but Koch (Ber. 5, 285) maintained that fisetin was probably an aldehyde of quercetin acid.

Schmid (Ber. 1886, 19, 1734), who carried out an exhaustive examination of this dyewood, obtained fisetin in a pure condition and proved that it was not identical with quercetin. He found that in addition to the free colouring matter, young fustic contains a glucoside of fisetin combined with tannic acid to which he gave the name of *fustin tannide*.

To prepare fisetin, Schmid (l.c.), and later Herzig (Monatsh. 12, 178), employed 'cotinin' (v. infra), a commercial preparation of young fustic which is no longer on the market. According to Perkin and Pate (Chem. Soc. Trans. 1895, 67, 648), fisetin is readily isolated from the dyewood as follows:—

Young fustic is extracted with boiling water, and the extract treated with lead acetate solution. The lead compound of the colouring matter is collected, made into a thin paste with water, and in a fine stream run into boiling dilute sulphuric acid. After removal of lead sulphate the dark-coloured filtrate, on cooling, deposits a semi-crystalline brownish mass, which is collected and purified by crystallisation from dilute alcohol.

Schmid assigned the formula $C_{23}H_{14}O_6$ to fisetin, but it was found by Herzig that the analyses agreed equally well with $C_{15}H_{10}O_6$, and that this formula was correct was supported by the work of Perkin and Pato (l.c.), who gave to fisetin sulphate the formula—

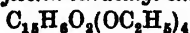


Fisetin forms yellow needles, melting at above 360°, easily soluble in alcohol. Alkaline solutions dissolve it with a deep yellow colour which, on exposure to air, gradually changes to brown; with alcoholic ferric chloride it gives a deep green coloration, and with lead acetate a bright orange-red precipitate. *Tetra-acetyl-fisetin* $C_{15}H_6O_8(C_2H_5O)_4$, m.p. 196°–198°, crystallises in colourless needles, and the *benzoyl* derivative $C_{15}H_6O_8(C_6H_5O)_4$, needles, melts at 180°–181° (Perkin and Pato), (Schmid, 184°–185°). Fisetin gives with mineral acids in the presence of acetic acid crystalline salts. *Fisetin sulphate* $C_{15}H_{10}O_6 \cdot H_2SO_4$, scarlet needles, *fisetin hydrobromide* $C_{15}H_{10}O_6 \cdot HBr$, orange needles, and *fisetin hydrochloride* have been prepared in this

manner (Perkin and Pate). These compounds are readily decomposed by water. *Mono-potassium fisetin* $C_{15}H_8O_6K$, yellow needles (Perkin, Chem. Soc. Trans. 1899, 75, 433), is obtained from fisetin by means of alcoholic potassium acetate.

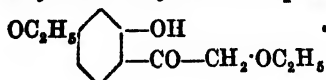
By fusion with alkali or oxidation of its alkaline solution by exposure to air fisetin gives *resorcinol* and *protocatechuic acid* (Herzig).

On ethylation with ethyl iodide fisetin is converted into *fisetin tetraethyl ether*

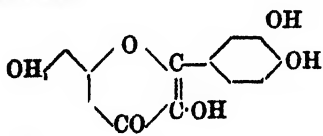


colourless needles, m.p. $106^\circ-107^\circ$; the corresponding methyl derivative $C_{16}H_{14}O_6(OC_2H_5)_4$ melts at $152^\circ-153^\circ$.

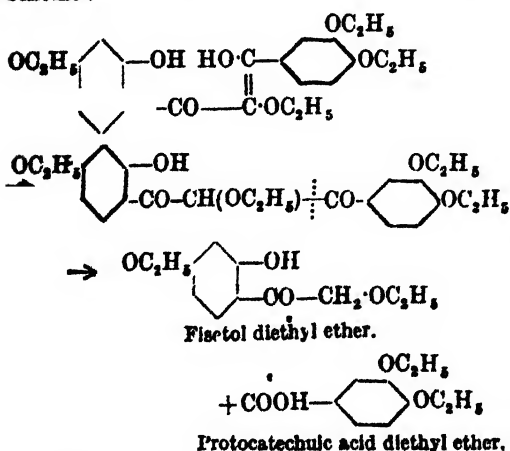
When fisetin tetraethyl ether is submitted to the action of boiling alcoholic potash it gives *protocatechuic acid diethyl ether*, and *fisetol diethyl ether* (Herzig), colourless needles, m.p. $42^\circ-44^\circ$. This latter compound, by oxidation with permanganate, is converted into the *monoethyl ether of resorcylic acid*, and the *monoethyl ether of resorcinolglyoxylic acid*, and consequently fisetol diethyl ether may be thus represented—



As a result of his investigation Herzig assigned to fisetin the constitution of a *tri-hydroxyflavonol*—

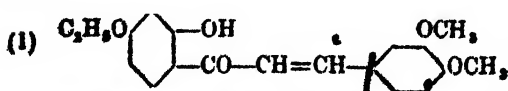


The tetraethyl derivative of this compound suffers hydrolysis according to the following scheme:—



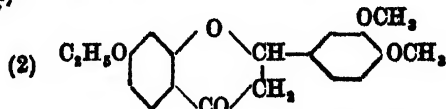
Fisetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 784).

2-Hydroxy-4-ethoxy-3':4'-dimethoxychalkone (1)—

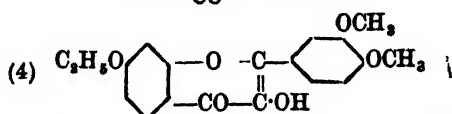
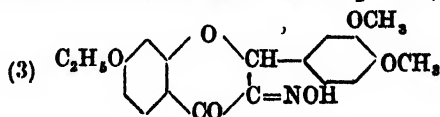


prepared by the condensation of resacetophenone monoethyl ether with veratric aldehyde, when digested with boiling dilute alcoholic sulphuric

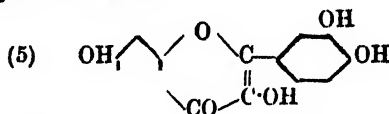
acid gives 3-ethoxy-3':4'-dimethoxyflavonone (2)—



and this, when treated with amyl nitrite and strong hydrochloric acid in alcoholic solution, is converted into the isonitroso compound (3)—



When boiled in acetic acid solution with 10 p.c. sulphuric acid this substance gives 3-ethoxy-3':4'-dimethoxyflavonol (4), from which fisetin (5) is readily produced by the action of boiling hydriodic acid—



The synthesis of fisetin has been more recently effected by Auwers and Pohl (Ber. 1915, 48, 85), from *m-p*-dimethoxy-benzylidene-6-methoxy-cumaranone, the yield being, however only 5 p.c.

Fisetin is a strong colouring matter and gives shades which are almost identical with those produced by quercetin, rhamnetin, and myricetin. The colours given with wool mordanted with chromium, aluminium, and tin are, respectively, red-brown, brown-orange, and bright red-orange (Perkin and Hummel, Chem. Soc. Trans. 1890, 69, 1290).

The glucoside of fisetin, according to Schmid (l.c.), is prepared as follows: A boiling aqueous extract of young fustic is treated with lead acetate, the precipitate removed, the clear liquid freed from lead by means of sulphuretted hydrogen, and saturated with salt. The mixture is filtered, the filtrate extracted with ethyl acetate, and the extract evaporated. There is thus obtained a residue consisting of the crude fustin-tannide, which is purified by solution in water, precipitation with salt, and extraction with ethyl acetate.

Fustin tannide crystallises in long yellowish-white needles, which are easily soluble in water, alcohol, and ether. When heated it decomposes above 200° . If a solution of fustin tannide in hot acetic acid is treated with water, and allowed to stand for some time, colourless crystals of *fustin* are gradually deposited.

Fustin crystallises from water in yellowish-white needles, m.p. $218^\circ-219^\circ$, and when digested with boiling dilute sulphuric acid gives *fisetin* and a sugar, the nature of which has not been determined. The formula given to this glucoside $C_{28}H_{24}O_{18}$ by Schmid cannot be regarded as correct, in view of the fact that the true formula of fisetin is now known to be $C_{15}H_{10}O_6$.

Dyeing properties of young fustic.—The colours derived from young fustic are all fugitive to light, hence this dyestuff has lost its importance. In silk dyeing it was formerly used for dyeing brown, the silk being mordanted with alum, and afterwards dyed with a decoction of young fustic, peachwood, and logwood. With the various metallic salts as mordants young fustic yields colours somewhat similar to those obtained from old fustic, the chromium colour is, however, much redder, being a reddish-brown, and the aluminium yellow is much duller; stannous chloride on the contrary gives an incomparably more brilliant orange, not unlike that obtainable from flavin or from Persian berries (Hummel).

Fisetin is present also as glucoside in the wood of the yellow cedar, *Rhodospachra rhodanthema*, and in the wood of the *Quebracho colorado* (l.c.).

The leaves of the *R. cotinus* contain myricetin.

A. G. P.

YPERITE. Syn. for $\beta\beta'$ -dichloroethyl sulphide; 'mustard gas' (q.v.). For a method of detecting and estimating yperite, see Grignard, Rivat and Scatchard, Ann. Chim. 1921, [ix.] 15, 5.

YTTERBIUM (*Neoytterbium*; *Aldebaranium*; *Cassiopaeum*). Sym. Yb. At.wt. 173.5. In 1878 Marignac, by the fractional decomposition of the nitrates, isolated from crude erbia the earth *ytterbia*, which has since been resolved by Urbain into two components *neoytterbia* and *lutecia* (Compt. rend. 1907, 145, 759; cf. Auer von Welsbach, Monatsh. 1906, 27, 935; 1908, 29, 181; 1913, 34, 1713; Wenzel, Zeitsch. anorg. Chem. 1909, 64, 119; Urbain, Chem. Zeit. 1908, 32, 730; Blumenfeld and Urbain, Compt. rend. 1914, 159, 323).

Occurrence.—Is found in xenotime, ytterbite (gadolinite), monazite.

Separation and purification. v. LUTECIUM (cf. Urbain, Congress of Applied Chemistry, 1909, x. 94).

Ytterbium oxide (*Ytterbia*) Yb_2O_3 , a colourless mass when free from thulia; it dissolves slowly in cold, and readily in hot, dilute acids. With the exception of scandia and lutecia, *ytterbia* (*neoytterbia*) is the weakest base of the yttrium earth series.

Ytterbium hydroxide $\text{Yb}(\text{OH})_3$ is a colourless gelatinous precipitate.

Ytterbium chloride $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (Matignon, Ann. Chim. 1906, [viii.] 8, 440), prepared by the action of hydrochloric acid on *ytterbia*, separates in deliquescent crystals, m.p. 150° – 155° ; it gives rise to the readily soluble platinum-chloride $2\text{YbCl}_3 \cdot \text{PtCl}_4 \cdot 22\text{H}_2\text{O}$, and aurichloride $\text{YbCl}_3 \cdot \text{AuCl}_3 \cdot 9\text{H}_2\text{O}$.

Ytterbium nitrate $\text{Yb}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ crystallises from strong nitric acid in transparent hygroscopic prisms; a trihydrate separating in colourless plates is obtained from solutions evaporated over strong sulphuric acid.

Ytterbium sulphate $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, lustrous colourless crystals, the solubility of which diminishes with rise of temperature; this salt is partially hydrolysed in dilute solutions.

Ytterbium orthophosphate $\text{YbPO}_4 \cdot 4\text{H}_2\text{O}$, a gelatinous precipitate obtained from soluble ytterbium salts and sodium phosphate; the metaphosphate $\text{Yb}(\text{PO}_3)_3$, a crystalline powder,

produced by melting together anhydrous ytterbium sulphate and metaphosphoric acid.

Ytterbium borate YbBO_3 , obtained by fusing together ytterbia and boric anhydride; is a crystalline mass insoluble in dilute hydrochloric acid.

Ytterbium carbonate $\text{Yb}_2(\text{CO}_3)_3 \cdot 4\text{H}_2\text{O}$, a gelatinous precipitate produced by mixing solutions of ytterbium nitrate and ammonium carbonate; the basic carbonate $\text{Yb}(\text{OH})\text{CO}_3 \cdot \text{H}_2\text{O}$ is formed by passing carbon dioxide through freshly-precipitated ytterbium hydroxide.

Ytterbium cobalticyanide $\text{Yb}_2(\text{CoC}_6\text{N}_6)_3 \cdot 9\text{H}_2\text{O}$, very slightly soluble in a 10 p.c. solution of hydrochloric acid; 1000 parts of a saturated solution contain 0.38 part of the salt.

Ytterbium oxalate $\text{Yb}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ is a crystalline powder distinctly more soluble in dilute sulphuric acid than the oxalates of yttrium and gadolinium (Nilson, Compt. rend. 1879, 89, 419; 1880, 91, 56, 118). The normal ytterbium salts of the lower fatty acids are very soluble substances.

Ytterbium dimethyl phosphate, long white needles, solubility 1.2 at 25° and 0.25 at 95° .

Spectra.—Spark spectrum (i.) visible region (Thalén, *ibid.* 1880, 91, 326); (ii.) ultra-violet (v. Welsbach, Monatsh. 1884, 5, 1; Crookes, Proc. Roy. Soc. 1906, 78, A, 154). Spark and arc spectrum (Exner and Haschek, Die Spektren der Elemente bei normalen Druck, 1912; Eder and Valenta, Atlas typischer Spektren, 1911; Kaiser, Akad. der Wissensch. Wien).

G. T. M.

YTTRIALITE. An amorphous mineral consisting of silicate of yttrium, thorium, &c., approximating to the formula $\text{R}_2\text{O}_3 \cdot 2\text{SiO}_2$. It contains Y_2O_3 46.5, ThO_2 12 p.c. The material is translucent with a dark olive-green colour on the fresh conchoidal fracture; externally it weathers to orange-yellow. Sp.gr. 4.58, H. 5–5½; soluble in hydrochloric acid. Masses up to 18 lb. in weight are found with gadolinite at Barringer Hill in Llano Co., Texas.

L. J. S.

YTTRIUM. Sym. Y. At.wt. 88.7 (Meyer and Weinheber); 90.12 (Egan and Balke); 88.9 (Smith and Balke); 89.33 (Kremers and Hopkins); 89.03 (Fogg and James). The individuality of yttria, the predominant and most basic constituent of the yttrium earths, was first recognised by Mosander in 1843, and is the most easily purified oxide of this series.

Sources.—The yttrium earths from the following minerals: ytterbite, xenotime, fergusonite, yttrotantalite, samarskite, polycrase, euxenite, yttracrasite (Amer. J. Sci. 1906, [iv.] 22, 515). It also occurs in smaller quantities in the rare earths from cerite and allied minerals (v. CERIUM METALS AND EARTHS).

Separation and purification.—In its basicity yttria follows the more basic cerite earths and is separated by methods founded on differences in basic strength from the other less basic yttrium earths, erbia, dysprosia, thulia, ytterbia, lutecia, and scandia, the following processes being employed for this purpose: (1) decomposition of nitrates; (2) the basic salt method (v. LANTHANUM AND SCANDIUM); (3) fractional precipitation with alkalis or aniline; (4) successive treatment with ammonium carbonate and acetic acid.

Crystallisation methods are less practicable in the yttrium than in the cerium group, because of the greater solubility of the salts and the instability of the double nitrates, which in the yttrium series are unstable at the ordinary temperatures in aqueous or nitric acid solutions. Nevertheless, the final purification of yttrium from erbium, &c., may be effected by fractionation of the bromates, chromates, formates, acetates, oxalates, acetylacetones, ethyl-sulphates, and ferrocyanides (*v. ERBIUM*).

According to Meyer and Wuorinen (*Zeitsch. anorg. Chem.* 1913, 80, 7), the following methods are suitable for the fractionation of mixtures containing yttrium. The precipitation of dichromate solutions with potassium chromate separates yttrium well from terbium and gadolinium, but is most applicable to mixtures from which most of the terbium group has been removed by other methods, when it yields pure yttria.

Fractional crystallisation of the ethyl sulphates is tedious, but is suitable for large quantities. Precipitation with potassium ferrocyanide furnishes nearly pure yttria, but the yield is small, and the precipitates are not readily filtered. Crystallisation of the double ammonium tartrates is unsuccessful, as is also the fractional hydrolysis of these salts by water, ammonia, or magnesia.

A method, depending on the hydrolysis of solutions of the phthalates by heat, rapidly removes the erbium group, and gives a large yield of a product consisting mainly of yttria, which is then conveniently purified by fractionally precipitating a slightly acid solution of the nitrates with potassium iodate.

By Muthmann and Bölin's chromate method small quantities of fairly pure yttria can be rapidly prepared from mixtures containing small amounts of erbium and holmium, but the method cannot be applied to the fractionation of mixtures containing didymium and gadolinium unless these are first removed by potassium sulphate (Egan and Balke, *J. Amer. Chem. Soc.* 1913, 35, 365). Holden and James (*J. Amer. Chem. Soc.* 1914, 36, 638) have investigated the various fractional precipitation methods in order to ascertain the best method of separating yttrium from the yttrium earths. The methods used were fractional precipitation of the dimethyl phosphates, the cacodylates, the phosphates, the monomethyl phosphates, the arsenates, the phosphites, the chromates, the iodides and bromates and hypophosphates. Of these the chromate and phosphate methods were found to be the most efficient. A still more effective method has been found in the fractional precipitation with sodium nitrite. The oxides are dissolved in nitric acid, the solution diluted and boiled, and a quantity of sodium nitrite added sufficient to precipitate the required fraction of the rare earth material. The yttrium concentrates in the later fractions. This method gives a larger yield, a more rapid separation and is less expensive than the phosphate or chromate method. It is not, however, very effective for the separation of yttrium from terbium (Holden and James, *l.c.* 1914, 36, 1418).

In the fractional electrolysis of the earths from xenotime, erbium collects in the early

fractions and yttrium in the later fractions (Dennis and Lemon, *J. Amer. Chem. Soc.* 1915, 37, 31).

Willand and James (*J. Amer. Chem. Soc.* 1916, 38, 1198) find that the best modes of separating yttrium, in relatively large quantity, from erbium, are by the use of the nitrite, cobalticyanide, and phosphate methods. Fractional precipitation with sodium nitrite is recommended for work on a large scale, on account of the cheapness of the salt and the ease of manipulation (*cf.* Bonardi and James, *J. Amer. Chem. Soc.* 1915, 37, 2642; Wichers, Hopkins and Balke, *ibid.* 1918, 40, 1615).

Yttria may also be separated from other rare earths by taking advantage of its solubility in ammonium nitrate solution (Prandtl, *Zeitsch. anorg. Chem.* 1925, 143, 277).

According to Whittemore and James (*J. Amer. Chem. Soc.* 1912, 34, 773) yttrium can be quantitatively separated from sodium by precipitation with ammonium sebacate and from potassium by a double precipitation with the same reagents. The separation of yttrium from iron, aluminium, lithium, and magnesium can be effected by its precipitation as oxalate by oxalic acid in presence of ammonium chloride.

Metallurgical yttrium has been obtained by the reduction of yttrium chloride or yttrium sodium chloride with sodium or by the electrolysis of the latter salt; it is an iron-grey substance melting at 1490°, easily oxidisable and decomposing hot water (Cleve, *Bull. Soc. chim.* 1873, [ii.] 18, 193, 289; 1874, [ii.] 21, 244; *cf.* Winkler, *Bor.* 1890, 23, 44, 120, 772, 2642). *See also* *Trans. Amer. Electrochem. Soc.* 1926, 49, 161.

Yttrium oxide (*Yttria*) Y_2O_3 , white powder, sp.gr. 4.84; sp.ht. 0.1173, absorbing carbon dioxide from the atmosphere; obtained crystalline by fusion with calcium chloride (*Compt. rend.* 1888, 107, 99; *J. Russ. Phys. Chem. Soc.* 1910, 42, 96).

Yttrium hydroxide $Y(OH)_3$, gelatinous precipitate; the product obtained with ammonia in presence of hydrogen peroxide is a hydrated peroxide $Y_4O_9 \cdot xH_2O$ (Cleve, *Bull. Soc. chim.* 1885, [ii.] 43, 53).

Yttrium carbide YC_2 , yellow crystalline mass, sp.gr. 4.13, produced by heating the oxide with carbon in the electric furnace, is decomposed by water evolving acetylene, mixed with hydrogen, methane, and ethylene (Moissan and Étard, *Compt. rend.* 1896, 122, 573).

The salts of yttrium with colourless acid radicals are devoid of colour, and their solutions show no selective absorption in the visible region of the spectrum.

Yttrium fluoride $YF_3 \cdot \frac{1}{2}H_2O$ is obtained in the wet way as a gelatinous precipitate; the anhydrous substance is produced by the action of fluorine on the carbide (Moissan and Étard, *l.c.*).

Yttrium chloride YCl_3 can be produced by the methods generally applicable for the preparation of the anhydrous chlorides of the rare earths (*v. CERIUM*). The hexahydrate

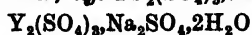


colourless deliquescent prisms, melts at 100°, and is readily soluble in water or alcohol (Matignon, *Ann. Chim.* 1906, [viii.] 8, 433).

The solubilities of the chloride, bromide, nitrate, and sulphate of yttrium have been deter-

mined by Crew, Steinert and Hopkins (J. Phys. Chem. 1925, 29, 34).

Yttrium sulphate $Y_2(SO_4)_3 \cdot 8H_2O$, monoclinic crystals, isomorphous with the octahydrated sulphates of erbium, neodymium, and praseodymium (Kraus, Zeitsch. Krist. 1901, 34, 307). The acid sulphate $Y(SO_4)H_2$ separates from concentrated solutions in sulphuric acid (Braunor and Pidék, Zeitsch. anorg. Chem. 1904, 38, 322). With alkali sulphates, yttrium forms soluble double sulphates, e.g. $2Y_2(SO_4)_3 \cdot 3K_2SO_4$;



$Y_2(SO_4)_3 \cdot 2(NH_4)_2SO_4 \cdot 9H_2O$; these salts crystallise on concentrating the aqueous solution of their components.

Yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$, very soluble deliquescent crystals; a dihydrate has also been described (Tanatar and Voljanski, J. Russ. Phys. Chem. Soc. 1910, 42, 586); basic nitrates, e.g. $3Y_2O_3 \cdot 4N_2O_5 \cdot 20H_2O$, are produced by the partial decomposition of the normal salt (James and Pratt, J. Amer. Chem. Soc. 1910, 32, 873).

Yttrium phosphates. The ortho-phosphate YPO_4 , which occurs native as xenotime (*v. supra*), has been obtained in lustrous needles by melting together yttrium chloride and the amorphous phosphate ('umpt. rend. 1875, 80, 304; 1888, 107, 622). When prepared in the wet way the crystalline salt has the composition $YPO_4 \cdot 2H_2O$. The normal pyro- and metaphosphates $Y_4(P_2O_7)_3$ and $Y(PO_3)_3$ have been described together with several acid and double phosphates (Cleve, *l.c.*; Johnson, Ber. 1889, 22, 976).

Yttrium carbonate $Y_2(CO_3)_3 \cdot 3H_2O$, white precipitate obtained either from a soluble yttrium salt and an alkali carbonate, or by passing carbon dioxide into freshly-precipitated yttrium hydroxide; it dissolves in excess of aqueous alkali carbonate forming double carbonates, e.g. $Y_2(CO_3)_3 \cdot Na_2CO_3 \cdot 4H_2O$.

Yttrium cobalticyanide $Y_2(CoN_6C_6)_3 \cdot 9H_2O$. Sparingly soluble in 10 p.c. hydrochloric acid solution; 1000 parts of a sat. solution contain 2.78 parts of the salt.

Yttrium ferrieyanide $YFe(CN)_6$ is precipitated from a mixture of dilute solutions of potassium ferrieyanide and yttrium chloride.

Yttrium oxalate $Y_2(C_2O_4)_3 \cdot 9H_2O$, a white crystalline powder, dissolving in aqueous potassium oxalate to form $Y_2(C_2O_4)_3 \cdot 4K_2C_2O_4 \cdot 12H_2O$; it is soluble in dilute sulphuric acid to approximately the same extent as lanthanum oxalate.

Yttrium dimethyl phosphate, long white needles, solubility 2.80 at 25° and about 0.55 at 95°.

Yttrium salts of other organic acids (*v. Cleve, l.c.*; Tanatar and Voljansky, *l.c.*; Benner, J. Amer. Chem. Soc. 1911, 33, 50; Jantsch and Meyer, Ber. 1920, 53, [B] 1577; Meyer and Müller, Zeitsch. anorg. Chem. 1919, 109, 1).

Spectra.—Spark spectrum; visible region (Thalén, Bull. Soc. chim. 1873, [ii.] 22, 250; Bunsen, Pogg. Ann. 1875, 155, 230, 366; v. Welsbach, Monatsh. 1884, 5, 1; Meggers, J. Washington Acad. Sci. 1924, 14, 419; Meggers and Moore, *ibid.* 1925, 15, 207); ultra-violet region (Lohse, Ber. Berlin Akad. 1897, 179; Exner and Haschek, Ber. Wien. Akad. 1900, 109, IIa, 122). Arc spectrum (Exner and Haschek, Die Wellenlängen der Bogenspektren,

1904; Eberhard, Zeitsch. wiss. Photograph. Photophysik. Photochem. 1909, 7, 245; Eder, Chem. Zeit. 1916, ii. 455). A complete list of the wave lengths determined from $\lambda 2243$ to $\lambda 4200$ is given by Yntema and Hopkins (Optical Soc. of America, 1922, J. 6, 121). Cathode luminescence (Crookes, Chem. Soc. Trans. 1889, 55, 255; Chem. News, 1889, 60, 27, 39, 51, 63; Muthmann and Baur, Ber. 1900, 33, 1748; Baur and Marc, *ibid.* 1901, 34, 2460).

G. T. M.

YTTROCERITE or YTTROFLUORITE. Calcium fluoride, or fluor-spar, containing varying amounts of yttrium and cerium fluorides in isomorphous mixture or solid solution, the general formula being $(Ca, Y, Ce)_2F_6$. Artificial fusions of calcium fluoride with these rare-earth fluorides give homogeneous mixed cubic crystals containing up to 50 p.c. YF_3 (there being a maximum melting-point at 1408° with 20 p.c. YF_3 , corresponding to $7CaF_2 \cdot YF_3$), and up to 55.8 p.c. CeF_3 . The former may be called *ytthrofluorite*, and the latter *cerfluorite* (T. Vogt, 1914). Yttrocerite was originally described by Gahn and Berzelius in 1814 from Finbo and Braddbo near Fahlun in Sweden; where, as white, yellowish, or dark violet, granular masses with octahedral cleavage and sp.gr. 3.45, it occurs sparingly with topaz and albite in quartz. The early analyses showed Ce_2O_3 , 16–18, Y_2O_3 , 8–9 p.c. Similar material has been found at Amity in New York; in a fluor-spar vein in Massachusetts; at Mount Mica near Paris, in Maine; and with topaz, felspar, and quartz in Colorado (probably Pike's Peak district). The Colorado mineral is violet-blue and resembles fluor-spar in appearance; analysis showed Y_2O_3 , 29.36, Ce_2O_3 , 18.19 p.c.; sp.gr. 4.31. In 1911 T. Vogt described, as a new mineral under the name *ytthrofluorite*, material from Hundholmen in Nordland, Norway. Here it occurs in considerable quantity forming a vein some metres in width in pegmatite intersecting granite. Associated minerals are fluor-spar, orthite, gadolinite, fergusonite, and xenotime. The composition is variable, one sample yielding on analysis Y_2O_3 , 17.35, Ce_2O_3 , 1.68 p.c., corresponding nearly to the formula $7CaF_2 \cdot YF_3$ mentioned above. This material resembles fluor-spar in appearance. It is pale yellow with an imperfect octahedral cleavage; sp.gr. 3.56, H. 4½, optically isotropic, n_D 1.4572 (of the material analysed).

L. J. S.

YTTROCRASITE. Hydrated titanate of yttrium, thorium, uranium, &c., crystallised in the orthorhombic system. Analysis shows $(Y, Er)_2O_3$, 25.67, Ce_2O_3 , etc., 2.92, ThO_2 , 8.75 p.c. The mineral is black with a bright pitchy lustre on the small-conchoidal fracture, resembling polycrase in appearance. Sp.gr. 4.804, H. 5½–6. Under the microscope thin splinters are transparent and colourless to pale yellow, and are seen to consist of a mixture of optically isotropic and feebly birefringent material. The mineral thus appears to have resulted from the alteration of an originally anhydrous species. It was found in Burnet Co., Texas, not far from the well-known gadolinite locality in Llano Co.

L. J. S.

YTTROFLUORITE v. YTTROCERITE.

YTTROTANTALITE. A complex mineral

consisting essentially of yttrium tantalate and crystallising in the orthorhombic system. It is black with a bright, conchoidal fracture, and closely resembles samarskite (*q.v.*) in appearance. Masses several pounds in weight have been

found in the felspar quarries at Ytterby and Fahlun in Sweden and in the south of Norway (W. C. Brögger, *Die Mineralien der süd-norwegischen Granitpegmatitgänge*, Vid.-Selsk. Skr. Kristiania, 1906, No. 6, 152). L. J. S.

Z

ZAFFRE. *Cobalt blue v. COBALT*; also **PIGMENTS**.

ZALA. A synonym for Borax.

ZAMIA STARCH is derived from the rhizomes of *Zamia floridana*, DC., a dioecious plant belonging to the Cycadaceae growing in Florida. Is present in the air-dried rhizomes to the extent of 37-75. The grains are spherical, ovoid, and dome-shaped, varying from 6 to 40 μ in length. Sometimes marketed as 'Florida Starch,' a term also applied to the starch derived from *Maranta arundinacea*, the true arrowroot starch, also produced in Southern Florida (Clevenger, *Amer. J. Pharm.* 1922, 94, 98).

ZANTHOXYLUM. The bark of the prickly ash, *Zanthoxylum americanum* (Mill.), and *Z. carolinianum*, which are rutaceous plants. Is used in medicine in the treatment of rheumatism and to relieve toothache. It contains a volatile oil and resin.

ZARATITE or **EMERALD-NICKEL.** Hydrated basic nickel carbonate



As thin mamillary crusts with an emerald-green colour and vitreous lustre it occurs generally on serpentine together with chromite, *e.g.* at Texas in Pennsylvania, Unst in Shetlands, Dun Mountain in New Zealand, Tasmania, &c. L. J. S.

ZAUBERIN. Trade name for the sodium compound of toluene para-sulphochloramide, used as a detergent and bleaching agent.

ZEIN *v. Maize*, art. ('EREALS).

ZEIODELITE. The name of a mixture obtained by stirring 24 parts of finely-powdered glass into 20 parts of melted sulphur; used as a cement and for taking casts instead of sulphur or plaster.

ZEOBROMAL. Dibromocinnamic ethylester.

ZEOLITES. A large group of minerals consisting of hydrated silicates of aluminium with alkalis and alkaline earths. A few of the more important are—

Natrolite (<i>q.v.</i>)	$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10} \cdot 2\text{H}_2\text{O}$
Stilbite	$\text{CaAl}_2\text{Si}_2\text{O}_{10} \cdot 6\text{H}_2\text{O}$
Heulandite	$\text{CaAl}_2\text{Si}_2\text{O}_{10} \cdot 5\text{H}_2\text{O}$
Chabazite	$\text{CaAl}_2\text{Si}_2\text{O}_{10} \cdot 6\text{H}_2\text{O}$
Analcime	$\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$
Thomsonite (<i>q.v.</i>)	$(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_2\text{O}_{10} \cdot 2\frac{1}{2}\text{H}_2\text{O}$

Harmotome and edingtonite contain barium; brewsterite contains some strontium; and potassium is present in phillipsite (*q.v.*). These minerals hold their water of crystallisation very loosely, and it is replaceable by a variety of substances (*e.g.* ammonia, alcohol, &c.). They lose readily with intumescence, hence the name *zeolite*, from *zein*, to boil, and *lithos*, a stone. They are readily decomposed by acids, usually with the separation of gelatinous silica; and by the action of various reagents several sub-

stitution products have been prepared. They are minerals of secondary origin, occurring usually in the steam-cavities of volcanic rocks, and have been derived from the decomposition of felspar and other alkali-bearing minerals (with which they show certain chemical analogies).

The zeolites present many points of mineralogical interest, and they afford beautifully crystallised specimens, but they are of no direct economic importance. They appear, however, to play an important part in soils by retaining in a readily soluble form the alkalis set free on the weathering of felspar. The indefinite zeolitic constituent of soils has been named *geolyte* (Ger. *Bodenzeolith*) (E. A. Wülfing, *Jahresh. Ver. Naturk. Württemberg*, 1900, 56, 35; R. Gans, *Zeolithe und ähnliche Verbindungen ihre Konstitution und Bedeutung für Technik und Landwirtschaft*, Jahrb. K. Preuss. Geol. Landesanst. Berlin, for 1905, 1906, 179-211).

On *permutite*, an artificial zeolite-like substance employed for softening water and for removing manganese and iron from water, and also used in sugar refining, and in gas-masks for absorbing gases, *v. R. Gans*, *Chem. Zentr.* 1909, i. 2031; *Chem. News*, 1919, 118, 15; also art. **WATER**. L. J. S.

ZEUNERITE *v. URANITE*.

ZIBETHONE *v. KETONES*.

ZINC. Sym. Zn. At.wt. 65.38, Richards and Roger; Baxter and Hodges. This metal was mentioned by Albertus Magnus, who died in 1280, the name then employed being 'golden marcasite.' The modern word zinc appears first in the writings of Paracelsus, about 1500, although the identification of zinc as the metal from blende is due to Homberg in 1695.

The metal had, however, been produced at a much earlier date, probably by accident. Zinc bracelets were discovered in the ruins of Cameros, destroyed circa 500 B.C. Libavins carefully examined the properties of zinc about 1595.

From the fact that the variation of the cubical expansion of zinc with temperature exhibits singular points at 176° and 320°, it is surmised by L. Losagn (Gazz. Chim. Ital. 1923, 53, 539) that this metal exists in at least three allotropic forms.

According to Egerton (*Nature*, 1922, 110, 773) it has been found possible to separate zinc by fractional distillation into a distillate and a residue, the densities of which bear to that of the initial metal the ratios 0.99971:1 and 1.00026:1, respectively, the differences being greater than the probable experimental error; see also Egerton and Lee, *Proc. Roy. Soc.* 1922, 103, 499.

Ores of zinc were known to the ancients, and were employed by them both for the manu-

facture of brass by the calamine process, and also in medicine. The working of zinc ores in Europe in modern times dates from the introduction of the use of brass, and there are records extant which show that in 1439 the Vieille Montagne calamine mines had been worked for a considerable time by the men of Aix. Metallic zinc was sometimes produced accidentally during the smelting of copper, but is stated to have been first made directly from calamine by Henckel in 1721 (Percy, Metallurgy, i. 520). A zinc factory was erected at Bristol by Champion in 1743; but the production in this country was small, the greater part of the metal required being imported from China and India, and zinc is stated to have sold in 1731 for £260 per ton, or more than eight times its present value. Other works were erected in the United Kingdom, and the demand gradually increased with the introduction of the direct method for the manufacture of brass. In England the process of distillation *per descensum* in fireclay crucibles was adopted; this has scarcely been used elsewhere, and is now completely abandoned in this country. The important zinc industry of Silesia in Germany was commenced in 1799 by Ruhberg, who had learned the process in England. The Liège (or Belgian) process was invented by Daniel Dony in 1809, and works were immediately erected for carrying out the process at Liège. These works ultimately developed into the Société de la Vieille Montagne in 1837, and this Société is now one of the largest zinc-producing companies in the world. Zinc smelting was not introduced into the United States until 1850. It was not till 1920 that the exports of zinc from England to India about equalled the total imports, and this country could be considered for the first time to supply itself with zinc. Since that time, however, the trade has fluctuated considerably, so that in 1864 the total production of zinc in the United Kingdom did not equal one half of that required in the Birmingham brass trade alone.

In recent years the world's production of zinc (or 'spelter') has steadily increased, though the industry is limited to comparatively few centres. On the continent smelting is conducted in Belgium, Westphalia, and Silesia; in America the centres are Kansas, Illinois, Oklahoma, and New Jersey; in Australasia, particularly in Tasmania; in the United Kingdom at Swansea, in Durham, and near Birmingham. The world's production of zinc in 1919 was about 520,000 tons, including 410,000 tons in the United States, but only about 20,000 tons in Great Britain, where the output was limited by shortage of ore and labour troubles. During 1919 British imports of spelter amounted to 94,226 tons.

According to the Imperial Mineral Resources Bureau, the following figures show the world's smelter production of metal for the year's covered by the publications:—

	1919	1920	1921
Zinc, long tons .	645,000	705,000	432,000

(J. Chem. Ind. 1923, 42, 966).

In 1919, 1920, and 1921, the contribution of the British Empire to the zinc production of the world was 11 p.c., 6 p.c., and 30 p.c. respectively, of the world's production, the low figure for 1920 being due primarily to the

strikes at the Broken Hill mines in Australia. In 1913 the United States consumed 308,000 tons, Germany 228,000 tons, and the United Kingdom 191,000 tons. Those three countries are the chief consumers of the metal. The British Empire meets only one-third of the requirements of the Mother Country.

The two most noticeable features in respect of zinc at the present time are: (1) The rising production of electrolytic zinc, notably in Tasmania, Canada, and the United States of America; and (2) the fact that, as a result of the war, the world's smelting capacity of zinc is largely in excess of the ore-production. The capacity in this respect of the United States alone is now 800,000 tons per annum. The electrolytic process is now an acknowledged commercial success, although still the greater part of the production is due to distillation (Redmayne, J. Soc. Arts. 1923; J. Soc. Chem. Ind. April 27, 1923).

The Derbyshire mines were once of great importance, but their output now is negligible. Between 1880 and 1910 the British production of zinc increased tenfold. At the end of the nineteenth century a very important zinc industry had grown up in Kansas. It depended largely on natural gas for fuel, and with the gradual exhaustion of the gas supply many spelter works were closed, and the industry migrated to the coalfields of Illinois or to Joplin.

Ores of zinc.—The most important ores of zinc are the sulphide and carbonate. *Zinc blende* (ZnS) is commonly called 'black jack' by the miner on account of its dead black colour and high lustre. The use of blende for the manufacture of zinc and brass was patented in 1758 by Champion of Bristol. Previously the source of the metal was the carbonate, *calamine* ($ZnCO_3$), and this was the only ore used in Belgium until about 1855, when roasting of blende was adopted. Both these ores are widely distributed and are now extensively employed. Of less importance are the oxide (which usually contains oxide of manganese, and from its colour is called red oxide of zinc), and the silicates.

In New Jersey red oxide of zinc occurs together with magnetic oxide of iron in *Franklinite* from which the zinc is first extracted, and the residue is afterwards smelted for spiegel-eisen in the blast furnace. For ores which consist largely of oxide of zinc, but with some iron, magnetic concentration is now employed, the magnetite being removed, and an ore suitable for the zinc smelter obtained. The flue dust from the blast furnace used in the manufacture of iron is also frequently sufficiently rich in zinc to render its extraction advantageous.

The greater part of the zinc smelted in the United Kingdom is now obtained from imported ores. Within the Empire are to be found some of the largest deposits of zinc ore in the world, e.g. Broken Hill, Australia, Bawdwin mines of Burma, Rhodesian Broken Hill, Tasmania, and British Columbia. Ores imported chiefly from Spain, Algeria, and Sardinia were prior to the war mostly used. Zinc ores are closely associated with those of lead, and the two metals are in many cases obtained from the same mine—just as in the case of lead. The United States of

America far exceeds any other country as producer of zinc.

Extraction of zinc.—It is necessary that the ores used for the extraction of zinc should be as rich and as uniform in character as possible. The ore as purchased by the smelter usually contains at least 50 p.c. of zinc, though 45 or even 40 p.c. ores are used if they contain other valuable materials to replace the decrease in zinc. The ores as they occur are often only poor in zinc, and require to be concentrated by washing in the case of calamine ores this is usually a simple matter, but with blendes which are frequently associated with other sulphides, concentration is a more complicated operation, though with modern appliances, careful sizing, and the necessary attention, a remarkably perfect separation can be effected. The slimes produced during concentration are again treated, 'true vanners' being now used for this purpose, and such portions as are rich in zinc are dried and smelted in mixture with other materials as afterwards described.

'Complex' ores, i.e. ores containing other metals in addition to zinc, have been the cause of considerable loss in times past, and enormous quantities of tailings were accumulated. These are now treated by flotation processes which separate the metallic sulphides from the gangue. In oil separation processes the dry, finely-crushed ore is mixed with a small quantity of oil, and is then washed with water. The metallic particles, or other bodies with smooth surfaces like sulphides, are wetted by the oil, and float upon the water, while the earthy portions sink to the bottom. In the Elmore oil vacuum process separation is assisted by the aid of partial exhaustion of a large metal receiver into which the oiled slimes and water enter. The air films surrounding the oiled particles are thus expanded and the separation much improved. In other cases diluted acid is employed, and with suitable ores gas bubbles are produced which cause the particles rich in metal to rise to the surface of the liquid. These flotation processes are now of such importance that from the Central mine at Broken Hill in Australia one-tenth of the total zinc ore of the world is obtained. The original ore contains 16.5 p.c. lead, 18.5 p.c. zinc, and 13 oz. of silver per ton. The concentrates account for 90 p.c. of the lead present, 85 p.c. of the zinc, and 88 p.c. of the silver (Sulman, Jour. Inst. Min. and Metallurgy, 1911, 47, 20).

Previous to the outbreak of war in 1914, the control of these Broken Hill concentrates was largely in German hands.

When the ores have been thus concentrated, they are calcined or roasted to convert them as completely as possible into zinc oxide. Calamine is readily calcined, and this is frequently conducted in kilns with the waste heat from the smelting furnaces. On the other hand, blende requires much care and experience in roasting, so as to prevent the formation of difficultly decomposable sulphate. Blende is generally roasted in multiple-bedded reverberatory furnaces, sometimes with the waste heat from the smelting furnaces. By the use of multiple-

roasting furnaces a considerable economy of fuel and more uniform heating are obtained. It has generally been considered that the presence of any sulphur in roasted blende leads

to loss of zinc, owing to sulphide being left in the retort, but, according to A. Voigt (J. Soc. Chem. Ind. 8, 1986), the zinc left in the retort is chiefly in the form of oxide, while the sulphur in roasted blende is in the form of sulphates of metals generally other than zinc, and the presence of a small quantity of sulphur in roasted blende does not reduce the yield of zinc.

In roasting blendes a quantity of zinc fume is produced, and may lead to a somewhat considerable loss of zinc. This fume has been utilised by Krause-Cöthen for the manufacture of zinc carbonate (Berg. u. Hütt. Zeit. 1891, 246). The blende roasted at Oberhausen contains 0.02 p.c. of mercury. The dust deposited from the roasting kilns contains about 7 p.c. of mercury, which is extracted, and the sulphur dioxide from the gases is used for the manufacture of sulphuric acid (Chem. Zeit. 10, 1039).

Great advances have been made in recent years in the furnaces used for roasting blende, the object being to economise fuel and labour, to obtain a more uniform product, and to utilise the sulphur dioxide evolved. This branch of the subject has been historically treated and fully illustrated by E. Schutz, Metallurgie, 1911, 635. One form of such furnace which has met with considerable favour is known as the Merton. It is multiple-bedded, and mechanically stirred.

After calcination the finely-divided ore is in all cases mixed with a suitable proportion of ground coal (non-caking), or other carbonaceous material, and heated to bright redness in a retort, the form and dimensions of which vary with the locality and the nature of the ore. The carbon unites with the oxygen of the ore to form carbon monoxide, and zinc is set free; the metal at the high temperature employed is converted into vapour, which is caused to pass into suitable receptacles, and condensed. The processes which are, or have been, used for the extraction of zinc differ merely in the form, arrangement, and number of the retorts, and in the methods adopted for supporting and heating them.

As the temperature at which the reaction $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$ takes place under ordinary atmospheric pressure is about 1050° , and nearly as high in a vacuum, the temperature of the retorts is necessarily high. The fuel consumption is therefore high, and the wear and tear of the retorts considerable. The difficulty of condensing the zinc vapour is increased by the fact that it is accompanied by carbon monoxide and other gases.

According to Lemaire (Compt. rend. 1920, 170, 807), zinc oxide is readily reduced directly by carbon without the necessary intermediate formation of carbon monoxide. The amount of carbon entering into the reaction is intermediate between the amounts necessary for the two possible actions $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$; $2\text{ZnO} + \text{C} = 2\text{Zn} + \text{CO}_2$. This is explained on the ground that the reduction of zinc oxide by carbon monoxide $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ takes place with a velocity greater than that of the reduction of carbon dioxide by carbon. The first reaction commences at 350° , and the second only at 400° (Chem. Soc. Abstr. 1920, ii. 313).

It is advantageous to crush the materials thoroughly, and to have as large a condensing space as possible. The condensers should be just sufficiently hot to keep the condensed metal

in the liquid state, as, if the receivers are too hot, zinc is lost by volatilisation, while if the temperature is too low a coarse crystalline product is obtained. It is necessary that the retorts should be kept filled with carbon monoxide; if carbon dioxide is present, part of the zinc is oxidised and zinc and zinc oxide distil over together. For this reason it is necessary to leave a little of the ore unreduced in the retort at the end of the process (Steger, J. Soc. Chem. Ind. 5, 607).

The following general principles have been laid down for the construction of zinc furnaces by M. F. Laur (Bull. Soc. Indust. Minérale, 1874, 3, 395; Inst. C. E. 41, 317):—

1. That it is not prudent to construct furnaces the internal capacity of which exceeds about 32·5 cubic yards.

2. The thickness of the charge to be reduced in the muffles should not exceed 7 ins., and the vessels should not exceed 20 ins. in height, or 5 ft. in length.

3. The maximum capacity which can be advantageously given to the retorts is about 22 gallons.

4. The total internal volume of the retorts should be about one-third of the volume of the furnace in which they are heated, since experience shows that about two-thirds of the space is required for supports and free circulation.

Four processes for the extraction of zinc have been actually worked on a considerable scale—namely, the English, Carinthian, Belgian, and Silesian.

1. In the *English process*, adopted by Champion at Bristol, large fire-clay crucibles were used, and the method was that known as distillation *per descensum*. The process involved the use of an excessive amount of fuel, and only a comparatively small amount of zinc could be produced. This manufacture forms a very interesting chapter in the metallurgy of zinc, and has been fully treated by Dr. Percy (Metallurgy, i. 550), but as it has been entirely superseded, will not be here described in detail.

2. The *Carinthian process*.—The process formerly adopted in Carinthia was in principle similar to the English method, the ore being charged into vertical pipes or retorts of fire-clay, and distillation being effected *per descensum*; a single furnace sometimes contained over 250 such pipes. This process is also now abandoned.

- 3 and 4. *Belgian and Silesian processes*.—The only processes now in extensive operation for the smelting of zinc are the Belgian and Silesian, neither of which is confined to the countries in which it was invented. The two systems are sometimes combined in the same furnace, the retorts in the lower or hotter part being on the Silesian principle, and in the upper part on the Belgian. In each case the retorts are of fire-clay, and are generally made on the premises. In this country they are still frequently moulded by hand, then air-dried for about a fortnight, and afterwards heated to redness in a separate furnace before being set in position. By an improvement, the invention of M. Dor, which has been largely adopted on the Continent, and to some extent in the United Kingdom, the retorts are subjected to a pressure of 3000 lbs. to the square inch during manufacture. Great care is taken in the selection of suitable clays, in

the preparation and tempering, and in pressing the retorts. They are thus made very thin, and yet possess great durability. The differences between the Belgian and Silesian systems are in the shape, size, and method of supporting the retorts, in the amount of charge used, and in the arrangement of the retorts in the furnace. In each system direct firing by coal was formerly universal and is still occasionally used, but gas-firing is now very generally employed. In Wales and in the United States regeneration by reversals, on the Siemens' principle, is generally adopted, but in Belgium continuous regeneration is preferred. In this system the gas producers are not separate from the furnace, but are placed in the furnace below the retorts. The products of combustion circulate by a zig-zag course through firebricks. The firebricks are provided with hollow channels, through which is drawn the air used for combustion. Such furnaces appear to work very satisfactorily and to require little attention or repair. The introduction of gas furnaces has led to considerable saving of fuel, which in Silesia was formerly 3·5 tons of coal per ton of ore, and is now about one-third of that quantity; gas firing has also led to the use of larger furnaces and given longer life to the retorts. The result has been that, in Silesia, while the number of works has actually decreased, the production of zinc has greatly increased (*v. M. Georgi, Zinc Industry of Upper Silesia*; Berg. u. Hütt. Zeitung, 36, 71, 78, 97; Inst. C. E. 49, 369).

The retorts used in the *Belgian process* are cylindrical or elliptical in shape, being closed at one end; these retorts are supported at the extremities, and are set in the furnace in tiers, each retort being inclined, and higher at the back than the front. The elliptical retorts are used for the lower tiers, where the temperature is highest, and they are sometimes air-cooled at the bottom. The introduction of the charge requires considerable skill. As the material is finely divided, particularly when fine concentrates are employed, it has been found advantageous to briquette the mixture by pressure, and this improvement is steadily gaining ground. Charging by electrically driven machines has also been successfully introduced. The mouths of the retorts are fitted with condensing tubes of clay in which the zinc collects, partly in the form of metal and partly in the form of more or less oxidised dust, which deposits chiefly in a sheet-iron nozzle fitted to the clay tube. The workman judges of the progress of the operation by the colour of the flame or vapours which are evolved. Brown vapours are first given off, and with these any cadmium passes over; they are succeeded by the characteristic flames of zinc, which continues until the operation is completed. The loss of zinc by the Belgian process is about 10–15 p.c. of that originally present in the ore; while in the Silesian process, in which poorer and more refractory ores are employed, the loss is 5, or even 10 p.c. greater (F. Juretzka, *Metallurgie*, 1911, viii. 1).

In the *Silesian process* the retorts are C-shaped; the width is the same as that of the Belgian retorts, but the height is greater, and as the retorts are supported in the furnace from beneath, they are made longer than in the Belgian process—consequently the charge is

greater. The retorts are usually placed in a single row in the furnace, which occasionally contains as many as forty such retorts, though about thirty-two is stated to give the best results, and a smaller number is frequently employed. At Freiberg the muffles were arranged in two rows one above the other, and each row contained sixteen muffles. In recent years the tendency has been to use a much larger number of retorts than formerly, so that the charge of ore per furnace has been raised from 15 cwt. to 8 or 10 tons.

In the lower part of the front of a Silesian muffle a hole is provided for the purpose of introducing the charge, and removing the residue after the distillation is complete. This method of charging, combined with the underneath support, gives greater durability to the Silesian muffles, so that, though in a given time the Belgian furnace may make more zinc, the annual production is rather in favour of the Silesian (*v. F. A. Thum, Notes on Zinc Smelting, Eng. and Min. Jour.* 1879, 275; *Inst. C. E.* 58, 407). The cost of calcining the ore, and smelting the zinc, in a modern works in South Wales, averaged about £3 per ton of spelter produced (1911).

The zinc works of Prince Hohenlohe in Silesia include three smelting works, with a total of 106 furnaces, and a separate calcining works for the preparation of zinc blende for distillation. The fourteen long double-bedded calcining furnaces employed have each an output of 220 lbs. of roasted ore every 5 hours. Each zinc furnace contains thirty-two muffles, heated by gas from Boetius producers. Every furnace is arranged with sixteen niches, each containing two muffles, while two furnaces are built together so as to form a double furnace. Two spaces are provided at either end of the double furnace, one for tempering the muffles, and the other for calcining the lump calamine. Most of the calamine is charged raw, as the carbon dioxide is driven off long before the temperature of reduction is reached. The charge per muffle weighs 507 lbs., and consists of a mixture of roasted blende, lump calamine, and dried slimes. The daily yield is about 108 lbs. of zinc. The zinc contains 3-4 p.c. of lead, which is reduced by refining to 1.07 p.c. The refining is conducted in a reverberatory furnace with an inclined base, in the well of which the metal collects, the lead at the bottom and the zinc above. Every 12 hours about half a ton of zinc is tapped, and the same amount of raw zinc is charged in; the lead is removed at longer intervals. An exactly similar process is used in Birmingham for refining Continental zinc previous to rolling. The refined zinc contains about 1 p.c. of lead, 0.02 p.c. of iron, and 0.04 p.c. of sulphur (*Berg. und Hütt. J.* 1889, 389; *Inst. C. E.* 101, 382).

For full particulars of modern practice in zinc smelting, especially in reference to the United States of America, W. R. Ingall's standard treatise on the Metallurgy of Zinc should be consulted. An excellent monograph by E. A. Smith, *The Zinc Industry* (Longmans, 1918), may also be read with advantage.

The demand for spelter of high chemical purity is now considerable, such metal being required for the production of the ductile brasses. One of the most remarkable advances in con-

nection with the metallurgy of zinc in recent years has been the improvement in the quality of the product when required for special purposes. Formerly 98 or 98.5 p.c. zinc was considered satisfactory, upwards of 1 p.c. of lead and a few tenths p.c. of iron being present. It is now possible to obtain regularly considerable quantities of metal guaranteed to contain over 99.75 p.c. of zinc, and upwards of 99.9 p.c. is also sold at a rather higher price. Such metal is either produced electrolytically, as afterwards mentioned, or by the use of a filter of carbon, firebrick, or other crushed and porous material placed in the mouth of the ordinary zinc retort. This filter retains the lead, while zinc vapour passes through and is condensed (*see Primrose, Production of Pure Spelter, Inst. of Metals, 1909, ii. 231; Bannister, Carbonaceous Filters in the Smelting of Zinc, Inst. of Metals, 1910, i. 213*).

Zinc of high chemical purity is also obtained by the distillation of 'hard zinc' produced in the galvanizing process (*see p. 576*). This hard zinc is an alloy of iron and zinc which is less fusible than zinc, and hence separates from the excess of zinc. Hard zinc is free from lead, and on distillation yields lead free zinc spelter.

Treatment of zinc ores in the blast furnace.—In order to reduce the consumption of fuel and labour in the extraction of zinc a number of attempts have been made to reduce zinc in the blast furnace, but hitherto without much success. The difficulty experienced is due to the fact that the vapour of zinc and the furnace gases must, in such a furnace, pass away together, and during the condensation which ensues a reaction takes place between the zinc and the carbon dioxide of the gases, thus $\text{Zn} + \text{CO}_2 = \text{ZnO} + \text{CO}$ reproducing oxide of zinc, and the ultimate result of the operation is merely to carry zinc oxide out of the blast furnace into the condensing apparatus. This action has been studied by Lencauhez (*Mém. Soc. Ingén. Civils*, 1877, 568; *Inst. C. E.* 51, 332), who found that zinc was still oxidised when the proportion of carbon dioxide was only 0.5 p.c. of the gas employed. Zinc vapour is also oxidised by any water vapour which may be present. By very rapid cooling of the gases Lencauhez succeeded in reducing the oxidation of the zinc to as little as 5 p.c., but after numerous experiments he concluded that this process is not likely to be commercially successful.

In some cases, with relatively poor complex ores containing zinc, a blast furnace smelting is adopted with the deliberate intention of volatilising the zinc as oxide. This is condensed, usually with the aid of bag filtration, and sold to the smelters to be dealt with in the ordinary way.

In 1878 Binon and Grandfils, in Stolberg, made the attempt to use a zinc oven with upright retorts. They aimed at making the Carinthian method continuous. The materials containing zinc were heated with reducing agents by gas in reduction spaces in the form of shafts, which were filled above and emptied below.

Electric smelting of zinc.—Considerable attention has been devoted to this subject during the past few years, and a lengthy list of patents has resulted. In the opinion of competent and disinterested observers the solution of the problem of the blast furnace reduction of zinc will come by means of the application of

electricity. Two typical processes may be here mentioned. In that of Snyder, adopted in British Columbia, complex ores are calcined to oxides, mixed with fluxes to give a slag melting at about 1050°, and treated in an electric furnace. The current passes through the molten slag, under which the lead is collected in a well. The zinc is volatilised and condensed in suitable chambers. The De Laval process, worked in Sweden, is conducted in an arc furnace into which the roasted ores are charged after mixing with flux and coal. The product is a coarse metal containing zinc, lead, and other impurities. This coarse metal is refined by distillation in another furnace, and zinc of high purity is obtained, together with zinc dust or fume and base lead bullion. One h.p. year is claimed to produce 800–1000 k. of metallic zinc, much of which is, however, in the form of dust. The current cost is about half the total charges. The electric processes depend for their success upon electricity from cheap water power, and are not likely seriously to compete with the old-established reduction centres, at all events for some time to come (*see* Sulman, J. Inst. Min. and Met. 1911, lxi.; Min. Mag. 1911, 310, 389).

Wet methods of extracting zinc.—One of the most difficult problems connected with the metallurgy of zinc is that of the treatment of complex ores. These may contain, in the aggregate, very considerable proportions of metallic constituents, but in that a number of metals are present together the ores cannot be treated by ordinary methods. Such ores usually contain about 12–28 p.c. of zinc, and 5–15 p.c. of lead, together with a few p.c. of copper, some ounces of silver per ton, and frequently small proportions of other constituents. Such ores are now frequently treated by oil vacuum or other concentration processes so as to classify the metalliferous portions into separate saleable products whenever possible. Various wet methods of extraction, usually connected with electro-deposition, have from time to time been suggested, and have been worked on a more or less considerable scale, though till recently without much commercial success. It was only after many trials that copper-refining by electro-deposition became a commercial success; and yet copper is worth more than double the price of zinc. The electro-motive force required for the deposition of copper is less than that necessary for zinc, and the strength of current that may be used with copper is greater. Thus electrolytic methods of extraction of zinc have to contend with the disadvantages of the comparatively low intrinsic value of the metal, and of comparatively slow deposition.

Where electro-deposition is employed, there are two methods open for extracting the zinc; in the first the ore itself may be used as anode; or, secondly, the ore may be roasted or treated with solvents to convert the zinc into a soluble form.

1. Luckow proposed to mix the ore with coke in order to render it a conductor, and to place it in an open chest in an electrolyte consisting of a somewhat strong and acid solution of common salt or zinc chloride (20–30 p.c. Zn). The metal was deposited either upon a zinc plate or upon a cathode of coke, (*Eng. Pat.* 9158, 1886) proposed a

method, but used magnesium chloride as electrolyte, and adopted special arrangements for collecting the evolved chlorine.

2. Many processes have been proposed for rendering the zinc in complex ores soluble, and in a number of these it is proposed to recover the zinc from solution by electro-deposition.

Lambotte and Doucet proposed to roast blende to oxide, dissolve in crude hydrochloric acid, precipitate the iron with chloride of lime and zinc oxide, and electrolyse the solution.

Parnell calcined complex ores to oxide, dissolved in dilute sulphuric acid, which was obtained as a by-product, precipitated the copper by metallic iron, and evaporated the liquor to a mud. Zinc sulphide was then added, and zinc oxide produced by heating the mixture strongly. The zinc oxide so obtained was sold to the smelters. Maxwell Lyte calcined the ore, and dissolved in hot dilute hydrochloric acid; the lead was allowed to separate as chloride on cooling, the iron precipitated by limestone, the copper with scrap iron, and the zinc as oxide by lime. Létrange was one of the earliest workers in the direction of electro-deposition of zinc; in his process blende was carefully roasted at low temperatures to produce zinc sulphate, which was dissolved with hot water and dilute sulphuric acid. The solution was then electrolysed, using an anode of lead (or carbon) and a cathode of zinc. The current used must have a high electro-motive force owing to the peroxidation of the surface of the lead.

Among other suggestions the following are worthy of notice. In 1886 Lea and Hammond (*Eng. Pat.* 10868) suggested the use of hydrochloric acid as a solvent for roasted ores previous to electro-deposition, while in the same year Squire and Currie (*Eng. Pats.* 12249 and 12630) proposed the use of an alkaline solution for the same purpose, and in 1887 Watt patented (*Eng. Pat.* 6294) the application of dilute vegetable acids for a similar object. Again, Burghardt (*Eng. Pats.* 8986 and 13182, 1888; 659, 1889) proposed the use of an alkaline solution made by adding the roasted ore, previously mixed with 3–7 p.c. of powdered coal or charcoal, to melted caustic potash or soda. The mass was extracted with water, the zinc electro-deposited, and the alkali recovered to be used over again. Croselmire (*Eng. Pat.* 4286, 1888) proposed to mix the ground ore with clay, and form into perforated pressed bricks which are roasted into sulphate in kilns. The roasted mass is extracted with hot water and an equivalent of dilute sulphuric acid, air is blown through the liquors to precipitate iron and manganese, and, after settling, the clear liquor is electrolysed, or the zinc may be precipitated by soda ash. In 1889, also, Cunningham (*Eng. Pat.* 9987) again patented the use of an alkaline solution obtained by fusion with caustic soda.

Among methods of another class proposed for the treatment of complex zinc ores may be mentioned that of Perino (*Eng. Pat.* 10657, 1888) who fused the blende in clay retorts at 150°–200° with ferric nitrate in the proportion of about 5 parts of nitrate of iron to 1 of zinc. The mass was extracted with water and a solution of zinc sulphate obtained. Arrangements were made for recovering the ferric nitrate, Siemens and Halske also (*Eng. Pat.* 3533,

1889) used ferric sulphate for extracting zinc from complex ores, while Seagall (Eng. Pat. 4871, 1889) employed a slightly acidified solution of ferric chloride for the same purpose.

The complex ores of Leadville, U.S.A., containing 25 p.c. zinc, 15 p.c. lead, 20 p.c. iron, are roasted to sulphate, extracted with water; the residue chlorinised to complete the extraction of the zinc, and the zinc precipitated from the solutions as oxide (J. Soc. Chem. Ind. 7, 572).

A process for the electrolytic production of zinc which was formerly conducted on a considerable scale in the United Kingdom is a modification of the Höpfer patent, introduced at Northwich by Messrs. Brunner, Mond, Ltd. The primary object is the production of chlorine from the calcium chloride liquors made in the ammonia-soda alkali process. These liquors are treated with zinc oxide (roasted zinc ores) and carbon dioxide, when calcium carbonate is produced and zinc chloride liquors obtained. This solution, after the removal of all the more electro-negative elements, is electrolysed, a current density of as much as 30 amperes per sq. ft. of cathode surface being allowable. The products are zinc and chlorine. The cathode consists of a series of discs of iron which revolve on a horizontal axis; the anodes are of carbon and are enclosed in wooden frames, the sides of which are enclosed with cloth diaphragms. The chlorine evolved is subsequently converted into bleaching powder. The zinc is stripped off the cathode plates, remelted, and cast into ingots. The great difficulty is to obtain a smooth adherent coating of zinc, and to prevent, as far as possible, the formation of spongy zinc. The exact nature of the latter product, and the cause of its formation, are still not thoroughly understood. More recently electrolytic zinc has been manufactured by Messrs. Chance and Hunt of Oldbury. It is understood that the method employed is similar in principle to that above described, though the details are kept secret. The zinc obtained is sold with a guaranteed purity of 99.96 p.c., which makes it of great value in the production of ductile brasses, and for other purposes where the presence of lead, &c. would be detrimental.

To avoid the necessity for electrolysis of the zinc solutions obtained from complex ores, processes have been introduced to precipitate the zinc in a form suitable for sale to the zinc smelter. A typical process is that in which sulphur dioxide, obtained from blende roasting, is used to extract zinc from roasted ores. With excess of sulphur dioxide the zinc passes into solution as bisulphite, and is separated from the residues. These contain lead, silver, &c., and are sold to the smelters. By the removal of half the sulphur dioxide from the solution insoluble zinc sulphite is thrown down. This sulphite is filtered off, dried, and calcined in a muffle at a low temperature. Zinc oxide is obtained in a form suitable for spelter production, and the sulphur dioxide is added to the calciner gases to enrich them for fresh leaching operations (Eng. Pat. 21759, 1908).

The foregoing process, after having been used for several years by one important British company, was replaced by a method which included roasting with partial sulphating of the zinc, extraction with dilute sulphuric acid,

precipitation of the iron and soluble silica by lime, and of the copper and cadmium by zinc. The solution was then electrolysed, and the sulphuric acid liquor used over again. For electrolysis the solution must not be too strong or too weak; in the latter case the resistance is unduly high. During the electrolysis of zinc sulphate zinc crystals are deposited in directions normal to the cathode surface. A peculiar ring structure is exhibited by sections parallel to the latter. Electro-deposition occurs most readily at angles, corners, and rough parts of the cathode.

The largest electrolytic zinc works in the British Empire is situated at Risdon, near Hobart, in Tasmania. It has a paid-up capital of upwards of £2,000,000, and was erected 1921 to treat Broken Hill concentrates as Tasmanian ores from the Mount Read and Rosebery mines. The former assay 47 p.c. zinc, 30 p.c. sulphur, 7 p.c. lead, and 10 oz. of silver per ton. The latter average 27 p.c. zinc, 7.3 p.c. lead, 9.5 oz. silver, and 2.5 dwts. gold per ton. The ores are roasted in multi-bedded mechanically rabbled calciners, the oxide of zinc extracted by dilute sulphuric acid, and the solution purified from iron and silica by addition of lime. The clear liquid is deprived of cadmium and copper by addition of zinc dust, and the purified zinc sulphate electrolysed. The lead-rich residue is dried and sold to smelters for the extraction of lead, silver, and gold. The cadmium is recovered, and is now one of the chief sources of the world's supply of that metal. The current available is 30,000 h.p.; it is supplied at a cheap rate, by the Tasmanian Government, at 11,000 volts a.c., the greater part of which is transformed to d.c. at 550 volts and delivered into the cell room. About 800 tons of zinc cathode sheets are produced weekly; they are melted and cast in slabs of about 50 lbs. weight, which contain 99.95 p.c. zinc. The British Government has undertaken to purchase a quantity not exceeding 45,000 tons per annum for a period of years.

The brittleness of electrolytic zinc is probably due to the presence of hydrogen, which in the case of the sample investigated was found to be present to the extent of 0.55 p.c. When electrolytic zinc is melted the hydrogen flame can be observed. When heated to 105°–110°C. for some hours a loss of weight of 0.025–0.04 p.c. occurs. A plate of zinc so treated becomes curved slightly, and a considerable volume of hydrogen is evolved. When heated to a temperature above 180°C. the plate becomes very curved, the concavity being directed towards the original cathode surface. The phenomenon is accompanied by a decrease of 0.7 in the value of the density of the metal. The electrical conductivity of electrolytic zinc is practically the same as that of pure zinc, but the value at 195°C. is much below the anticipated value. This decrease and the decrease of density occurring at about the same temperature are not reversible phenomena, but are connected with the evolution of hydrogen. Determinations of hardness at high temperatures are in agreement with the customary values. Very little, if any, hydrogen is dissolved in electrolytic zinc or electrolytic iron which has been stored for a long period (M. von Schwab,

Zeitsch. Elektrochem. 1923, 29, 188; J. Soc. Chem. Ind. 1923, 42, 607 A).

Properties.—Zinc is a bluish-white metal, which at ordinary temperatures is brittle, and when pure exhibits a beautifully crystalline fracture. Large crystals are often found in zinc rods which have been worked mechanically. The presence of impurities usually renders the fracture closer in the grain and less brilliant. Zinc melts at 419.4° , and boils at 930° . It can, however, be readily distilled in glass vessels in a vacuum, under atmospheric pressure. The vapour pressure of molten zinc up to 2 atm. is represented by

$$\log p = -66.55/T - 1.147 \log T + 12.046$$

Both zinc and cadmium have a constant atomic heat over the range of temperature from the melting-point to the boiling-point. The values are 7.5 (cadmium), 7.24 (zinc) (Braune, *Zeitsch. anorg. Chem.* 1920, 111, 109; cf. Nair and Turner, *Chem. Soc. Trans.* 1913, 103, 1534; Rodebush and Dixon, *J. Amer. Chem. Soc.* 1925, 47, 1036). Zinc undergoes two marked changes in electric conductivity, one at 170° , and the second at 340° . It is, therefore believed by Benedicks to exist in three allotropic modifications (Metallurgie, 1910, 7, 531). From observations of electrical resistance, thermal E.M.F., electrolytic potential, specific gravity, hardness, mechanical properties, thermal curves, and microstructure of the pure metal (99.97 p.c. Zn), Bingham (*Inst. of Metals J.* 24, 333) also concludes that zinc exists in three allotropic forms, the transformation temperatures being approximately 180° and 310° (cf. Laschtschenko, *J. Russ. Phys. Chem. Soc.* 1913, 45, 552; Werner, *Zeitsch. anorg. Chem.* 1913, 83, 275; Cohen and Helderman, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, 16, 505; Le Chatelier, *Compt. rend.* 1890, 414, 454; Benedicks and Arpi, *Zeitsch. anorg. Chem.* 1914, 88, 237; Lorenz and Plumbridge, *ibid.* 1913, 83, 228; Janecke, *ibid.* 1915, 90, 313). According to measurements of various kinds of zinc, it exhibits two singular points, at 174°C. and 322°C. , the former corresponding with the transformation of the α to the β modification, and the latter that of the β to the γ modification. If traces of iron or tin occur in the zinc, the lower transformation point disappears, whilst the presence of cadmium causes the two transformation points to approach (L. Losana, *Gazz. chim. ital.* 1923, 53, 539-545; *J. Soc. Chem. Ind.* 42, 1923, 1075 A). Its tensile strength varies greatly according to the mode of preparation; cast zinc has a tenacity of only 1.2 tons per square inch, whilst an annealed rod gave a tenacity of 7.9 tons per square inch, and zinc wire 10 tons per square inch. Its hardness is intermediate between that of tin and copper, being equal to 6 on Turner's Sclerometer and $2\frac{1}{2}$ on Mohs' scale. Pure zinc has a density of 7.1400 at 16.3° (Egerton and Lee). The coefficient of expansion between 100° and 300° Abs. has been measured by Borelius and Johansson (*Ann. Physik.* 1924 iv, 75, 23).

Two sets of distillations of pure zinc were carried out in high vacuum under conditions to obtain a slightly different concentration of the isotopes in the final residue of the last distillate. For the determination of densities,

the metal was cast in a vacuum and seeded with about 1 mg. of a particular kind of zinc. The first set of distillations gave a residue of slightly increased density, but the distillate was of the same density as the original zinc. The second set of distillations, carried out under improved conditions, yielded a residue of increased density (about 1 part in 3700 parts), and a distillate of decreased density (about 1 part in 3600 parts). The density of ordinary zinc at 16.3° , determined from seven samples of the metal prepared as described, was found to be 7.1400 ± 0.0006 . The possibility of attributing the difference of densities to flaws, allotropes, different physical conditions, and impurities is discussed and shown to be improbable. The degree of separation obtained agrees with Dempster's observations of isotopes of weights 64-70, but is less than half what might be found for equal parts of an isotope of mass 64, and of isotopes 66, 68, and 70 (A. C. Egerton and W. B. Lee, *Proc. Roy. Soc.* 1923, [A] 103, 499; *Chem. Soc. Abstracts*, July, 1923, 490).

Though zinc is brittle at ordinary temperatures, and so tender above 200° that it can readily be crushed to powder, it can be rolled into sheet or drawn into wire at an intermediate temperature of about 100° - 150° . It is a remarkable fact that the metal when so treated retains its malleability in the cold. Zinc was first rolled early in the present century in Birmingham, and rolled zinc now forms one of the most important varieties of the commercial metal, the greater part of the zinc produced in Europe being used for this purpose. Commercial zinc always contains more or less lead and iron, together with traces of cadmium, arsenic, and sulphur, the lead being volatilised with the zinc in the process of manufacture. Kosmann has also found comparatively large quantities of thallium in commercial zinc (*Chem. Zeit.* 10, 762). The chief technical methods for the assay of zinc have been described and discussed in connection with a paper by Greenwood and Briske (*Inst. of Metals*, 1909, 2, 249). The presence of lead, which is objectionable in zinc to be used for the manufacture of the best qualities of strong brass, is an advantage in zinc that is to be rolled. For the influence of foreign metals on the rolling of zinc, see Post and Van de Casteele, *Bull. Soc. chim. Belg.* 1913, 27, 175. Ingall has studied the effect of annealing rolled zinc, and shows that sheets are stronger across the direction of rolling than with the grain (*Inst. Metals J.* 26, 281). As English zinc is relatively free from lead, it is usual to employ this variety for the production of alloys in which lead would be objectionable, while Continental zinc is imported for rolling. If the state of the market renders it advantageous to roll English zinc, this can be improved by the addition of a small proportion of lead. In addition to what is made here, more than 20,000 tons of sheet zinc is annually imported into the United Kingdom. The density of zinc varies from 6.8 to about 7.2, according to the mode of preparation. The change of density of melted zinc with temperature may be represented by the formula

$$d = 6.59 - 0.00097(t - 419)$$

When heated in the air much above its melting-point, zinc readily burns with a brilliant

greenish-white flame, producing the oxide (ZnO) which condenses in a bulky flocculent condition formerly known as 'philosopher's wool.' The white fume produced when casting brass or other zinc alloys that melt at a tolerably high temperature consists of zinc oxide. Though zinc is readily volatile, the oxide is fixed at all ordinary furnace temperatures. For remarks on the toxicity of zinc vapour, see Drinker, *J. Ind. Hyg.* 1922, 4, 177. Zinc is not affected by dry air at ordinary temperatures, but tarnishes superficially in moist air. The metal is also not attacked by mineral lubricating oils, and of ordinary animal oils it is attacked most by sperm oil and least by lard oil (Redwood, *J. Soc. Chem. Ind.* 5, 362). Zinc, both pure and commercial, dissolves readily in alkalis. Pure zinc is unattacked by water at boiling-point, and is almost unaffected by ordinary acids either diluted or strong. Commercial zinc, on the other hand, decomposes boiling water with the evolution of hydrogen, and is readily attacked by diluted sulphuric acid and by hydrochloric acid either diluted or strong. Impure zinc when amalgamated resists the action of acids exactly like pure zinc, and hence the zinc plates used in electric batteries are amalgamated so as to prevent the loss due to 'local action.'

For heat of solution of zinc in hydrochloric acid, see Richards and Thorvaldson (*J. Amer. Chem. Soc.* 1922, 44, 1051). The influence of impurities on the solubility of zinc in acids has been studied by Vandraček and Izák-Křižko (*Rec. trav. chim.* 1925, 44, 376).

This difference in the behaviour of pure and impure zinc towards acids has attracted much attention from chemists since the fact was first pointed out by A. de la Rive in 1830. Among the more important observations on the subject are those of Pullinger (*Chem. Soc. Trans.* 57, 815), Weeren (*Ber.* 24, 1785), and Centnerszwer and Sachs (*Zeitsch. physikal. Chem.* 1914, 87, 692).

Pullinger's conclusions are as follows:—Pure zinc with a perfectly smooth surface is not acted upon by dilute sulphuric acid that has been previously well boiled; pure zinc with a rough surface is readily acted upon, but less by acids that have been boiled than by those which have not. The presence of oxidising agents such as nitric acid, hydrogen peroxide, or electrolysed sulphuric acid, increases the rate of dissolution, while a reducing agent, such as hydriodic acid, almost entirely prevents dissolution; but reducing agents containing sulphur, such as sulphur dioxide, are without effect. It is not improbable that when zinc with a rough surface dissolves in dilute sulphuric acid the cause of dissolution is persulphuric acid, which acts catalytically, and in all probability pure dilute sulphuric acid would be without action upon metallic zinc, whether the surface of the latter be rough or smooth.

The solubility of impure zinc in diluted acids has been generally explained on the supposition that local electric currents are set up owing to the presence of the impurities, whilst with pure zinc no such currents are produced. Weeren, however, shows (*loc. cit.*) that the insolubility of pure zinc is due simply to the formation of a layer of condensed hydrogen on the surface of the metal, and thus the further action of the acid is stopped. Oxidising agents remove this

film and assist dissolution; in impure zinc the hydrogen, obeying ordinary electrical laws, is evolved from the surface of the impurities. The fact that dissolution is much promoted by simply brushing the surface of the metal, or by allowing the action to take place in a vacuum, appears to afford strong support of this view, which is also quite in harmony with the fact that pure zinc dissolves much more rapidly in boiling dilute sulphuric acid, when the ebullition of the liquid removes any hydrogen from the surface of the metal, than at 98° where no ebullition occurs. Pure zinc with a rough surface, as Pullinger has shown, dissolves much more readily in diluted sulphuric acid than the same metal when the surface is perfectly smooth. Weeren suggests from the above facts that the difference in the action of diluted sulphuric acid on pure and impure zinc is capable of a simple mechanical explanation.

Centnerszwer and Sachs made experiments with (1) polished zinc, (2) etched zinc, (3) rolled zinc, (4) slowly cooled zinc, (5) rapidly cooled zinc, and zinc which had been kept at 400° for eight days. Zinc slowly increases its rate of solution in a given acid to a maximum, after which the rate slowly falls off in accordance with the law of Boguski, $dx/dt = kF(c-x)$ in which dx/dt is the velocity, F the surface exposed to the acid, c the concentration of the acid, x the amount dissolved at time t , and k the velocity constant. The solution of the zinc passes through an induction period. Zinc which has been etched in hydrochloric acid dissolves more rapidly than unetched zinc. Zinc which has reached its maximum velocity of solution in 2N-hydrochloric acid, on removal from the acid and immersion in fresh acid, immediately begins to dissolve with the maximum velocity, and the rate of solution then falls off in accordance with Boguski's law. In acids of equal hydrogen-ion concentration, sulphuric acid dissolves zinc more slowly than hydrochloric acid. Specimens of zinc from the same rod show different solution-velocities, which is to be explained by the different crystal habitat. Plates of rolled zinc, on the other hand, give velocities which are uniform. Zinc which has been rubbed with emery paper dissolves much more quickly than polished zinc, and the finer the emery the more rapid the rate of solution. Zinc plates which have been immersed in iodine solution dissolve more readily than fresh zinc. The velocity of solution of zinc in acids of different concentration increases more rapidly than the concentration of the acid. A mixing of the solution increases the rate of solution. A black deposit is formed on the surface of the zinc during solution; this accelerates the rate of solution, and when it is mechanically removed the velocity decreases. Zinc which has passed through the induction period of solution retains its activity when allowed to remain in water, but loses it if kept in the air and allowed to dry. Rapidly cooled zinc has a longer induction period than slowly cooled zinc, but after the surface has been etched, both dissolve at the same rate. When slowly cooled zinc is heated to 400° for prolonged periods its induction period is increased (*Chem. Soc. Abstracts*, 1914, ii, 550; also Centnerszwer and Drukar, *J. Russ. Phys. Chem. Soc.* 1915, 47, 439; *Chem. Soc.*

Abstr. 1915, ii. 562.) For the hydrogen over-voltage of zinc, see G. M. Westrip (Chem. Soc. Trans. 1924, 125, 1112).

The question of the corrosion of zinc sheet and pipes, and of articles coated with zinc, when in use, is of great commercial importance. In dry pure air, as for instance in parts far removed from manufactories and towns, zinc roofing, when properly attached, lasts almost indefinitely with only a surface oxidation. But in the neighbourhood of towns, and especially in the vicinity of chemical manufactories, commercial zinc is rapidly corroded and spoiled. The presence of the slightest trace of free sulphuric or hydrochloric acid in the drainage water is very prejudicial. The presence of copper in any form in contact with zinc should also be carefully avoided. Thus Müller has shown (Dingl. poly. J. 269, 280) that the zinc pipes which carried the drainage water from the copper dome of the royal castle at Brunswick were rapidly attacked and corroded, while similar pipes on the opposite side of the same building were unaffected. The explanation of this difference probably was that in the presence of ammonia or of acids in the atmosphere some copper was dissolved by the rain water, and this copper being afterwards deposited on the surface of the zinc, set up an electric action resulting in the destruction of the pipes.

The presence of lead, cadmium, or iron causes an increase in corrosion by acidic agents. Minute traces of arsenic, antimony, copper, or tin can considerably increase the tendency of zinc to corrode, and this influence is particularly marked in the cases of arsenic and antimony.

G. Ducker (Zeitsch. Elektrochem, 1923, 29, 412-415) placed test pieces of pure zinc, commercial zinc, and specially prepared alloys in a bath of sal-ammoniac and determined the loss in weight. Traces of iron in the zinc or the solution produced serious effects owing to electrolytic action. The effect of cadmium is due to its influence on the structure of the metal. The effect of lead, which is a minimum at concentrations of about 1 p.c., is partly electrochemical and partly due to its influence on the structure of the metal. This is confirmed by the fact that any treatment of the metal which tends to alter the structure will increase the rate of attack. Small impurities in the sal-ammoniac increase the corrosion, especially in strong solutions, with the pure salt solutions, the attack is slowest with the stronger concentrations, which is probably due to the protective action of the reaction products. The author advocates the use of sal-ammoniac free from iron, and re-distilled zinc in the preparation of primary cells (Sci. Abstr. 1924, 27, 238). To determine the relative corrosion of zinc and lead in solutions of inorganic salts, the metal plates were suspended in salt solutions of high concentrations, and the corrosion was expressed as percentage loss of weight, the loss of weight from similar plates suspended in distilled water being taken as 100. With zinc plates, the rate of corrosion rapidly reached a maximum with increasing concentration, beyond which the rate of corrosion steadily decreased. Sulphates and chlorides gave similar results, the former producing a more pronounced decrease the critical concentration. Nitrates,

however, caused a rapid decrease in the corrosion rate throughout. The conditions influencing corrosion are the chemical action of the dissolved salt on the metal, the solubility of oxygen in the solution, the rate of solution of oxygen by the quiescent salt solution, and the physical and chemical action of the products of corrosion (J. N. Friend and J. S. Tidmus, Inst. Metals, Mar. 1924; J. Soc. Chem. Ind. 1924, 43, B. 337).

The use of galvanised iron tanks for water-cisterns has led to much controversy, particularly in the colonies, as to the effect of such storage on the health of persons who drink the water so stored. According to Bunte, the use of zinc-coated iron water-pipes is not deleterious to health, and this view is supported by Dr. Ehmann, late director of the water supply of Württemberg, and by Dr. Boardman, of Boston (J. Soc. Chem. Ind. 6, 557). But a strong feeling exists to the contrary, and, after careful inquiry, the use of galvanised tanks for drinking-water was condemned in the British and French Navies. From the well-known properties of zinc it might be anticipated that some waters, which are either slightly acid or alkaline, would attack zinc vessels, while other waters might be almost without action. The presence of chlorides would probably also be prejudicial. It is not unlikely, therefore, that the differences in the action of water on zinc cisterns, as noticed by various observers, is due in great measure to the character of the water. It is, however, certain that zinc or galvanised vessels should not be employed with acid waters.

Experiments have been conducted to determine the degree to which ordinary galvanised iron buckets are corroded by tap water, distilled water, carbonated water, milk, orangeade, and lemonade. Quantities of 1 gallon of each of these liquids (1 quart of milk) were placed in buckets and samples analysed for zinc at the end of 17 and 41 hours. The orangeade and lemonade contained the juice of twelve oranges and twelve lemons respectively and 1 lb. of sugar to each gallon. The number of mg. of zinc per litre found in the five liquids after the periods named were: tap water, 5, 21; distilled water, 9, 27; carbonated water, 193, 181; milk, 438, 1054; orangeade, 530, 854; lemonade, 1411, 2,700. The hydrogen ion concentration and titratable acidity, with phenolphthalein as indicator, were also determined in the solutions. The quantity of zinc found after 17 hours increases directly with the hydrogen ion concentration and titratable acidity. The buckets which had contained the milk, orangeade, and lemonade were visibly corroded, especially in the last-named case (J. W. Sale and C. H. Badger, Ind. Eng. Chem. 1924, 16, 164; J. Soc. Chem. Ind. 1924, 43, B. 273).

Zinc-dust is employed somewhat largely as a reducing agent, as a precipitant for gold in the cyanide process for the extraction of gold from gold ores, and in the manufacture of fireworks. It is obtained, mixed with more or less oxide, in the distillation of the metal, or can be produced by crushing the metal in a mortar at a temperature somewhat below its melting-point.

In castings zinc takes a very sharp impression of the mould, and, as it melts at a low

temperature, it has been used to a considerable extent, especially in France, for the production of statuettes and other objects of beauty, which are afterwards usually coloured or bronzed. Some of these bronzes contain about 17 p.c. of copper; this alloy expands in the mould, and gives very sharp and clear impressions (see Turner and Murray, *Inst. of Metals*, 1909, ii. 115). The introduction of photo-engraving has also in recent years led to the use of considerable quantities of sheet zinc of special quality.

Galvanising.—An important application of zinc, known as galvanising, was patented by Crawfurd in 1837. The object of the process is to coat the surface of iron with a thin layer of zinc, which protects the metal underneath from oxidation. In this respect zinc acts more perfectly than tin, which is negative to iron; in the case of tin plates the protection only lasts so long as the surface of the iron is covered with tin, but as soon as any portion of the iron is exposed to the action of the atmosphere oxidation proceeds more rapidly than in the absence of tin. Zinc, on the contrary, is more positive than iron, and thus, even though the coating of zinc may be removed in places, the protection continues so long as any zinc remains. Galvanised iron, however, cannot be used in contact with acids or alkalis, nor for the canning of fruits, meat, &c., on account of the action of vegetable acids and animal juices on the surface of the zinc.

A micro-section through a piece of galvanised iron indicates that between the iron and the zinc there is at least one layer of intermediate compound of iron and zinc (see p. 579). It is probable that the excellent wearing qualities of galvanised iron depend to a considerable extent upon the presence of this hard crystalline layer.

According to H. Bablik (*Stahl. u. Eisen*, 1924, 44, 223), the zinc coating obtained in the usual process of galvanising consists essentially of three layers—an extremely thin cementing layer very rich in iron, a slightly thicker layer of FeZn_2 and FeZn_7 , and a thicker layer of pure zinc. The lower layers are very hard and brittle and tend to make the coating crack on bending. In the new process the formation of the intermediate layers is prevented and a pliable coating is obtained, whilst economies are effected in the amount of fluxes used, and in the proportion of zinc lost in ashes and hard zinc. The apparatus consists of a cast-iron vessel having a cylindrical fireclay collar; the vessel is filled with soft lead on which a thin layer (3-6 cm. thick) of zinc floats so as to come in contact solely with the fireclay collar. A smaller fireclay cylinder dips through the zinc layer into the lead and is filled with a flux containing ammonium chloride. The articles to be galvanised are pickled in hot dilute sulphuric acid immediately before being passed through the flux layer into the lead, then up through the zinc layer. The resulting coating has a duller colour and is more coarsely crystalline than usual, but the size of the crystals can be reduced and the colour greatly improved by adding 1-2 p.c. Al to the zinc before use. The aluminium also retards the formation of oxide crusts and of hard zinc. Figures show the production of sheets together with the consumption

of zinc and lead during a year's working of the process (*J. Soc. Chem. Ind.* 1924, 43, B. 299).

The operation of galvanising is not in any way an electric process, as might be inferred from its name, but is simply a method of coating clean iron with zinc by immersion in a molten bath of the latter metal. Numerous patents have been obtained for suggested improvements in galvanising since Crawfurd introduced the process, particularly by Mallet and Morewood, but the old process is still almost universally adopted with a few improvements in details for saving of labour and the production of a better surface with a smaller consumption of zinc. Galvanising is conducted largely in the United Kingdom, and particularly in the neighbourhood of Birmingham and Wolverhampton, and in South Wales.

The iron or steel which is to be galvanised is received in the black state, coated with scale from the process of manufacture. Sheets are close annealed (i.e. annealed in large iron boxes, while carefully protected from access of air) to render them soft, but many other articles are treated without annealing. The scale is next removed by pickling in hydrochloric acid, which is used cold, or nearly cold, and which is contained in stone troughs. Tanks built of blue brick, set with sulphur joints, are also frequently used for containing the pickling acid. The strength of the acid depends on the character of the work; for wire 12 p.c. of real HCl is sufficient; for tubes, buckets, and general work an intermediate strength is best; while for sheets about 20 p.c. is generally used, and sometimes the undiluted muriatic acid of commerce (26-30 p.c.) is employed. By this method of working, pickling is usually complete in a few minutes; but on the Continent, where acid is dearer and economy is necessary, a dilute pickle is used, the water is heated, and the sheets are allowed to remain in the pickle for about 2 hours. The scale having been thus dissolved or loosened, the iron is washed with water, and, if necessary, rubbed with sand to complete the cleansing. The molten zinc is contained in a wrought-iron pot, the dimensions of which vary according to the character of the work to be done, and which is heated by means of a slow coke fire around the sides and under the bottom of the pot. The surface of the zinc is covered with powdered sal-ammoniac, which acts as a flux, and when best sheets are being treated it is usual to add about 2 or 3 p.c. of tin to the bath so as to assist in the production of a crystalline appearance of 'spangle' on the surface. In other cases remelted zinc, i.e. zinc containing some tin and lead solder, is added to the bath for the same purpose.

According to Hannab and Ithead, tin alone does not produce 'spangle' when added to the zinc bath. The action is much facilitated by the presence of lead or bismuth (*J. Inst. Metals*, 30, p. 79). In galvanising sheets also it is usual to have a pair of rolls in the bath to guide the sheet in its passage through the zinc and to improve the surface. The consumption of zinc can be somewhat reduced, and the surface considerably improved, by the use of rolls or wire brushes as the sheet leaves the bath. Koffler and Breden (*Eng. Pat.* 12485, 1885; and 18674, 1888) have patented the use of wire brushes for

this purpose; whilst Heathfield (Eng. Pat. 10089, 1886; and 1682, 1890) has introduced brushes which press evenly on the surface of the sheet, as it leaves the bath, and he also adds fine wire brushes, together with improved rolls for feeding in the sheets. Corrugated sheets form a considerable portion of the trade; these are galvanised plain, and afterwards passed through corrugating machines in the cold. In galvanising wire, it is reeled through the pickle trough and the zinc-bath continuously, while netting is woven in the black, and afterwards reeled like wire. A continuous arrangement for this purpose has been patented by Vibart (Eng. Pat. 14297, 1889). The proportion of zinc taken up by the iron in galvanising varies considerably, being as high as 25 p.c. with moderately small wire, and less than one-fourth of this with many articles such as anchors, chains, and large elbows. In some galvanising works the sheets are pickled with hot diluted sulphuric acid, and the molten zinc is covered with zinc chloride instead of ammonium chloride; but the process above described is in much more general use.

The molten zinc gradually takes up iron during the galvanising process, and forms an alloy which is heavier than zinc, and which sinks to the bottom of the bath. This is removed from time to time and cast in plates, which, when broken, exhibit a close-grained fracture with black spots. This alloy is known as 'hard zinc,' and contains from about 2 to 5 p.c. of metallic iron. It is usually re-melted at a higher temperature, when it separates into two portions, one being tolerably pure zinc. The other portion is much less fusible, and forms a crystalline or granular material of the colour of zinc; it is very friable, and frequently exhibits surface colorations of great beauty. In this form it is generally sold to the smelter, and contains about 7.5 p.c. of iron, corresponding to FeZn_{10} , though exceptionally compounds are produced which contain upwards of 25 p.c. of iron (cf. Taboury, *Compt. rend.* 1914, 159, 241; Le Chatelier *ibid.* 1914, 159, 356).

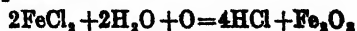
The ammonium chloride used as a flux in galvanising is gradually lost during the process, and fresh additions have to be made as required. This loss is doubtless due in part to volatilisation of the salt itself, but also to a reaction which takes place, whereby zinc chloride is formed and ammonia set free. It has been proposed to collect the fume of ammonium compounds evolved from the galvanising bath by suitable exhausting arrangements and scrubbers in which the gases are washed by diluted acid, and it is stated that such an arrangement not only very much improves the atmosphere of the manufactory, but actually yields a profit in working.

The result of the action of the ammonium chloride and of atmospheric oxygen on the molten zinc during galvanising is the production of a scum which is known as 'flux skimmings,' and which is removed from time to time. This material consists of chloride and oxide of zinc, together with some ammonium chloride and dirt; it is usually sold to the smelters. Heathfield (Eng. Pat. 14411, 1885) proposed to dissolve the chlorides in water and deposit the zinc electrically; Richards (Eng. Pat.

13982, 1885) dissolves the oxide of zinc, together with the chlorides, in the minimum quantity of hydrochloric acid, and after evaporation electrolyses the concentrated solution of zinc chloride (cf. Ingalls, *Metallurgy of Zinc*, 2nd ed. 578).

The electrolytic method has also been applied to the treatment of the zinc scum obtained during desilverising, and Rosing states (*Dingl. poly. J.* 263, 87) that this method is the most suitable for the purpose of any process at present known. The powdered scum is spread on a lead plate at the bottom of a wooden vat which is filled with a solution of zinc sulphate. The lead plate acts as anode, and when the current is passed, zinc deposits on the cathode, and a corresponding weight of zinc is dissolved from the scum. When the surface zinc has been thus removed, the residual mass is dried and heated to redness in a cupellation furnace and again electrolysed.

The quantity of hydrochloric acid annually used for pickling in the country is very great, as a number of firms engaged in the galvanising trade each require some thousands of tons of commercial muriatic acid (26-30 p.c.) per annum, but no statistics on this point are available. When the works are situated near the sea the waste pickle is readily disposed of, but the Midland manufacturers have during the last few years met with increasing difficulty in getting rid of their waste acid. The nuisance has become intolerable, and costly litigation has been undertaken by the local corporations to enforce some efficient system of treatment. Hitherto the usual system has been that of neutralisation with lime and subsequent filtration, with or without subsequent roasting of the ferrous precipitate, to convert it into red oxide of iron. Turner (Eng. Pat. 1889, 1890) introduced a method of recovering the hydrochloric acid, and the process has been in operation in South Staffordshire for over 30 years. The waste liquor, which consists of an acid solution of ferrous chloride, contains slightly under 10 p.c. of iron and about 15 p.c. of acid, chiefly in combination. The liquor is allowed to trickle slowly into a fire-brick reverberatory furnace of special construction; this is connected with condensers for the acid, which are arranged in the ordinary way. A bath of concentrated ferrous chloride solution is maintained in the furnace and thus prevents leakage, as the saturated solution penetrates any crack, and solidifies in coming in contact with the cool exterior of the furnace. The ferrous chloride is more strongly heated near the firebridge, and decomposes thus:—



Hydrochloric acid is thus recovered and used over again, while the ferric oxide is raked out of the furnace and used as fettling in the puddling process. The fuel consumption is about 4 cwt. of gas coke per ton of waste liquor treated.

When sulphuric acid is used for pickling, the solution is evaporated and crystallised to produce copperas (commercial ferrous sulphate), for which there is a limited demand. In a few instances the copperas is afterwards decomposed by heat for the production of rouge, and other varieties of bright-red ferric oxide.

Dry galvanising.—In the process known as 'sherardising,' introduced by S. Cowper-Coles, the articles which are to be coated with zinc are carefully cleaned and placed in closed boxes with zinc in a state of fine division. The boxes with their contents are then heated to a temperature insufficient to cause the zinc-dust to melt, and the vapour evolved gradually combines with the surface of the iron, and produces a closely adherent and protective coating of zinc. This process has been applied on a considerable scale, and is specially suited for articles which have sharp patterns upon their surfaces, or crevices which would be obliterated or filled up with zinc in the usual processes of dipping in molten zinc. The surface is somewhat less bright than usual, but is pleasing in appearance, and its wear is quite satisfactory.

Electro-galvanising.—Iron or steel articles are now also frequently covered with zinc by deposition, with the electric current, from a neutral solution of zinc sulphate, or from zinc salts dissolved in caustic alkali. This process is not used for the general run of galvanising work, but more particularly for articles which are in a partly finished condition, or which are of such a special size or shape as to render the ordinary process unsuitable. Zinc coatings can thus be obtained which are quite satisfactory in wear and appearance, but they are apt at times to be soft and spongy, and not to adhere firmly to the surface of the iron. They are also more than usually subject to trouble from the development of black spots on the surface when exposed to moist air.

The nature of the zinc coating obtained by various processes has been studied in detail by Guertler, *Metallographie*, 1911, 353. The most complete account of the various processes of galvanising is that given by M. A. Sing (*Le Zingage du fer et de l'acier*, *Revue de Metallurgie*, 1912, 1, 78, 160).

ALLOYS OF ZINC.

Zinc readily unites with most metals when the temperature is raised sufficiently to insure fusion. The binary alloys of zinc are generally white, crystalline, brittle materials of limited importance. These alloys are usually of uniform composition; with lead and with bismuth, however, zinc unites at a temperature above its melting-point, but the alloys separate on cooling into two distinct layers, the upper layer in each case consisting of nearly pure zinc. The most important series of binary alloys of zinc is the copper-zinc (or brass) series, which is separately described.

With aluminium zinc readily unites when the metals are melted together in any proportions. The constitution of the series of alloys has been studied by Heycock and Neville (*Chem. Soc. Trans.* 1897, 389); Shepherd (*J. Phys. Chem.* 1906, 9, 504); Ewen and Turner (*Journ. Inst. of Metals*, 1910, 2, 140); Rosenhain and Archbutt (*Phil. Trans. A*, 211, 315; also 10th Report Alloys Research, 1912); Eger (*Intern. Zeitsch. Metall.* 1913, 4, 29); Bauer and Vogel (*Mitt. K. Mat. Prüfungsamt*, 33, 146); Tanabe (*J. Inst. Metals*, 1924, 32, 415). Their thermal expansion has been measured by Smirnoff (*Compt. rend.*, 1912, 155, 351). The phases

which are recognised are α , which is zinc, or a solid solution containing less than 1 p.c. of aluminium; β , which is a definite compound, probably Al_2Zn_3 ; and γ , which is a solid solution of zinc in aluminium, and may contain as much as 40 p.c. of zinc. There is one eutectic, with 95 p.c. of zinc, melting at 380° , there is also a small break on the freezing-point curve at 85 p.c. of zinc, and an inversion at 256° , when the β -phase on cooling breaks up into α and γ . The compound Al_2Zn_3 appears to be stable only above 256° (Fraenkel and Goetz, *Z. Metallk.* 1925, 17, 12). The commercially interesting alloys are at the aluminium end of the series, and these have assumed very considerable importance in recent years (*cf.* Levi-Malvano and Marantonio, *Gazz. chim. ital.* 1912, 42, 1, 353; Carpenter and Edwards, *Intern. Zeitsch. Metall.* 1912, 2, 209). The so-called aluminium (used for motor cylinders and many purposes usually contain about 10 p.c. of zinc; not unfrequently a few p.c. of copper or other metal or metals, and the residue aluminium. These alloys are rather more fusible than pure aluminium and are stronger and work better. They are also slightly cheaper. Alloys containing up to 25 p.c. of zinc can be rolled hot, at suitable temperatures, and material with tensile strength up to 34 tons per sq. in. obtained. The strength of these alloys is thus equal to that of mild steel, and as their density is only about 3.32 they have found considerable applications where lightness and strength are required. Tensile tests have also been made on large crystals of an alloy containing 15.6 p.c. of zinc (Elam, *Proc. Roy. Soc.* 1925, A, 109, 143). Duralumin, the light alloy used for aircraft and similar purposes, is of this class; its properties depend not only upon its composition, but also upon suitable mechanical and heat treatment. In sand-cast alloys the maximum tensile strength is obtained with from 20 to 60 p.c. of aluminium, and the maximum hardness is within the same range. The tensile strength of all these alloys rapidly falls as the temperature rises. They are, therefore, not suitable for use when subjected to the effect of heat. See also Vol. IV. p. 295.

The density of the zinc-aluminium alloys agrees closely with that calculated from their composition; chilled castings are slightly less dense than theory would indicate, and sand castings slightly lighter than chilled castings. The volume changes which occur on alloying are, however, not such as can be detected without careful tests. According to O. Bauer and W. Heidenhain (*Mitt. Materialpruf.* 1923, 41, 50), the relation between the contraction on freezing and the constitution of aluminium-zinc alloys has been determined. In all samples tested the chill-cast alloys showed a greater total shrinkage (from liquid to solid at ordinary temperature) than the sand-cast alloys. The great difference in the shrinkage of chill-cast and sand-cast zinc practically disappears when only 0.5 p.c. of aluminium is added to the metal. Further additions of aluminium reduce the contraction to a minimum at 2.5 p.c. Al, then increase that of the chill-cast alloy to a maximum at the eutectic point without, however, influencing that of the sand-cast metal. From the point at which the primary separation of Al_2Zn_3 from the liquid mass begins the contraction of both sand-cast

and chill-cast alloys falls, reaching a minimum at a composition corresponding to Al_2Zn_3 , then slowly rises to a maximum at 55 p.c. Al (limit of γ -mixed crystal phase), falls somewhat, and finally rises steeply to the high value of pure aluminium. The curve in general provides a confirmation of Rosenhain and Archbutt's equilibrium diagram for the aluminium-zinc alloys (J. Soc. Chem. Ind. 1911, 1166) and evidence for the existence of the compound Al_2Zn_3 (J. Soc. Chem. Ind. 1924, 43, B. 520). Zinc-copper-aluminium alloys are only satisfactory for use at ordinary temperatures, as they become brittle on heating; an alloy containing 12.5-14.5 p.c. Zn and 2.5-3 p.c. Cu has a tensile strength of more than 11 tons per sq. in., and an elongation of 4 p.c. on 2 in. at 15°; the tensile strength falls to 4 tons at 250°, and to 1.5 tons at 350°. Some copper zinc-aluminium alloys of high zinc content exhibit the phenomena of season cracking if annealed at too high temperature, but this tendency in the over-annealed metal may be greatly overcome by hot working, so as to effect a total reduction of cross-sectional area of 50 p.c.; the alloys of this series also corrode badly on exposure to seawater, although they are stable in the air (Alloys Research Committee, 11th Report, J. Soc. Chem. Ind. 1921, 851 A.).

Magnesium and zinc form a definite compound MgZn_2 , which can be distilled unchanged.

With *antimony*, zinc readily unites in all proportions; the resulting alloys are brittle, and exhibit a close-grained, dark-grey fracture when much antimony is present; when antimony is in excess, the surface of the alloys readily tarnishes during the process of casting, and the ingot becomes coated with a dark-grey crust of oxide. When the constituent metals are present in about equal proportions, surface colorations of great beauty can be obtained by oxidation, the tints obtainable including yellow, green, red, purple, and blue. A small proportion of antimony renders the surface colour of cast zinc distinctly more blue than usual, and with care the presence of 0.5 p.c. of antimony can be readily detected by this test. The usual colour of the surface of ingots, of equal parts of antimony and zinc, is a bright sky-blue, and the alloy has the peculiar property of marking glass (Turner). Antimony-zinc alloys are readily fusible, and in this respect the influence of antimony is quite different from that of arsenic or phosphorus, both of which raise the melting-point of zinc. The most stable compound of antimony and zinc appears to be ZnSb , m.p. 537° (Tammann and Dahl, Zeitsch. anorg. Chem. 1925, 144, 1). Zinc-antimony alloys have met with an application for the production of thermopiles, for which purpose they are well suited.

With *bismuth*, zinc unites when the metals are melted together, but on cooling the alloy separates into two layers, the upper consisting of zinc containing bismuth, while the lower layer consists of bismuth containing zinc. The composition of the two layers varies with the temperature, the solubility of each metal in the other steadily increasing as the temperature rises until at about 850° the whole is of uniform composition (Heycock and Neville, Chem. Soc. Trans. 1897, 71, 390). With *gold*, zinc forms a series of alloys which are pale yellow, with

excess of gold, and greenish as the proportion of zinc increases; all these alloys are more or less brittle. In the production of jewellery part of the copper used in the preparation of the gold alloys is often replaced by brass, as the colour of the resulting gold can be thus improved, while the cost of the alloy is slightly reduced. The presence of much zinc renders the gold hard and difficult to work, and as the zinc is volatile at high temperatures this alloy is not suitable for use where the article has to be reheated during manufacture. The compound AuZn , with 75.1 p.c. Au, can be obtained by distilling off the excess of zinc from gold zinc alloys, in a vacuum, at 500° (see Groves and Turner, Chem. Soc. Trans. 1912, 585).

With *iron*, zinc forms a series of alloys which are generally white, hard, and brittle. With not more than 5 p.c. of iron the alloys are close-grained and darker in colour than pure zinc; such alloys are produced in the process of galvanising, and are known as 'hard zinc.' With more iron the character of the alloy varies according to the method of preparation. The ferri-ferrous residue left on liquating 'hard zinc' is very friable, and readily crushes into a coarse dust, consisting of bright flakes or spangles; on the other hand, the material obtained by fusion is compact, white, hard, and brittle. The alloy of zinc and iron obtained by saturating zinc near to its temperature of volatilisation with iron is not attracted by a magnet; it does not rust, nor give sparks by friction or blows. It is dense in structure, but is only semi-metallic in fracture, and contains about 22 p.c. of iron. These alloys have a somewhat important application in the preparation of 'delta metal,' and also of Aich, stereo, and Gedge's metal, all of which are yellow brasses containing about 60 p.c. of copper and nearly 40 p.c. of zinc. The addition of iron to these brasses, first suggested by Keir in 1779, imparts special hardness, toughness, tenacity, and wearing properties, while the alloy can be rolled either hot or cold, and the constituents of the mixture are relatively cheap. The proportion of iron present usually varies from about $\frac{1}{4}$ to 4 p.c., according to the purpose for which the alloy is to be applied. The zinc-iron alloy can be prepared by one of the following methods:—

1. By immersing clean iron wire, or sheet, in a bath of molten zinc heated to near its boiling-point. The addition of a little charcoal and some solid ammonium chloride assists the action. Where the presence of a little tin in the alloy is not objectionable (as for stereo-metal) a convenient method is to employ clean tin-plate scrap; the coating of tin readily unites with the zinc and leaves a clean surface of iron exposed to the action of the molten metal.

2. In order to reduce the waste of zinc usually accompanying the production of such alloys, a zinc of high boiling-point may be advantageously used in some cases. Bull (Eng. Pat. 4086, 1888) proposed the addition of phosphorus or arsenic for this purpose, while the addition of a little copper to the zinc assists the action without the introduction of any injurious constituent.

3. Alloys rich in iron can also be obtained by liquating the 'hard zinc' from galvanising works, and strongly heating the ferri-ferrous

residue in a closed crucible. The excess of zinc is volatilised, and the percentage of iron increases with the temperature employed. The alloys actually used in practice contain from about 7 to nearly 30 p.c. of metallic iron.

The equilibrium of the iron-zinc series has been studied by V. Vegesack (Zeitsch. anorg. Chem. 52, 1907, 30). The diagram is somewhat complicated. At the iron end there is a series of solid solutions in α , β , and γ iron with a maximum of about 35 p.c. of zinc at 1100°. At the zinc end two compounds are recognised, FeZn_2 (or perhaps FeZn_3) and FeZn_{11} . These compounds undergo decomposition at 777° and 662° respectively. W. Guertler (Metallographic, 1911, 353) has recognised the compound FeZn_3 as an intermediate, electro-negative layer in the coating of galvanised iron, and occurring between the iron and the zinc coating. He has also recognised crystals of FeZn_2 in the external coating of zinc (cf. Vigouroux, Ducehiez and Bourbon, Bull. Soc. chim. 1912, [iv.] 11, 480; Raydt and Tammann, Zeitsch. anorg. Chem. 1913, 83, 257).

With *cobalt*, zinc combines to form a definite compound CoZn_4 . Alloys of these two metals, containing more than 81.6 p.c. of zinc, are non-magnetic and become more brittle as the quantity of zinc diminishes. When powdered and treated with cold 1 p.c. hydrochloric acid or dilute nitric acid they leave a residue of CoZn_4 , D° 7.43 (Ducehiez, Bull. Soc. chim. 1911, [iv.] 9, 1017).

With *manganese*, zinc forms MnZn_2 and MnZn_3 , the fusion diagram being similar to that of the zinc-iron alloys. The alloys are hard and brittle; those containing 5–20 p.c. of manganese are porous, but those with a greater proportion of manganese are more compact (Parravano and Perret, Gazz. chim. ital. 1915, 45, i. 1).

With *lead*, zinc readily combines when the two metals are melted together, but on cooling the mixture, or allowing it to remain at rest, the zinc collects as a layer at the upper surface, while the lead is found at the bottom of the mass. Neither of the metals is, however, quite pure, for the lead on cooling retains 1.6 p.c. of zinc, while the zinc retains 1.2 p.c. of lead (Percy, Metallurgy, 90). These proportions vary according to the method of treatment and the temperature employed. Thus E. Kraut has examined the behaviour of zinc containing lead on remelting (J. Soc. Chem. Ind. 5, 537). The sample was melted, well mixed, and a quantity removed and granulated. The residue was allowed to cool slowly, and the top, middle, and bottom of the mass separately analysed. The top contained 0.943 p.c. of lead, the middle 2.847 p.c., and a small quantity at the bottom as much as 4.121 p.c.; whilst the original zinc contained 1.543 p.c. of lead. In these experiments only 2 kilos. of metal was employed; on the large scale the separation of the two metals is still more complete.

The rolled zinc of commerce is a nearly saturated solution of lead in zinc, and usually contains about 1 p.c. of lead. An excess of lead injuriously affects the rolling properties; hence it is usual when rolling Continental zinc to remelt it in a reverberatory furnace with an inclined bed. The metal is allowed to remain fluid at a temperature a little above its melting-

point, and the zinc is ladled off from the top from time to time. The excess of lead separates and collects as a layer in the lower end or 'sump' of the furnace, beneath the zinc, and is removed at suitable intervals.

On strongly heating lead-zinc alloys, the excess of zinc is at first volatilised, but as the temperature rises both lead and zinc distil over together. This curious volatility of lead in the presence of zinc is doubtless the cause of the occurrence of lead in commercial zinc, obtained from ores containing lead. The presence of a small proportion of zinc in commercial lead communicates hardness and allows the lead to receive a good polish without destroying its malleability.

With *mercury*, zinc readily unites to form a series of white brittle amalgams which become pasty when mercury is in excess. Zinc amalgams are easily obtained by mixing mercury with molten zinc, or by adding zinc to mercury heated nearly to its boiling-point. Zinc plates for galvanic batteries are coated with mercury by first cleansing the surface of the zinc with dilute sulphuric acid and then rubbing the mercury over the clean surface. An amalgam of zinc and tin is used on the rubbers of frictional electrical machines. (On the literature of zinc-amalgams v. J. Soc. Chem. Ind. 9, 512; cf. Hildebrand, 8th Inter. Cong. Appl. Chem. 1912, 22, 117).

For the use of zinc amalgam in the evolution method for the determination of sulphur in iron and steel, see Teruo Ashida (Memoirs of the Coll. of Science, Kyoto Imperial University, Series A. Vol. 7, No. 1983).

With *silver*, zinc does not very rapidly unite at the melting-point of the latter, but at higher temperatures the metals readily combine, forming a series of alloys which are whiter than zinc, and the use of which has been proposed for coinage and other purposes. With 5, 10, or 20 p.c. of zinc, silver forms white ductile alloys, which can be rolled like standard silver, and which are more fusible than the corresponding copper alloys (Percy, Gold and Silver, 169–171; cf. Heycock and Neville, Chem. Soc. Trans. 1897, 71, 407; Carpenter and Whiteley, Intern. Zeitsch. Metall. 1912, 3m 145).

When lead which contains silver or gold is melted with zinc and allowed to cool, the zinc separates, rises to the top, and solidifies first. This solid crust of zinc contains the precious metals, and this fact was applied by Parkes in the well-known process for desilverising argentiferous lead. The zinc scum is distilled to remove the zinc, much of which is recovered in the metallic state. The silver is melted, refined, and cast into ingots. The separation of the two metals is practically complete at 700° in a vacuum (Groves and Turner).

According to W. G. Traub (Am. Electrochem. Soc. Trans. 42, p. 55; Disc. 59, 1922) experiments were made to determine the cause of the disappearance of certain metals that had been deposited on zinc. The results indicate that copper, brass, gold, and silver are diffused into zinc; whereas nickel, which does not diffuse into zinc, can be used as a preventive against diffusion of other metals deposited over it (Sci. Abstr. 1924, 27, 300).

With *tin*, zinc readily unites in all propor-

tions, the resulting alloys being generally harder than tin but softer than zinc. The colour of the alloys is in all cases white, and the fracture is crystalline, although its appearance varies with the mode of preparation. The alloys of tin and zinc are not quite uniform in composition, as the tin tends to separate and collect at the bottom on cooling. Tin-zinc alloys are used for castings of patterns for ornamental purposes. A detailed description of these alloys, based on the work of Guettier and Rudberg, is given in Hiorns' *Mixed Metals*, 249-253.

With cerium, zinc forms two compounds Ce_2Zn and Ce_3Zn (Clotofski, *Zeitsch. anorg. Chem.* 1920, 114, 1).

The vapour pressures of molten cadmium and of its alloys with zinc have been measured at two temperatures, and Raoult's law is found to hold. The internal pressure of cadmium, indicated by compressibility and expansion coefficients, is much the same as that of zinc at the temperatures investigated (A. C. Egerton and F. V. Raleigh, *Chem. Soc. Trans.* 1923, 123 3321, *J. Soc. Chem. Ind.* 1923, 10, 2, 55).

NICKEL SILVER, BRASS, &c.

In addition to the binary and other zinc alloys above mentioned, zinc enters into the composition of a number of alloys containing three or more metals, of which the following are the most important.

Nickel silver (also known as German Silver, Packfong, White Copper, Electrum, Nevac Silver, &c.) consists of copper, zinc, and nickel. It is an alloy of white, or nearly white colour, of high tenacity, and capable of being cast, rolled, spun, and otherwise worked. One of its most important properties is its relative permanence in the air, and this has led to the use of the alloy on a very extensive scale. It usually contains about 50-60 p.c. of copper, the proportions of zinc and nickel varying according to the price and use of the alloy; the zinc is seldom less than 11 or more than 30 p.c. of the whole. For castings a little lead is frequently added. Generally an alloy of about equal weights of zinc and nickel is first prepared, and to this 'temper' the necessary quantities of copper and brass are added to give the required composition. A good description of the copper-nickel-zinc alloys will be found in Hiorns' *Mixed Metals*, 235-248.

One of the chief applications of nickel silver is in the electro-plate trade, for the production of articles of which teapots, forks, and spoons may be taken as examples. The alloys are melted in crucibles, deoxidised usually with manganese, cast into strips in metal moulds, and rolled, with several annealings, to the required gauge. For the production of ductile alloys pure metals must be used, and the temperature and character of the annealings carefully regulated. The character of the silver deposit on such articles has been studied by McWilliam and Barclay (*Inst. of Metals*, 1911, 1, 212), who conclude that when the proportion of nickel exceeds 14 p.c. the silver is more liable to strip off irregularly in actual use. With more nickel the strength and hardness increase and the alloy more nearly resembles silver in colour. Alloys containing

10-22 p.c. of nickel are specified for best work, and by suitable methods adherent coatings of silver of excellent quality can be obtained (*ibid.* 226).

Part of the tin in *gun metal* and in *bearing metal* is frequently replaced by zinc, as it is found that the density and wearing properties of the alloy are thereby increased (*v. Bronze*, art. Tin). For the same reason the bronze coinage of this country contains 1 p.c. of zinc. Zinc is also present in some varieties of aluminium bronze, and phosphor bronze, in manganese bronze, and other similar alloys. The 'Biddery Ware,' manufactured in India, usually contains about 90 p.c. of zinc together with copper, lead, and tin in different proportions.

Copper alloys—Brass. *History.*—Although the word brass frequently occurs in the Old Testament, there is little evidence that an alloy of zinc and copper was known in early times, unless, indeed, the suggestion be accepted that brass was sometimes accidentally produced in the manufacture of copper. The word translated 'brass' might equally well be rendered copper or bronze, both of which were in common use for a considerable period before the introduction of copper-zinc alloys (*v. Bronze*, art. Tin).

There is abundant evidence, however, that brass was known to the Romans about the beginning of the Christian era; that it was used for coinage purposes, and that it formed one of the yellow alloys known as *orichalcum*. The analytical and historical evidence on these points have been summarised by Dr. Percy (*Metallurgy*, i. 518-528; *cf. Gowland, Presidential Address, Inst. of Metals*, 1912). In the middle ages the Germans were famous for the production of brass, which was imported into this country chiefly in the form of sheet or *latten*, which was employed for the 'brasses' of churches, particularly in the Eastern counties. Over 4000 such brasses are known to exist in various churches, &c. in the United Kingdom, which is far richer in this respect than any other country. The first brass manufactory in England is stated to have been erected by a German in Surrey about the middle of the seventeenth century. Brass works were started in Bristol in 1702, whilst the first works for making brass in Birmingham (now the centre of the brass trade) were erected about 1740 by Turner. Up till the middle of last century the only method used in the production of brass was the calamine, or cementation, process, in which copper, in the form of bean shot or sheet, was heated in crucibles in contact with calamine and carbon, with the result that zinc was liberated and volatilised, being afterwards absorbed by the copper. The brass thus produced was then melted down and cast. This process was slow and laborious, and only yielded a brass tolerably rich in copper. In 1781 James Emerson patented the direct production of brass from copper and zinc, although there is evidence that the method had been previously used to a limited extent. The calamine process was gradually superseded by the direct method of production; the last calamine brass works in this country were closed about 1850. Some of the most important factors in the development of the brass trade have been the introduction of rolling mills in the early part

of last century, with the subsequent application of powerful machinery; the application of the stamp and die in 1769, whereby articles were produced more rapidly, with better finish, and with less metal than by the old process of casting; the introduction of gas fittings in the early part of the nineteenth century; the use of brass and copper tubes in locomotives and marine engines; the introduction of yellow metal sheathing; of brass cases for cartridges; the extruding and hot stamping of brass; and the extended use of engineers' brass work and steam and water fittings, and lastly the applications to electric fittings. These and many other circumstances have resulted in an enormous development of the brass trade, so that there are normally employed in the brass trade of Birmingham alone over 35,000 persons (male and female), while the consumption of metal is valued at 4 millions sterling (*v. A Short History of the Brass Trade*, J. W. Davis; also *Encyc. Brit. art. Brasses*; Thomson, *Hist. of Chemistry*, i. 55, 62, &c.; *Midland Hardware District*, 228-240; Percy, *Metallurgy*, 504; Holzapfel's *Mechanical Manipulations*, 312; *Useful Metals and their Alloys*, 566).

General properties of zinc-copper alloys.—

Zinc and copper unite in all proportions, the resulting alloys being of remarkably uniform composition throughout the mass (Laurie, *Chem. Soc. Trans.* 53, 106; 55, 677). The experiments of Tilden (*J. Soc. Chem. Ind.* 9, 84) also show the great uniformity in composition of commercial sheet brass, although on the other hand Hiorns (*Mixed Metals*, 107) gives analyses showing the copper to be less at the top than at the bottom of ingots of cast brass. The alloys containing upwards of 60 p.c. of copper are red or red-yellow in colour; those containing less than 48 p.c. of copper are grey or white; the intermediate alloys are yellow. The hardness of the alloys is usually greater, while the melting-point is higher, and the density greater, than that calculated from the mean of the constituents. Copper-zinc alloys containing 7-28 p.c. Cu expand to a greater or lesser extent on solidification, the maximum expansion occurring with the alloy containing 15 p.c. Cu. The range of composition in which marked expansion takes place has a large freezing interval, and chill-cast alloys within this range exhibit to a considerable degree the phenomenon of inverse segregation. The degree of segregation in chill-cast bars is proportional to the expansion that takes place in sand-cast bars and has the same range and maximum copper content. The force of expansion in alloys containing 10-20 p.c. Cu is sufficiently great to break the crucible in which the metal is cooled, and the resulting metal contains many cracks and voids, whilst its hardness and elastic limit are low. Microscopical examination of alloys within this range revealed in all cases a very indefinite structure containing many minute cracks and holes; this appears to be due to the fact that these alloys consist almost entirely of ϵ , which has the property of expanding and becoming very soft, so that the crystal boundaries become obliterated. The expansion of the ϵ phase proceeds very quickly after the alloy has cooled through the β peritectic line (K. Iokibe, *Inst. of Metals*, 1924; *J. Soc. Chem. Ind.* 1924, 43, B. 297). The

addition of zinc to copper produces remarkable alterations in the working properties of the product, varying, however, with the proportion of zinc present. Thus, pure copper can be rolled hot or cold, although in the latter case frequent annealing is necessary, and rolling hot is much cheaper and more expeditious. The addition of only a trace of zinc renders copper 'red short,' although it does not interfere with the malleability of the metal when cold. Hence alloys which contain from about 62 to 100 parts of copper p.c., and the residue zinc, are not generally rolled hot, or if so rolled require special treatment. Usually these alloys are rolled cold, and are annealed and pickled from time to time as the metal becomes hard and brittle from the work put upon it. But alloys with about 60 p.c. of copper can be rolled either hot or cold, and the cost of production is thus reduced. These alloys are, however, less ductile and tough than those which contain more copper. Their tensile strength is greater, but their ductility less than with alloys higher in the series. The alloy of 60 parts of copper and 40 of zinc was patented by Muntz for the production of sheathing for wooden ships, and is now largely prepared under the name of 'yellow metal,' for the production of the cheaper varieties of brass sheet, tubes, and wire. The standard size of yellow metal sheets is 14 by 48 ins., and the thickness is returned according to the Birmingham metal gauge. Alloys containing about 56 to 58 p.c. of copper, and consisting almost entirely of the β phase, are extruded into rods, while red hot, by means of suitable presses. Such alloys will forge at a red heat. Alloys of about this composition are used for material which has to be turned or otherwise finished by automatic machinery. According to Heathcote, the presence of from 1.5 to 2 p.c. of lead in the alloy gives the best results when machining (*J. Inst. of Metals*, 1917, 17, 56). Alloys containing about 50 p.c. of copper are light yellow in colour; but cannot be rolled either hot or cold. The chief application of alloys containing rather more than half their weight of copper is for the production of 'brazing' solder for use with copper, brass, &c. These alloys form what is usually known as 'hard' solder, in contradistinction to lead-tin alloys or 'soft' solder. But in the brass trade different varieties of solder are used, containing from about 45 to 56 p.c. of copper, according to the temperature to be employed. The brazing solders containing more copper are called 'hard,' and those with more zinc 'soft.' The solder most commonly employed contains about 51 p.c. of copper, and is usually sold in the form of powder, which is prepared by heating a mass of the alloy to a particular temperature below its melting-point, when it is struck a sharp blow with a mallet. At this temperature the alloy is very friable, and readily crumbles into powder when treated as above described. If it is too hot or too cold it cannot be powdered in this way.

With more than 50 p.c. of zinc the alloys lose their yellow colour and become white, brittle, and more fusible. Though all these white alloys are brittle when hot or when cold, they can usually be laminated at some intermediate temperature, and in this respect they

zinc. This proper temperature varies according to the proportion of copper present, being as low as 150° in zinc, and at a red heat, probably about 600° , in yellow metal. As the copper increases beyond 60 p.c., as before explained, brass can no longer be rolled hot, but is laminated in the cold with repeated annealing.

For the corrosion of Muntz metal in sea water, see W. Donovan and T. E. Perks, *J. Soc. Chem. Ind.* 1924, 43, 72 T. For the corrosive action of brackish waters on metals, see T. E. Perks, *J. Soc. Chem. Ind.* 1924, 43, 75 T.

According to Mallet (*Construction of Artillery*, 82), the alloy CuZn_2 , containing about 33 p.c. copper and 67 p.c. zinc, is used for watch-maker's brass, and possesses the greatest tenacity of the whole series. This statement has been copied into many well-known works on the subject, but it is evidently an error. Laurie has shown by his investigations on the electro-motive force of zinc-copper alloys (see above) that only one definite alloy exists in this series. This compound is white, hard, and brittle, and corresponds very closely in composition to Mallet's alloy above mentioned. All other zinc-copper alloys may be considered as solidified solutions of this definite compound in excess of one or other of the constituent metals. Guertler (*Zeitsch. anorg. Chem.* 1906, 51, 397; 1907, 54, 58) and Murray and Turner (*J. Inst. of Metals*, 1909, 2, 131) support the view of only one definite compound in the copper-zinc series, viz. Cu_2Zn_3 with 39.36 p.c. Cu. This compound is a brilliant white brittle substance, harder than mild steel. Of itself it is of little or no practical value, but by its union with various proportions of copper, which alone is too soft, a whole series of alloys is obtained which possess most valuable and remarkable graduated properties.

The equilibrium of the copper-zinc series was studied by Roberts-Austen (4th Report Alloys Research); Shepherd (*J. Phys. Chem.* 1904, 8, 421), Tafel (*Metallurgie*, 5, 13), Hudson (*J. Soc. Chem. Ind.* 1906, 503), Murray and Turner (*J. Inst. of Metals*, 1909, 2, 103), and Carpenter and Edwards (*ibid.* 1911, 5, 127). The latest form of the equilibrium diagram of this series has been given and discussed by Rosenhain in the article on METALLOGRAPHY, and will, therefore, only receive brief reference here. The alloys, which are of commercial importance, contain from about 45 to 100 p.c. of copper. Within this range there are three constituents which are respectively designated by the Greek letters α , β , and γ . The α constituent is a solid solution of zinc in copper, the maximum content of zinc being about 36 p.c. at 400° . The γ constituent was regarded by Shepherd as a solid solution, but by Murray and Turner as the compound Cu_2Zn_3 , containing about 40 p.c. copper. The β constituent contains about 53 p.c. copper. It has the properties of a solid solution, but was believed by Carpenter (*J. Inst. of Metals*, 1912) to be an intimate mixture of α and γ below a critical temperature of 470° , but this view is not now generally accepted. This critical temperature is noted with alloys containing from 60 p.c. of zinc down to 28 p.c., and probably less. The α phase is relatively soft and ductile: the β phase is harder and more brittle, while the γ phase is still harder, and practically has no ductility. It can be

readily powdered in a mortar. The effect of adding zinc to copper is, therefore, as shown by Charpy, to increase the tenacity and to diminish the ductility. Beyond 40 p.c. the tenacity very rapidly falls away again, whilst the ductility is diminished after 30 p.c. Hence where ductility and strength are required together, as with cold-drawn tubes, or cartridge cases, about 70 p.c. copper is preferred. The chief commercial alloys may be classed as follows (Hudson):—

1. 100–71 p.c. Cu. Consist entirely of α at all temperatures.
2. 71–64 p.c. Cu. Entirely α below 400° ; $\alpha + \beta$ above.
3. 64–63 p.c. Cu. Consist of $\alpha + \beta$ at all temperatures.
4. 63–53.5 p.c. Cu. $\alpha + \beta$ at low temperatures; β only at some higher temperatures.
5. 53.5–51 p.c. Cu. Consist of β entirely at all temperatures.
6. 51–40 p.c. Cu. $\beta + \gamma$ at low temperatures β only at a higher temperature.

It will be noted that the proportion of the β constituent increases as the temperature rises, and this fact has important bearings on the heat treatment of brass. The brittle ranges in the brasses have been studied by D. Bunting (*Inst. of Metals*, 7, 31).

Cast brass. All brass is now made by melting together copper and zinc, but the term 'cast brass' is applied when the article to be made receives its form in the mould, and does not require to be afterwards rolled, drawn, hammered, or spun. For this purpose the charge is melted in graphite or clay crucibles, which usually contain about 90 lbs. of metal, and which are heated in small wind furnaces by coke. Generally each furnace contains but one pot, but sometimes two or four pots are placed in a single furnace, which is made proportionately larger in such cases. In Birmingham clay crucibles were formerly used for brass, and plumbago for bronze castings. Larger crucibles, holding 250 lbs. of metal, are often used in big foundries. Small cranes are then provided. Tilting furnaces are also now very frequently employed. Electrically heated furnaces are used in many of the larger brass works in the United States. In practice it is necessary to add a quantity of scrap brass to the charge, and this is generally introduced first into the red-hot crucible together with a small quantity of flux, which is added to remove the oxide and dirt adhering to the scrap. When only new metal is used the flux is either much reduced or altogether omitted. The fluxes most commonly employed are ground fluor-spar, together with more or less glass, and *sal enizum* or acid potassium sulphate. Calcined borax, often with the addition of some boracic acid, is also used as a flux. When the scrap is hot the copper is charged into the crucible, usually in the form of ingots, though occasionally bean shot copper is used. After the copper has thoroughly melted, the zinc is cautiously added in as large pieces as possible. The use of large pieces of zinc reduces the loss, and moderates the violence of the combination. In any case considerable heat is produced by the union of zinc and copper, and some of the zinc burns with a dazzling brilliancy. After allowing the crucible to remain in the furnace for a short time to permit

the metal to become sufficiently fluid, it is poured into moulds, which for brass casting are generally of 'green' sand. While the brass is hot, zinc gradually volatilises and burns at the mouth of the crucible, forming zinc oxide; this produces the white fume which fills the casting house while the metal is being poured, and as a protection against the deleterious effects of inhaling the fume it is customary for the workman to keep his mouth and nostrils covered with a cloth. Regulations are now in force to ensure the proper ventilation of brass foundries. When the metal has set, the castings are turned out and dipped while warm into water, which detaches most of the adhering sand; the processes of dressing, grinding, polishing, dipping, and burnishing are necessary to give the required surface, while the finished article is lacquered to preserve it against atmospheric influences. The proportion of copper in cast brass varies considerably according to the purpose for which it is required; in some cases cheapness is of prime importance, in others the metal must 'dip' well when immersed in acid, while not unfrequently the shade of colour of the resulting alloy is of the utmost moment. Best cast brass generally contains from 70 to 75 p.c. of copper; ordinary good English brass 66·6 p.c. (i.e. 2 p.c. of copper to 1 of zinc); while common cast brass contains about 62 p.c. of copper. A little lead is generally added in preparing cast brass; this gives sounder castings and produces a metal which turns much better in the lathe than ordinary brass. Although not unfrequently as much as 2 p.c. of lead is added to the charge, most of this is removed by oxidation and usually only about 0·3-0·5 p.c. remains. The loss of metal in melting and casting is usually about 3 p.c., but this is greater when much small scrap is used. It may be added that in the preparation of cast brass it is not so necessary to ensure the absence of very small quantities of metals such as antimony, bismuth, and silver as is the case when the alloy has afterwards to be rolled or drawn. When special ductility or malleability is required in the final product, it is of the utmost importance that the purest obtainable materials should be employed.

When alloys of the copper zinc series are cast in bars in sand moulds, and the length of the bars during cooling is observed by means of an extensometer, it is found that in some cases marked expansion occurs, while with other compositions there is little or no expansion. There are three maxima, which in order of magnitude occur with 15, 80, and 50 p.c. of copper respectively. The nature of the marked expansion with about 15 p.c. of copper has been studied by K. Iokibe (*Inst. Metals Jour.* 31). It does not occur if the alloys are cooled quickly; in the rapidly cooled alloys there is marked 'inverse segregation,' i.e. the copper concentrates towards the middle of the ingot. The series has four maxima on the hardness curve, which are with 40, 80, 65, and 10 p.c. respectively. The 40 p.c. alloy is exceptionally hard (Turner and Murray, *J. Inst. of Metals*, 1909, 2, 98; F. W. Harris, *Inst. of Metals J.* 28, 327).

Sheet brass. One of the most important applications of brass is for the production of sheets, as sheet brass is not only needed for a multitude of useful and ornamental purposes

itself, but it forms the starting-point for the manufacture of the greater part of the brass wire and tubing that is dealt with in commerce.

For the production of 'yellow metal' it is customary to prepare the alloy by melting copper on the bed of a small reverberatory furnace and adding the requisite quantity of zinc. But in preparing other varieties of sheet brass it is usual to employ crucibles heated in coke fires as described for cast brass. Gas- or oil-fired furnaces are also employed, and are coming steadily into favour. The crucibles generally hold about 120 lbs. of metal. In either case the alloy when melted is cast in iron moulds into flat bars, varying in size, but of which one about $4\frac{1}{2}$ in. \times $\frac{1}{2}$ in. \times 90 in. may be taken as an example. These are known as 'strips' and the operation is known as 'strip casting.'

The strips are then 'broken down' by being passed cold through a pair of rolls, the operation being repeated as often as the metal will allow. The work done upon the metal soon causes it to become hard, and if the rolling were continued the strip would readily develop cracks. To obviate this the metal is annealed at a red heat, about 650°C., and the surface is cleaned from oxide by pickling in dilute sulphuric acid. After washing with water, the operations of rolling, annealing, pickling, and washing are repeated, in order, until the desired shape and thickness are obtained. During the process of rolling the original crystalline structure of the alloy is largely broken down and an amorphous hard matrix is produced. This subject has been fully dealt with by Beilby (*Hard and Soft States in Metals*, *J. Inst. of Metals*, 1911, 6, 5). On annealing, the first effect is to restore the crystalline structure of the alloys. At the same time it becomes soft and ductile. If, however, the temperature of annealing be too high, or the time unduly prolonged, the crystals increase in size, and ultimately become so large that the material is quite weak, brittle, and worthless for practical purposes. The proper annealing temperature varies with the composition of the alloy, and the whole question has been studied by Hudson and Bengough (*J. Inst. of Metals*, 4, 1910, 92), and by Bengough (*ibid.* 7, 1912). With 70-30 p.c. brass the best annealing temperature is between 600° and 700°, but brass may become coarsely crystallised or 'burnt' at 100° below the solidus line if maintained for sufficient time, while it may be safely heated to within a few degrees of the solidus if the time does not exceed half an hour. Annealing commences at a lower temperature with brass which has received much cold work; in such cases even 300°C. may produce a marked effect (Matthewson and Phillips, *Amer. Inst. Min. Engs.* Feb. 1916). As sheet brass is used for so many purposes, its composition varies over a wide range, extending in fact from a mere trace to 40 p.c. of zinc. Turner has shown (*Chem. News*, 63, 227, 64, 143) that the use of impure washing water containing chloride leads to the production of copper-red stains and smears, on the surface of the finished brass, which is a cause of frequent loss and trouble. The cause of red stains has been more fully studied by E. A. Bolton (*Inst. Metals J.* 30, 35), who concludes the copper oxide reacting with the pickle deposits copper and causes the stains.

Since the ductility of the alloy increases with the proportion of copper, alloys such as best red brass, gilding metal, and percussion-cap metal contain from 80 to 90 p.c. of copper. Dutch metal contains 80–85 p.c.; Prince's metal, 75 p.c.; best English sheet brass, 70–72 p.c.; ordinary, 66.6 p.c.; common, 63 p.c.; and yellow metal, 60 p.c. As already explained, this last alloy, though somewhat deficient in ductility, is strong and possesses the great advantage that it can be rolled either hot or cold. White metal alloys are used in the form of sheet to a limited extent, and these contain less than 50 p.c. of copper. The cheaper yellow alloys, rich in zinc, do not 'stand the fire' so well in soldering, and it is not usual to solder anything containing less than 60 p.c. copper. Even with this composition a special soft solder has to be employed, whilst red brass stands the fire best, and can be used with the hardest solder.

Brass wire is made from sheet brass, the sheet of suitable thickness being slit into thin strips by cutters, and the strips are then drawn into wire at the draw bench. The chief varieties of wire arranged in order of ductility are as follows:—Red metal, Prince's metal, ordinary, common, and yellow metal. The first two of these were formerly used in the button trade, as in soldering on the shanks with hard solder they 'stood the fire' well. The other varieties can all be soldered with suitable solder of low melting-point, but the difficulty of soldering increases with the proportion of zinc.

Brass tubes. There are two principal methods of producing brass tubes. By the original process, which is still largely employed, sheet brass of the required composition and thickness is cut into strips of the necessary length; the strips are then drawn through a die, which imparts a circular shape, and the edges are soldered together by the use of powdered solder and borax made into a cream with water. Small tubes are soldered by being drawn through a small furnace fired with small coal or coke, but large tubes are now generally united by the use of a gas blowpipe, which gives a local and easily regulated heat. In the second and more modern method of manufacture brass tubes are solid-drawn, and thus the operation of soldering is dispensed with. This process is chiefly employed for large tubes and for tubes of special quality, as the soldered joint in tubes made in the ordinary way is always more brittle than the rest of the material. The soldered joint is also frequently a cause of corrosion in tubes exposed to steam or salt water. For solid-drawn brass tubes a short hollow cylinder of metal is cast in suitable moulds, and by drawing on a mandril, with frequent annealings, this hollow cylinder is gradually elongated to the required dimensions.

Condenser tubes are generally made of 70 p.c. copper, 30 p.c. zinc; or, according to the Admiralty specification, in which 1 p.c. of the zinc is replaced by tin. The corrosion of condenser tubes is a source of considerable loss and trouble, especially in the mercantile marine. The causes which lead to such corrosion have been studied by Brühl (*J. Inst. of Metals*, 6, 279) and by Bengough (*ibid.* 1911, 5, 28, and in a series of later reports to the Corrosion Committee of the Institute of Metals).

Ornamental patterns on brass tubes when parallel with the length of the tube are produced by passing the plain tubes through a set of suitably arranged rolls, on the surface of which the desired pattern is cut. But when the pattern is of a spiral form it is usual to draw the plain tube through a die of the requisite shape, arrangements being made for either the tube or the die to rotate during the operation. Best drawn tubes for locomotives and similar purposes contain 70–72 p.c. of copper; the composition of other tubes varies according to the quality of the sheet brass used in the process of manufacture.

Colouring of brass. A considerable proportion of the goods originally made of brass are so coloured before passing into commerce that the tint of the metal itself is no longer to be recognised. The most important applications of colouring are the following:—Bronzing in various shades, such as black, grey, red, green, &c.; lacquering in many shades; and bright colouring with highly coloured, transparent lacquers. These processes of colouring may be divided into two classes according as to whether they are conducted before or during the operation of lacquering.

As has been pointed out by Löwenherz, a variety of shades of colour can be obtained by carefully heating bright clean brass to definite and regulated temperatures. These colours so produced are formed in the following order:

- | | |
|-------------------------|---------------------|
| 1. Orange yellow. | 6. Rose-red gold. |
| 2. Clear golden yellow. | 7. Violet-rose red. |
| 3. Orange gold. | 8. Clear rose. |
| 4. Dark gold. | 9. Steel white. |
| 5. Brown gold. | |

Some of the colours are of great firmness and beauty, and the process is full of promise for special purposes, but has not hitherto been successfully adopted on any considerable scale.

The methods of bronzing, applied before lacquering, include the following:

Copper bronzing.—To develop a copper-coloured surface on brass the metal may be cautiously rubbed with hydrochloric acid, or, still better, it may be immersed in a slightly acid dilute solution of copper nitrate until the desired depth of colour is obtained. To produce a dark copper-bronze colour, treat as above, and blacken the surface with plumbago before lacquering.

Grey bronze.—A cheap grey bronze is produced by rubbing with plumbago and using a nearly colourless lacquer. A more permanent grey bronze is produced by the use of a solution of arsenic trioxide in hydrochloric acid; the addition of iron salts improves the effect. For common work, which is *not soldered*, an aqueous solution of mercuric chloride rendered acid with vinegar is frequently used.

Black bronze.—The very beautiful and permanent black bronze used for mathematical and scientific instruments is produced by the application of a dilute aqueous solution of platinum tetrachloride which was introduced for this purpose about the year 1860.

Green bronze.—A cheap green bronze which was formerly much in favour was obtained by the use of plumbago followed by a transparent yellow lacquer.

Ordinary lacquer is a solution of shellac in proof spirit, but other gums and solvents are also used. A colourless 'dip' lacquer (i.e. one in which the articles may be dipped, instead of the lacquer being applied by means of a brush to the warm surface as usual) is made by dissolving nitrocellulose in amyl acetate. For ordinary purposes many shades of lacquer from colourless, through yellow, to brown are regularly employed. For the cheaper kinds of bronzing special bronze lacquers of a variety of colours are used; and in addition richly coloured transparent lacquers of numerous shades are produced for the manufacture of brightly coloured thin sheet metal for ornamental purposes. In this branch of manufacture the use of aniline derivatives has led to numerous improvements.

T. T.

COMPOUNDS OF ZINC.

Zinc oxide ZnO . This substance, the *nix alba*, 'philosophical wool,' or 'flowers of zinc' of the alchemists, the *tutia* or *pompholyx* of the ancients, occurs as the mineral zincite or red zinc ore which is a mixture of zinc oxide and 7-12 p.c. red manganese oxide. It is often found in red or orange-yellow hexagonal crystals or in granular masses. Zinc oxide is occasionally found crystalline in zinc and brass melting furnaces.

Zinc oxide is known in commerce as zinc white, and is generally prepared on the large scale by burning zinc or its ores in retorts, or in an electric furnace, the zinc fumes being led into chambers where they meet a current of air and the oxide thus formed is led into a second chamber and allowed to condense; or the ore may be heated with anthracite or charcoal, and the resulting hot fumes treated with air. The New Jersey Zinc Company, working on franklinite ore, a zinc-iron-manganese spinel, make the greater part of the zinc oxide on the American market. The ore is washed, crushed, and passed by a belt conveyor over a separating table where the franklinite is removed by an electro-magnet. This is mixed with coal and spread on grates through which air is blown. The reduced zinc is converted into oxide which is drawn by the aid of fans through cooling pipes into fabric bags which are tapped at the bottom from time to time (see Eng. Pats. 16129, 1891; 11233, 1894; 4310, 1894; 12274, 1901; 18015, 1903; 4058, 1904; 21787, 19339, 1906; U.S. Pat. 902280, 1908; Fr. Pat. 403681, 1909; amongst others; J. Soc. Chem. Ind. 1894, 401; *ibid.* 1901, 911; *ibid.* 1903, 1138; *ibid.* 1906, 1056; *ibid.* 1907, 1150; *ibid.* 1910, 88; Schnabel, Eng. and Mining J. 1892, 9, 26295).

Zinc oxide may also be prepared by heating zinc sulphate with carbon for about 2 hours at about 650° (Eng. Pat. 3906; D. R. P. 93315).

A hot solution of sodium sulphate or other alkali salt is electrolysed with zinc electrodes; zinc sulphate is formed at the anode, and sodium hydroxide at the cathode. These react forming zinc hydroxide, which is then calcined (Fr. Pats. 328491, 1903; 348294, 1904; U.S. Pat. 771025, 1903; Ind. Elektrochem., 1904, 8, 29).

The zinc oxide of pharmacy is prepared either by burning the metal or by precipitating very pure zinc sulphate with a hot solution of

sodium, magnesium, or other carbonate, and heating the dried carbonate to expel carbon dioxide (Jansen, Mag. Pharm. 26, 74; Dulk, Berl. Jahrb. Pharm. 24, 2, 74; 29, i. 59; D. R. PP. 21987, 151022; Rigg, Eng. Min. J. 75, 626).

Crystalline zinc oxide of sp.gr. 5.782 may be obtained by heating the nitrate (Brügelmann, Zeitsch. anal. Chem. 29, 126); by heating zinc chloride in a stream of water vapour (Daubrée, Compt. rend. 1854, 39, 153); and by a number of other methods (Sidot, *ibid.* 1869, 69, 202; Goigou, *ibid.* 1887, 104, 120).

A large number of patents have been taken out for the preparation of the oxide by various methods, of which the following may be mentioned: Fr. Pats. 338977, 1903; 373027, 373953, 1906; 406150, 1908; 404840, 1909; 412214, 411672, 1920; Eng. Pats. 2532, 1905; 24526, 1906; U.S. Pats. 815516, 1906; 849322, 900088, 1908; 919375, 919376, 920336, 921909; J. Soc. Chem. Ind. 1897, 182; 1033; 1904, 1034; 1906, 325, 374; 1907, 1910, 233, 425, 1016.

Zinc oxide is a white powder of sp.gr. 5.6 (see Fuchs and Schiff, *ibid.* 1896, 363), which, on heating, becomes lemon-yellow, but on cooling again becomes white.

According to Schüpphaus, the yellow colour is due to the formation of a suboxide (*ibid.* 1899, 987). Zinc oxide volatilises in the electric furnace, the vapours condensing in long, transparent crystals (Moissan, Compt. rend. 1892, 115, 1034). In a current of air it commences to volatilise at 1100° (Doeltz, Metallurgie, 1906, 3, 212). At a bright red heat the oxide is probably polymerised to some extent (de Forcrand, Compt. rend. 1902, 134, 1426; *ibid.* 135, 36; Ann. Chim. Phys. 1902, [vii.] 27, 26). Water dissolves about 0.003 grm. per litre (Remy and Kuhlmann, Zeitsch. anal. Chem. 1924, 65, 161). Zinc oxide commences to be reduced by carbon in an atmosphere of nitrogen at 800°, by carbon dioxide at 600°, reduction in both cases increasing rapidly with rise in temperature (Doeltz and Graumann, Metallurgie, 1907, 4, 290). By magnesium it is reduced with explosive violence (Winkler, Ber. 1890, 23, 120). It may be reduced on heating it in dry hydrogen.

The reaction between zinc oxide and carbon monoxide has been examined by passing a stream of gas over the heated oxide in a quartz boat and determining the carbon dioxide in the issuing gases and the amount of zinc reduced by the loss in weight of the zinc oxide boat due to volatilisation of the metal. The velocity of the reaction $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2$ is very small at 420°, but increases rapidly with rise of temperature. At the same time the relative proportion of carbon dioxide formed increases owing to decomposition of the carbon monoxide into dioxide and free carbon. On the other hand, especially on cooling to temperatures below those at which reduction of the zinc oxide takes place, a certain amount of carbon dioxide becomes reduced again to monoxide by the metallic zinc formed in the early stages. Above 700° no further deposition of carbon takes place, showing that carbon is no longer in equilibrium with the products of the reaction. The proportion of zinc reduced depends not on the quantity of carbon monoxide passing through the apparatus, but on the time

of contact. Experiments on the reduction of zinc oxide by carbon showed that the presence of small quantities of oxygen accelerates the reaction considerably; in the total absence of oxygen a temperature of over 1000° is necessary in order to obtain any dissociation of zinc oxide in the presence of carbon. It therefore appears that the reduction of zinc oxide by carbon takes place, under commercial conditions, through the intermediate action of carbon monoxide (A. d'Hooghe, Bull. Acad. roy. Belg. Cl. Sci. 1923, 9, 323; Chem. Zentr. 1924, 95, 1; J. Soc. Chem. Ind. 1924, 43, B. 260).

When strongly heated in the oxyhydrogen flame it emits an intense white light, and is seen to phosphoresce when cooled in the dark. The character of the light emitted by incandescent zinc oxide has been examined by E. L. Nichol and B. W. Snow (Phil. Mag. [v.] 32, 420; and [5] 33, 19; see also Schmidt, Ann. Physik. 1904 [iv.] 13, 622; Tafel, *ibid.* 14, 206), who have studied the behaviour of zinc oxide under the action of canal rays.

Certain preparations of zinc oxide when illuminated with ultra-violet rays become luminous, the luminescence slowly increasing in intensity to a maximum and on removing the exciting rays immediately disappears. A weak and transient phosphorescence is shown at the same time (Winther, Zeitsch. wiss. Photochem. 1921, 21, 45).

One part of the oxide dissolves in 230 parts of water (Dupré and Bialas, Zeitsch. angew. Chem. 1903, 16, 54). If quite pure it dissolves completely in ammonia. It is readily soluble in acids, forming the corresponding zinc salts which are colourless substances having a disagreeable taste, are often poisonous to plants and animals, act as emetics, and are employed in medicine, chiefly for external application.

Zinc white has been recommended as a useful, efficient, and more healthy substitute for white lead for oil painting, and in the preparation of varnishes (Livache, Compt. rend. 1901, 132, 1230; Bull. Soc. d'Encouragement, 1908, 110, 516; 1902, 103, 690; Lenoble, J. Soc. Chem. Ind. 1904, 829). For this purpose zinc white, alone, or mixed with finely-ground silica and calcium carbonate, is made into an emulsion with linseed or a similar oil (Eng. Pat. 4870, 1893; Fr. Pat. 366465, 1906; D. R. P. 175402, 178983; J. Soc. Chem. Ind. 1894, 22; *ibid.* 1906, 1056).

Many fast colouring matters, inorganic and organic, are, however, bleached by light when mixed with zinc oxide and gum, especially in glass. White lead and cadmium yellow are blackened by light when mixed with zinc oxide and glycerol. Eosin and cyanin are more rapidly bleached in the presence of zinc oxide, fuchsin is not. The zinc oxide itself is chemically unchanged when acting as a photo-catalyst (Winther, Zeitsch. wiss. Photochem. 1922, 21, 141).

A mixture of zinc hydroxide and hydrocarbonate, used as a white pigment, is prepared by intimately pulverising zinc ore with quicklime, then extracting the mixture with liquid ammonia. After removing foreign metals by ordinary methods the ammoniacal liquid is distilled in a vacuum with or without the application of heat (Fr. Pats. 309079, 2001, 1903).

A mixture of ground zinc white and hydrated oxide of zinc precipitated in the cold or at 50° – 80° , is said to be a useful enamel pigment when used in the proportions represented by the formula $2\text{ZnO} + \text{Zn}(\text{OH})_2$, whilst for matt-surface paints the proportion should be $6\text{ZnO} + \text{Zn}(\text{OH})_2$. As a second coat for enamelling, zinc carbonate may be substituted for a part or the whole of the zinc oxide (Joannis, J. Soc. Chem. Ind. 1906, 486).

Zinc soaps are manufactured by thoroughly mixing about 0.25 p.c. oleic or other aliphatic acid with zinc oxide and a little water. The resulting zinc soap can now be mixed into an emulsion with raw or boiled oil, a thick paste thus being formed, the constituents of which do not separate even on prolonged standing (Fr. Pat. 368755, 1906).

Zinc lead pigment consists of zinc oxide and sulphate, lead oxide and sulphate, some sulphur dioxide and water (Buskett, Eng. and Ming. J. 1907, 83, 760).

Zinc oxide is used in the manufacture of cements (D. R. P. 56958; Fr. Pats. 332788, 333671, 1903). When mixed with aluminium phosphate it is used as a dental cement (Grenet, Chem. Zeit. 1909, 33, 610).

It is also employed in the glass industry (J. 1894, 151, 354; Zschimmer, Chem. Zentr. 1907, ii. 1461; Walker, J. Amer. Chem. Soc. 1905, 27, 865); and in the preparation of crystalline glazes (Holdercroft, Trans. Eng. Ceramic Soc. 1909–10, 9, 37).

Crystalline zinc glazes are formed by the separation of zinc silicate on slow cooling of the glaze. It has a smaller coefficient of expansion than other glazes, and when melted on to pottery or stone ware is less liable to 'craze' than lead glaze.

By addition of different oxides, characteristic colour effects can be obtained with zinc glazes. Zinc oxide may also be used in place of the more costly tin oxide for producing opalescent glazes (Petrik, Chem. Zeit. 1908, 32, Rep. 490).

Crystalline zinc glazes are prepared by mixing 27.389 parts by weight of zinc oxide with 7.382 potassium nitrate, 13.770 borax, 7.000 whiting, 4.466 flaky boric acid, 0.600 cupric oxide, and 39.693 flint. The glaze should be ground as finely as possible and applied to the surface to be glazed with dextrin as an adhesive (Riddle, Trans. Amer. Ceramic Soc. 1906, 8, 336; Minton, *ibid.* 1907, 9, 782). It is also used for the production of white and colour resists employed in printing processes (Leuber, Zeitsch. Farben. and Textil Ind. 1904, 3, 417); for the preparation of certain sizing materials (D. R. P. 194726; J. Soc. Chem. Ind. 1908, 634); and to some extent in analytical processes in the laboratory (Meineke, Zeitsch. angew. Chem. 1888, 252; Koninek, Chem. Zeit. 1906, 29, Rep. 5).

For the estimation of zinc oxide in zinc paints and lithopones, see J. Soc. Chem. Ind. 1907, 977; Stromeyer, Arch. Pharm. 27, 549.

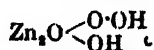
Zinc grey is obtained as a by-product in the manufacture of zinc white. Made into a paste with wood oil it is used as a cement for steam joints (Livache, Bull. Soc. d'Encouragement, 1905, 107, 568). It also forms a good, silver-grey oil paint.

Zinc hydroxide $\text{Zn}(\text{OH})_2$ is obtained as a

white powder by adding caustic potash or soda or ammonia to a solution of a zinc salt. It may be obtained crystalline by allowing zinc to remain in contact with iron or copper under a layer of ammonia or by allowing its saturated solution in caustic potash to stand, or by the action of water on zinc oxide (de Forcrand, *l.c.*). It may be obtained in two different crystalline forms: thin needles or short thick rhombic crystals (Fricke, *Amer. J. Sci.* 1925, v. 9, 145). It is stable in air up to 85°, loses nearly all its water at 130°–140°, is readily soluble in excess of ammonia and alkalis towards which it behaves as a weak acid, H_2ZnO_2 (Herz, *Zeitsch. anorg. Chem.* 1901, 26, 90; Rubenbauer, *ibid.* 1902, 30, 331; Hantzsch, *ibid.* 289; Bonsdorff, *ibid.* 1904, 41, 132; Moir, *Chem. Soc. Proc.* 9105, 310; Dawson and McCrac, *Chem. Soc. Trans.* 1900, 1239; Euler, *Ber.* 1903, 36, 3400; Kuriloff, *Zeitsch. Elektrochem.* 1906, 12, 209; *Bull. Acad. St. Petersburg*, 1901, 1, 95). It has been supposed that the zinc hydroxide in alkaline solution is mainly present as a colloidal modification. It can exist as H_2ZnO_2 , and in two modifications of $Zn(OH)_2$, characterised by different solubilities, one variety forms regular crystals (Klein, *Zeitsch. anorg. Chem.* 1912, 74, 157). A mixture of zinc ammonium hydroxide and copper ammonium hydroxide has been used for pectinising cellulose and similar substances to produce a kind of vegetable parchment (*J. Soc. Chem. Ind.* 1904, 122).

Zinc peroxide ZnO_2 , also known under the trade names *Zinkonal*, *Dermogen*, *Ektogan*, and *Zinc perhydrol*, is formed by the action of hydrogen peroxide on zinc oxide or hydroxide, or on an ammoniacal solution of zinc nitrate. It may also be made by adding a solution of zinc sulphate in excess to a solution of sodium hydroxide containing hydrogen peroxide when the zinc is totally precipitated as hydroperoxide (Kuriloff, *J. Russ. Phys. Chem. Soc.* 1890, 22, 171; de Forcrand, *Compt. rend.* 1902, 134, 601; *ibid.* 135, 103; *D. R. P.* 171372; Kazaneky, *J. Russ. Phys. Chem. Soc.* 1910, 42, 1452; Carrasco, *Gazz. chim. ital.* 1911, 41, i. 16). It has also been formed by subjecting an aqueous solution of barium peroxide to the action of a zinc salt, the acid radicle of which forms a soluble salt with barium (*U.S. Pats.* 709086, 1902; 740832, 1903); or better, by the electrolysis of a zinc chloride solution contained in a vessel with a porous diaphragm, hydrogen peroxide being added to the cathode compartment and platinum or carbon being used as anodes and platinum or tin as cathodes (*D. R. P.* 151129; for another method, see *J. Soc. Chem. Ind.* 1905, 947; also *Fr. Pat.* 364825, 1906). A number of peroxides have been described, but, according to Kuriloff (*Compt. rend.* 1903, 137, 618; see also de Forcrand, *ibid.* 1904, 138, 129), the only one which is a definite chemical compound has the composition $ZnO_2 \cdot Zn(OH)_2$.

or

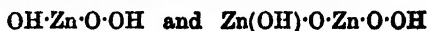


the others all being mixtures of varying quantities of zinc peroxide with zinc oxide or zinc hydroxide (Lemaire, *Rép. Pharm.* 1910, 22, 1; Hengeler and Philipp, *J. Soc. Chem. Ind.* 1906, 226; Ebler and Krause, *Zeitsch. anorg. Chem.*

71, 150; Riesenfeld and Nottebohm, *ibid.* 1911, 1915, 90, 150). According to Sjöström, (*ibid.* 1917, 100, 237) zinc perhydrate is not a simple chemical individual, since by trituration with water it can be separated into fractions containing varying quantities of active oxygen. It is to be regarded as a mixture of substances derived from the two compounds $Zn(OH)_2$ and



the hydroperoxides being of the types



Zinc peroxide is a yellowish-white, tasteless, odourless, non-hygroscopic antiseptic, non-irritant powder. It is stable in the autoclave to 130°, and at a dry heat to 150°, is insoluble in water, and gives all the ordinary reactions of a peroxide.

Mixed with tartaric acid it is applied as a dressing to wounds, chronic ulcers, &c. It thus liberates hydrogen peroxide *in situ*, and is therefore more active than the same quantity of the latter applied in the usual way. For eczema and other skin diseases it is applied mixed with half its weight of potassium iodide and some tartaric acid (*Chem. Zentr.* 1906, ii. 548; *D. R. PP.* 14821, 157737; Homeyer, *Apoth. Zeit.* 1902, 17, 697; *J. Soc. Chem. Ind.* 1905, 947).

Zinc chloride $ZnCl_2$, the *oleum lapidis calaminaris* of Glauber, who first described it in 1648, may be prepared in the anhydrous state by distilling zinc oxide with sal ammoniac, forming the 'butter of zinc' of Hellot; by distilling zinc with corrosive sublimate (Pott); by the action of chlorine on the metal (Westrumb), or by heating dehydrated zinc sulphate with calcium chloride (Persoz) (*Eng. Pats.* 982, 1892; 13813, 1895; *D. R. PP.* 154518, 158089).

On the large scale it is usually obtained by placing scrap zinc in a stone, cast iron, or wooden vessel containing hydrochloric acid. The solution is neutralised with sodium carbonate, warmed to 40° or 50°, and mixed with bleaching powder to precipitate iron and manganese. The clear zinc chloride solution is siphoned off and boiled down in enamelled iron pots. The evaporation is continued until the temperature of the liquor is 230° or 240°, a little potassium chlorate is added to oxidise any organic matter, and some pure hydrochloric acid carefully poured into the hot solution to dissolve any basic salt. The mass is then allowed to solidify, the agitation being kept up all the time, and while still warm it is packed in iron drums of 30–50 kilos. capacity, which are at once closed air-tight.

According to a more recent patent (*Fr. Pat.* 385448, 1907), zinc-heating material is intimately mixed with sawdust or similar substance containing cellulose in earthenware or cast-iron twin tubular retorts, which are used alternately. The first retort is heated to 120°–180°, and chlorine is passed in at the base, hydrochloric acid is thus generated *in situ*, and the temperature rises spontaneously to 230°–250°. The products of combustion pass from the upper part of the retort to a receptacle where the tar is deposited and thence to the base of the second retort where the excess chlorine is fixed and the products then pass out into a second receptacle,

where the tar is again fixed, and thence into a coil and receiver cooled by water. The mass thus obtained is lixiviated with water. Iron and manganese are then oxidised with chlorine and calcium hypochlorite, the iron is precipitated by zinc oxide, the manganese, if necessary, by lead peroxide (D. R. P. 154085; 136521), and the other metals by agitation with zinc. The remaining liquor is then finally evaporated to obtain pure zinc chloride.

It may also be obtained almost pure by treating zinc compounds with ferrous chloride (D. R. P. 136521); by heating zinc ore to 550° passing hydrogen chloride over it, and finally lixiviating the mass so obtained (D. R. P. 158087). A large number of patents exist for the preparation and purification of zinc chloride by the above and other methods (Eng. Pat. 22826, 22827, 1894; 5662, 8449, 7561, 1895; 24573, 1896; 19878, 1900; D. R. P. 155066; 172460; U.S. Pat. 845868, 1907; 883426; 1908; Mallet and Guye, Chem. Zeit. 1904, 28; 763; J. Soc. Chem. Ind. 1893, 276; *ibid.* 1896, 450, 595; *ibid.* 1896, 198, 356; *ibid.* 1897, 1015; *ibid.* 1900, 146; *ibid.* 1905, 497).

Pure anhydrous zinc chloride can be prepared by dissolving 40 grms. of the chloride in 20 c.c. of hydrochloric acid (sp.gr. 1.19), an evaporating the solution in a tube of refractor glass through which a stream of hydrogen chloride is passed. The temperature is gradually raised, and after some time the mass solidifies with evolution of hydrogen chloride. The solid chloride is fused again rapidly in a current of the same gas. The dehydration is complete in 75 mins. (Grünauer, Zeitsch. anorg. Chem. 1904, 39, 389; see Vogel, Faraday Soc. Trans. 1906, May 5; see also D. R. P. 120970).

Zinc chloride is a white or greyish-white mass or powder, of sp.gr. 2.907 at 25°/4° (Baxter and Lamb, Amer. Chem. J. 1904, 31, 229). Its m.p. is variously given as 100° (Davy), 210° (Lorenz), 262° (Braun, Mylius, and Dietz), 290°–300° (Schulze). According to Grünauer the completely anhydrous chloride has m.p. 300°. It is very hygroscopic and deliquescent, odorless, poisonous, with a metallic astringent taste. It melts to a clear, mobile, highly refractive liquid, b.p. 730°–732°; in a current of chlorine it sublimes, forming acicular crystals. It forms hydrates with 1, 1.5, 2.5, 3, and 4 molecules of water (Dietz, Ber. 1899, 32, 90; Mylius and Dietz, *ibid.* 1905, 38, 921) and is probably monomeric or less hydrolysed in solution. Its aqueous solution dissolves paper and cotton, and it should therefore be filtered through asbestos or glass, not paper. When evaporated or boiled with zinc oxide, oxychlorides are formed (Perrot, Bull. Soc. chim. 1895, [iii.] 13, 975; Driot, Compt. rend. 1910, 150, 426), whilst if a solution of sp.gr. 1.7 be boiled with an excess of zinc oxide, the resulting liquid dissolves silk, and can be employed for separating the latter from wool, cotton, or linen. Zinc oxychloride is sometimes also used in the preparation of some dental cements, and as a pigment.

When zinc chloride is electrolysed, chlorine is evolved and crystalline zinc is deposited (Sapozhnikoff, J. Russ. Phys. Chem. Soc. 1905, 37, 153; see also Schultze, Zeitsch. anorg. Chem. 1899, 20, 323; Grünauer, l.c.).

form of rods or tablets. It is a powerful caustic, distinguished by its property of burning deeply and not spreading sideways. It is applied in substance, or made into a paste with starch or gypsum, to cancers, sloughing or unhealthy sores, and nævi (Lauder Brunton).

In dilute solution it is also used as an astringent, an antiseptic, a disinfectant, and as a deodorant.

A solution of zinc chloride, in the proportion of 1 lb. of the salt to 5 gallons of water, was patented by Sir W. Burnett (Eng. Pat. 7747, 1838) for the preservation of timber, and such a solution is still occasionally used for disinfecting and deodorising.

For the preservation of wood it has been recommended to employ an emulsion of aqueous zinc chloride, and wood-tar oil (D. R. P. 139441, 152179; Chem. Zentr. 1903, i. 749; *ibid.* 1904, ii. 379); or a 15 p.c. solution of a mixture of ammonium sulphate and a soluble zinc salt (D. R. P. 109324).

Zinc chloride is employed for weighting cotton goods (Furth, Färber Zeit. 1901, 12, 1; D. R. P. 214372, 215702; Chem. Zentr. 1900, ii. 1509, 1905), and for crimping cotton, wool, and silk (Bull. Soc. Ind. Mulhouse, 1898, 68, 350, 348; see also Flintoff, J. Soc. Dyers, 1896, 15, 151).

Solutions of zinc chloride were also employed by Mercer for treating cotton in the operation of 'mercerising' (v. CELLULOSE).

Zinc chloride is of considerable use as a condensing agent in many organic reactions, its reactivity being probably due to its tendency to form additive compounds which act catalytically.

Zinc chloride dissolves casein and these solutions have been employed for preparing artificial silk and hair. Zinc chloride has also been used in the production of hydrochloric acid from hydrogen and chlorine (Fr. Pat. 352419; Chem. Zeit. 1905, 29, 993); for the prevention of the rusting of iron (Reed, Trans. Amer. Electrochem. Soc. 1903, 3, 149); in the preparation of glass etching liquids (J. 1894, 354), and in the laboratory as an analytical, dehydrating and condensing agent and in the synthesis of a large number of organic compounds (Kondakoff, J. Russ. Phys. Chem. Soc. 1892, 24, 114, 309; J. pr. Chem. [u.] 48, 467; Dott, Pharm. J. 1905, [iv.] 21, 136; among others).

Primary alcohols are found to react readily with concentrated hydrogen chloride solution in presence of zinc chloride. This seems to indicate that the rôle of zinc chloride in reactions of this type is not that of a dehydrating agent, but of a catalyst operating by means of the formation of a molecular compound with the alcohol (J. F. Norris, Ind. Eng. Chem. 1924, 16, 184; Chem. Soc. Abstr. 1924, 126, i. 381).

By the gradual addition of zinc to fused zinc chloride until it ceases to be dissolved zincos-zinc chloride $\text{ZnCl}_2 \cdot 2\text{ZnCl}_2$ is obtained as a bluish-white hygroscopic solid.

Zinc chloride forms double chlorides with the alkali and other metals (Wells and Campbell, Zeitsch. anorg. Chem. 1894, 5, 273; Ephraïm, *ibid.* 1908, 59, 756; Ephraïm and Model, *ibid.* 1910, 67, 376, 379; Baxter and Lamb, l.c.; Gewecke, Annalen, 1909, 366, 217), with copper oxide (Mailhe, Compt. rend. 1901, 133, 226), an iodo chloride $\text{ZnCl}_2 \cdot 2\text{ICl}_2 \cdot 8\text{H}_2\text{O}$ (Weinland and

Schlegelmilch, *Zeitsch. anorg. Chem.* 1902, 30, 134), a *chlorobromate* (Löwenthal, *ibid.* 1894, 6, 355), and a *chloroborate* $6\text{ZnO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{ZnCl}_2$ (Rousseau and Allaire, *Compt. rend.* 1894, 118, 1255). Zinc chloride also forms double compounds with ammonia, such as $\text{ZnCl}_2 \cdot \text{NH}_3$, $\text{ZnCl}_2 \cdot 2\text{NH}_3$ (Thoms, *Chem. Zentr.* 1889, ii, 965; Kwasnick, *Arch. Pharm.* 229, 310; Jaeger, *Ber.* 1902, 35, 3405), and with ammonium chloride (Curtius and Schrader, *J. pr. Chem.* 1894, [ii.] 50, 311; Meerburg, *Zeitsch. anorg. Chem.* 1903, 37, 199).

A solution of zinc ammonium chloride is used in soldering for the purpose of removing oxide from the surface of the metals.

Zinc perchlorate $\text{Zn}(\text{ClO}_4)_2$ may be obtained by dissolving the metal, its oxide, or carbonate in aqueous perchloric acid. The salt crystallises with 4 and 6 mols. of water, and is highly hygroscopic. When heated it decomposes before all the water is expelled, so that the anhydrous perchlorate cannot exist. The water in the hexahydrate may be replaced by ammonia. The ammoniated perchlorate is liable to explode when heated.

Zinc bromide ZnBr_2 is readily made by digesting granulated zinc with bromine water. It resembles the chloride, and is used to a small extent in medicine in the treatment of epilepsy.

In the absence of moisture zinc reacts with a mixture of ethylene dibromide, or ethylene di-iodide, and acetone to give the zinc halide with acetone of crystallisation. At the commencement of the reaction ethylene is evolved.

Zinc bromide-acetone, $2\text{ZnBr}_2 \cdot 3\text{C}_2\text{H}_5\text{O}$, colourless needles, m.p. $32^\circ\text{--}34^\circ$, is easily soluble in water, with slow deposition of zinc hydroxide. **Zinc iodide-acetone**, $\text{ZnI}_2 \cdot 2\text{C}_2\text{H}_5\text{O}$, pale yellow, elongated prisms, m.p. $45^\circ\text{--}47^\circ$, is deliquescent and slowly decomposed by water (I. Coucoulesco, *Bul. Soc. Chim. Romania*, 1924, 6, 36; *Chem. Soc. Abstr.* 1924, 126, ii, 411).

Zinc iodide ZnI_2 is also employed in medicine, as an application to enlarged tonsils and in the form of ointment to reduce swellings. It is also administered internally in cases of scrofula, chorea, and hysteria. It has found a limited application in photography.

For a number of double compounds of the bromide and iodide with other metallic compounds, see Ephraim, *l.c.*; Ephraim and Model, *l.c.*; Rousseau and Allaire, *Compt. rend.* 1893, 116, 1445; *ibid.* 119, 71; Tassiliy, *ibid.* 1896, 123, 323; Dubois, *ibid.* 1903, 143, 40; Chrétien, *Ann. Chim.* 1898, [vii.] 15, 358; Mosnier, *ibid.* 1897, [vii.] 374.

Zinc fluoride ZnF_2 is formed by the action of hydrofluoric acid on zinc or on zinc oxide at a red heat, or on zinc chloride at $800^\circ\text{--}900^\circ$ (Poulesco, *Compt. rend.* 1893, 116, 581). It forms slender, colourless, transparent needles, sp.gr. 4.84 at 15° , sparingly soluble in cold water, soluble in boiling mineral acids. It is reduced by hydrogen at a red heat; when heated in air it forms zinc oxide. When dissolved in hydrofluoric acid, or when zinc is dissolved in excess of hydrofluoric acid, it forms the compound $\text{ZnF}_2 \cdot \text{HF}$, which has been recommended for use in the preservation of wood, particularly of telegraph poles (Nowotny, *Chem. Zentr.* 1906, ii, 355). Like the other halides, zinc fluoride

yields a number of double salts (Helmolt, *Zeitsch. anorg. Chem.* 1893, 3, 115; Weinland and Köppen, *ibid.* 1899, 22, 286; Georgia, *Gazz. chim. ital.* 22, i, 55; Higley, *J. Amer. Chem. Soc.* 1904, 26, 613; Rimbach and Kilian, *Annalen*, 1909, 368, 101).

The electrolysis of fused anhydrous zinc fluoride or a fused mixture of the fluoride and sodium chloride has been recommended as a mode of making electrolytic zinc (Gallo, *Gazz. chim. ital.* 1913, 43, i, 361).

Zinc sulphate ZnSO_4 . This salt has long been known under the name which it still bears, of 'white vitriol.' It was obtained, on a manufacturing scale, as far back as the sixteenth century, by lixiviating roasted zinc sulphide by means of water, and crystallising the solution—a method still practised, with certain modifications (U.S. Pat. 851639, 1907; *J. Soc. Chem. Ind.* 1907, 608).

In some processes the zinc pyrites is previously treated with sulphuric acid, after which it is roasted (D. R. P. 154518). It is then sometimes further treated with oxidising agents. In some cases again the ore is treated with a mixture of dilute sulphuric acid, ferrous sulphate, and a little sodium chloride (D. R. P. 197044), or with ferric sulphate alone (D. R. P. 200613). According to D. R. P. 135056, after converting the sulphide ore into the sulphate in the ordinary way, the product is roasted with calcium hydroxide and sodium nitrate in a muffle furnace in order to drive off the impurities, or to convert them into insoluble compounds. When the process is finished, the zinc sulphate is lixiviated out (see also D. R. P. 120822, 135182; Knokloch, *Pharm. Zeit.* 40, 472; Hofmann, *Amer. Inst. Mining Eng. Trans.* 1905, 117; *Fr. Pat.* 384904, 1907).

Native zinc sulphate or *goslarite* is occasionally found in zinc mines, being probably formed by the oxidation of zinc sulphide.

Zinc sulphate separates from its solution at the ordinary temperature in right rhombic prisms, isomorphous with magnesium sulphate, and of the composition $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; sp.gr. 1.95; 2.036 (Mohs). It has a strong metallic styptic taste, and effloresces slightly in dry air. According to Poggiale, 100 parts of water dissolve the following amounts of zinc sulphate at different temperatures (see also Callendar and Barnes, *J. Phys. Chem.* 1897, 2, 536, who give slightly different figures):—

	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Anhydrous salt
10°	138.2	48.3
20°	161.5	53.1
30°	191.0	58.5
50°	263.8	68.7
100°	653.6	95.6

The solubility of the hexahydrate and of the heptahydrate has been determined by Bury (*Chem. Soc. Trans.* 1924, 125, 2538), and Cohn and Hettenschij (*Zeitsch. physikal. Chem.* 1925, 115, 440).

The solution has an acid reaction and is poisonous. The salt is insoluble in absolute alcohol.

Solutions of zinc sulphate keep clearer in the light than in dark (Verda, *Chem. Zentr.* 1907, i, 1392).

A hexahydrated salt $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is obtained

by crystallising the solution at 40°; sp. gr. 2.072 (Thorpe and Watts); a pentahydrated salt $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ by boiling the salt with alcohol (sp. gr. 0.825) (sp. gr. 2.206, Thorpe and Watts), and a dihydrated salt by pouring a cold saturated solution of zinc sulphate into strong sulphuric acid; and washing the precipitate with absolute alcohol until free from uncombined acid; sp. gr. 2.368 (Thorpe and Watts). The monohydrate salt is formed by heating the heptahydrated salt to 110° until it ceases to lose weight; sp. gr. 3.284 (Thorpe and Watts). The anhydrous salt is obtained by heating the heptahydrate to 300 sp. gr. 3.4. At a red heat all the sulphates are decomposed, yielding a residue of zinc oxide.

Zinc sulphate is used in dyeing and calico printing, in the manufacture of varnishes and drying oils for painting.

Coloured zinc pigments are prepared by intimately mixing together zinc sulphate with 6–30 p.c. of the sulphate of other metals which yield a coloured oxide, such as nickel, iron, cobalt, or manganese. The mixture is dried, finely divided carbon is added, and the whole is heated carefully at 650°. To produce a more delicately-tinted pigment, the zinc sulphate should first be purified by stirring zinc oxide into its solution and passing a current of chlorine through it, whereby the impurities are thrown down (Eng. Pat. 17031, 1896; Fr. Pat. 36657, 1908; J. Soc. Chem. Ind. 1903, 1074).

It is also used for the preparation of zinc white and other zinc compounds, and in pharmacy as an astringent, and in lotions, washes, and gargles. It is also occasionally employed as an emetic, and in the treatment of convulsive diseases. A number of basic sulphates, formed by digesting the oxide or hydroxide with strong solutions of zinc vitriol, or precipitating such solutions with varying quantities of potash, can be formed.

Zinc sulphate combines with ammonia and with other sulphates to form double salts (Curtius and Schrader, *l.c.*; Tröger and Evers, Arch. Pharm. 235, 644; Mallet, Chem. Soc. Trans. 1900, 77, 220; Tutton, *ibid.* 1905, 87, 23; Koppel, Zeitsch. physikal. Chem. 1905, 52, 85).

The compound $\text{ZnSO}_4 \cdot 3\text{H}_2\text{SO}_4$ has been separated from the acid in the first chamber in the manufacture of sulphuric acid from zinc blende (Hoffmann, Zeitsch. angew. Chem. 1910, 23, 1672).

Anhydrous zinc sulphate behaves towards alcohols as a mixed catalyst, its action being both dehydrating and dehydrogenating. The latter action preponderates as in the case of zinc oxide, and it is suggested that the sulphate may function as a basic salt. Its action is more marked than that of the oxide. A proportion of the aldehyde formed is condensed, but isobutylaldehyde and isovaleraldehyde may be obtained readily and in good yield, whilst glycerol yields acetaldehyde by internal dehydration. The action on acetone results in the formation of a small quantity of mesityl oxide and of phosgene (G. Brus, Bull. Soc. Chim. 1923, 33, 1433; Chem. Soc. Abstr. 1924, 128, i. 2).

According to Kolthoff and Verzyl (Rec. trav. chim. 1924, 43, 389) only potassium ferrocyanide is suitable for the potentiometric titration of zinc, the composition of the precipitate being $\text{K}_2\text{Zn}_2(\text{Fe}(\text{CN})_6)_3$. The addition of

a caesium salt causes the end point to be less sharp (cf. Treadwell and Chervet, J. Soc. Chem. Ind. 1922, 890 A). Ferrocyanides of sodium, magnesium, and calcium give with zinc salts a precipitate of zinc ferrocyanide, which forms a double salt with excess of the reagent. Barium ferrocyanide does not form a double salt with zinc ferrocyanide (J. Soc. Chem. Ind. 1924, 43, B. 539).

The results obtained by potentiometric titration of a zinc sulphate solution with M/40 potassium ferrocyanide at the ordinary temperature are about 1 p.c. too low, but substantially accurate results are obtained if considerable quantities of ammonium sulphate are added to the solution. The presence of large quantities of sodium, magnesium, calcium, and aluminium salts causes low results. Manganese, cadmium, and copper should not be present; ferric compounds are rendered harmless by addition of ammonium fluoride and sulphuric acid. The potassium ferrocyanide solution should contain 1 p.c. of ferricyanide. This renders it more sensitive to decomposition by light, but it can be kept indefinitely in vessels of dark brown glass (E. J. A. H. Verzyl and I. M. Kolthoff, Rec. trav. chim. 1924, 43, 380; J. Soc. Chem. Ind. 1924, 43, B. 539).

Zinc hydro- or hyposulphite ZnS_2O_4 is obtained by passing a current of sulphur dioxide into a mixture of zinc-dust and alcohol or water at a temperature above 40°. On stirring, a crystalline paste of the hydrosulphite is formed, which is washed with methylated spirits and dried *in vacuo* below 70° (Eng. Pat. 3811, 1907; D. R. P. 184564, 103403, 137494, 144281; Fr. Pat. 331095, 1903; Brunck, Annalen, 1903, 327, 240; Bazlen, Ber. 1905, 38, 1061).

Soluble double salts of zinc hydrosulphite with ammonium salts are obtained by the action of zinc-dust on alkali disulphite in the presence of acid and an ammonium salt (D. R. P. 203846, 1907).

Zinc hydrosulphite forms microscopic rhombic crystals, very soluble in water, giving, very readily, supersaturated solutions. It is employed as a reducing agent in the indigo dyeing industry.

Zinc sulphite ZnSO_3 is prepared by the action of sodium sulphite on zinc sulphate (Denigès, Bull. Soc. chim. 1892, [iii.] 7, 569). It forms a number of hydrates, double salts, and basic salts (Seubert, Arch. Pharm. 1891, 229, 316; Seubert and Elten, Zeitsch. anorg. Chem. 1893, 4, 61; Rammelsberg, Pogg. Ann. 67, 255).

It is used to a very limited extent in medicine.

Zinc sulphide ZnS , *ls. blende*, is one of the most important ores of zinc. Its value as an ore of zinc was first demonstrated by Brandt in 1735, it being formerly regarded as a worthless lead ore, *galena inanis*. It is found crystallised in forms derived from the regular system, usually of a red, brown, or black colour, due to the presence of foreign metals. Occasionally it is met with of a light yellow colour; sp. gr. 3.5–4.2. When heated under pressure (100–105 atm.) it fuses at 1800°–1900°. The solidified fused sulphide has a lustrous appearance and a bright greenish-yellow colour. It is the hexagonal modification (*wurtzite*). It occurs native in enantiomeric forms *α-ZnS* (*wurtzite*) and

β -ZnS (sphalerite), which become mutually transformed on heating.

It is obtained artificially as a white amorphous precipitate by adding an alkaline sulphide or sulphuretted hydrogen to a solution of a zinc salt (Eng. Pats. 396541, 25965, 1908).

In Schneider's method for the precipitation of zinc sulphide from feebly acid (sulphuric) solutions, proper neutralisation is a decisive factor for the success of the operation. The solution, to which a piece of Congo paper is added as indicator, should not be too dilute, it is made distinctly ammoniacal, acidified with sulphuric acid, then treated with strong ammonia solution, drop by drop, until the alkaline reaction persists after 5-10 seconds' stirring. The prescribed small excess of sulphuric acid, calculated on the subsequent dilution desired, is then added (O. Hackl, Chem. Zeit. 1924, 48, 326; Analyst, 1924, 49, 352).

A mixture of zinc sulphate (230 lbs.), water (90 gallons), ammonia of sp.gr. 0.91 (230 lbs.) is introduced into an enamelled digester and about 60 lbs. of carbon disulphide are added. The vessel is closed and heated to 100° with constant stirring, until the pressure is about 60 lbs. After 4 hours the pressure begins to fall, and in 10 hours it will have fallen to about 22 lbs., when the process is complete. The zinc sulphide is collected, washed, and dried. It is very finely divided and is suitable for use as a pigment (Eng. Pat. 11108, 1900).

Zinc sulphide is sometimes separated from its ores by immersing the crushed ore in a solution of sodium sulphate, disulphate, or nitrate, and skimming off the sulphide which rises to the surface (Eng. Pats. 26279, 1902; 27132, 1903; 20160, 20159, 1904; U.S. Pat. 780281; Fr. Pats. 326866, 326867, 1902). For other methods of preparing the sulphide, see Eng. Pat. 16272, 1902; Fr. Pats. 397631, 396541, 1908; 415605, 1910; D. R. PP. 132916, 137801, 149557, 167172, 167498, 171872, 179022).

It may also be obtained by dissolving zinc in an alkali hydroxide and then adding just sufficient alkali sulphide to precipitate the zinc (Fr. Pats. 353496, 353480); or by passing zinc chloride vapour over barium or stannous sulphide (Fr. Pat. 338322, 1903; Viard, Compt. rend. 1903, 136, 892). On exposure to light or by heating at 60° or 70° it is tinged light grey to light brown, especially when containing chlorides or sulphates of magnesium, calcium, or zinc. The darkening of zinc sulphide is due to the formation of free zinc. In order that a specimen should be sensitive to light, it must be phosphorescent and hygroscopic; it is more sensitive the more these conditions are satisfied. The darkening is due to the following series of changes. The preparation of the sulphide, involving ignition, affords a metastable product. Incident radiation raises the metastable molecules to a critical state, and, if the sample be dry, it simply emits radiation and reverts to the previous, metastable, condition. When, however, it has deliquesced slightly, hydrolysis occurs, producing hydrogen sulphide and zinc hydroxide. During illumination, a critical molecule of the sulphide reacts with the hydroxide, giving zinc and sulphurous acid, which with hydrogen sulphide affords sulphur, zinc pentathionate also being produced. The main

products are thus zinc and sulphur (André Job and Guy Emachwiller, Compt. rend. 1923, 177, 313-316; J. Chem. Soc. 1923, 124, ii. 600).

Zinc sulphide prepared by precipitation did not darken under any conditions of illumination. Ignited zinc sulphide, freed from materials with which it had been heated, showed a sensitiveness towards light from a quartz mercury lamp when the temperature of ignition was so high that measurable quantities of wurtzite were formed. The zinc blonde form of zinc sulphide was not affected by ultra-violet light from a quartz mercury lamp. The presence of small quantities of heavy metals made no change in the action of light in these cases. Crystallised zinc sulphide containing halogen compounds was sensitive to the long wave-length ultra-violet and the presence of small quantities of heavy metals intensified the action. The sensitiveness of zinc sulphide containing halogens was removed by washing the material, so far as the long wave-length ultra-violet was concerned, but this had no effect on the short wave-length ultra-violet effect or on the phosphorescence. Sensitiveness to long wave-length ultra-violet light was apparently induced by fusing zinc sulphide (wurtzite) with a halogen salt (M. Herter and W. Kordatzki, Zeitsch. physikal. Chem. 1923, 106, 386; J. Soc. Chem. Ind. 1924, 42, 1233 A).

E. Maas and R. Kempf have examined the various hypotheses put forward to explain the blackening of zinc sulphide, and discuss them in the light of their own and other experiments. They conclude that the phenomenon is due to the zinc sulphide forming zinc disulphide and finely divided metallic zinc on the surface of the mass. The mechanism of the process, they consider, is the same as that referred by Fajans to the action of light on silver bromide (Chem. Zeit. 1922, 46, 910). The ultra-violet rays in the light cause the transference of an electron from a negatively charged sulphur ion on the surface of the crystal lattice of zinc sulphide to a neighbouring positively charged zinc ion, whereby free uncharged atoms of zinc and sulphur are formed. The zinc appears as finely divided metal, the sulphur atom combines with neighbouring zinc and sulphur ions to form zinc disulphide. Amorphous freshly precipitated zinc sulphide not possessing a lattice structure is not sensitive to light; neither is zinc sulphide which has been ground in a mortar, since here the lattice arrangement has been disturbed. Blackened lithopone brightens in the dark, owing to oxidation of the metallic zinc, for it remains black if no oxygen is present (E. Maas and R. Kempf, Zeitsch. angew. Chem. 1923, 36, 293; J. Chem. Soc. Abstr. July, 1923, p. 491). According to A. Job and G. Emachwiller (Compt. rend. 1923, 177, 313-316) the darkening of zinc sulphide under the influence of light is dependent on the phosphorescence and hygroscopicity of a sample, and is due to the formation of zinc and sulphur. Hydrogen and zinc pentathionate are also formed, hydrogen sulphide being an intermediate product (cf. J. Chem. Soc. 1923, ii. 600; J. Chem. Soc. Ind. 1923, xlii. 896 A).

Zinc sulphide is soluble in dilute mineral acids, but is insoluble in acetic acid. When heated in a stream of sulphuretted hydrogen,

or in an electric furnace, it forms hexagonal crystals identical in form with the naturally occurring variety known as *wurtzite* (Mourlot, Compt. rend. 1896, 123, 45; Traube, Jahrb. Min. 9, 147). This is also formed when zinc oxide is heated in sulphuretted hydrogen. For other methods of converting the amorphous sulphide into the crystalline variety, see Villiers, Compt. rend. 1895, 120, 97, 149, 322, 498; Viard *ibid.* l.c.; Spring, Zeitsch. physikal. Chem. 1895, 18, 553; Staněk, Zeitsch. anorg. Chem. 1898, 17, 124.

Pure zinc sulphide melts at 1600°–1700° forming a light greenish-yellow lustrous mass and is distinctly volatile at higher temperature (Friedrich, Metallurgie, 1908, 5, 114). According to Krutwig (J. Soc. Chem. Ind. 1906, 267 the precipitated sulphide decomposes much more readily than natural zinc blende. Heated in a current of carbon dioxide it is readily decomposed at 1000° according to the equation $\text{ZnS} + 3\text{CO}_2 = \text{ZnO} + \text{SO}_2 + 3\text{CO}$. When treated with hot concentrated sulphuric acid, zinc sulphide evolves sulphur dioxide, whilst with the cold dilute acid, sulphuretted hydrogen is formed (Berthelot, Ann. Chim. 1898, [v.] 14, 176). Zinc sulphide may be completely reduced by heating it with spongy metallic iron at 1300° (Graumann, Metallurgie, 1907, 4, 6). Freshly precipitated zinc sulphide dissolves in potassium cyanide forming a double salt which is precipitated on boiling (Berthelot, Compt. rend. 1890, 128, 711).

When zinc sulphide is heated with carbon in nitrogen at 1300–1400°, a volatile compound is formed, which, if the containing vessel is of quartz, reacts with the silicon forming a volatile compound ZnSSi , which may also be obtained by heating zinc sulphide with silicon at 1300°. The compound ZnSSi forms hard brown crystals of homogeneous structure. It may be polished like a metal, has an electrical conductivity less than silicon, reacts with acids forming sulphuretted hydrogen and with alkalis with evolution of hydrogen (Fraenkel, Metallurgie, 1909, 6, 62).

Natural zinc sulphide crystals have the property of phosphorescing after exposure to light (Mourel, Compt. rend. 1890, 128, 57; Verneuil, *ibid.* 1888, 106, 1104), and the phosphorescent sulphide may be prepared artificially by heating precipitated zinc sulphide to redness in the presence of alkali chlorides or the sulphides of other metals (Eng. Pat. 385096, 1907; D. P. 163648; Henry, Compt. rend. 1892, 115, 35; Grüne, Ber. 1904, 37, 3076; Hofmann and D. P. 163648; Jorissen and Ringer, *ibid.* 1903, 33; Chem. Zentr. 1906, i. 644; see also D. P. 200998). The various factors which are concerned in the production of phosphorescent sulphide have been studied by MacDermott, Stewart and Wright (Chem. Soc. Trans. 1911, 663). The main results are as follows: Pure zinc sulphide prepared in various ways can be obtained in a phosphorescent condition. The addition of certain impurities has a marked effect in some cases, and this effect may take the form of inhibiting the phosphorescence (as with iron) or altering its tint (as is the case with manganese). The presence of a chloride, whether it be zinc chloride or the chloride of some other element, has an advantageous influence. The factor which has the greatest

influence is the temperature to which the zinc sulphide is heated. This temperature effect can be varied within limits; thus a sample heated for a very short time to a high temperature will give effects similar to those observed in another sample heated for a longer time at a lower temperature, provided that the lower temperature is not less than about 750°. Washing, rubbing, or disturbing the final product in any way tends to diminish its phosphorescent power. Exposure to ultra-violet light also decreases it (Loeb and Schmiedeskamp). Amorphous sulphide does not phosphoresce, nor does purely crystalline sulphide show such good phosphorescence phenomena as samples which contain semi-crystalline material. Specimens made from zinc salts not containing chlorides do not show such brilliant phosphorescence as those produced in the presence of chlorides (l.c. p. 681). With respect to the colour, most impurities influence the phosphorescence tint only slightly, the range of colours extending from lemon tint to green and bluish-green; but in the case of manganese the emitted light is golden to orange (cf. Tiede and Schleede, Ber. 1920, 53, [B.] 1721; 1923, 56, 674). The wurtzite and sphalerite forms of zinc sulphide prepared by heating the precipitated sulphide are both phosphorescent. The phosphorescence of the wurtzite form is the more persistent, but in both cases the decrease of luminous intensity is extremely rapid. Under the influence of heat and shock the two varieties are very thermoluminescent and triboluminescent (Guntz, Compt. rend. 1922, 174, 1356).

Schmidt has described the preparation of highly phosphorescent zinc sulphide, and has been drawn to the conclusion that its phosphorescence is inhibited by the presence of metals which yield black sulphides. This observation is directly opposed to the observations of Tomaschek (A. 1921, ii. 588). It is pointed out that Schmidt's procedure does not give any guarantee that the necessary amounts of copper are not introduced with the many salts employed, and that it is therefore quite possible that subsequent additions of the element may cause its concentration to exceed the narrow limits required for optimal effect. A specific action in Schmidt's method cannot be attributed to the chlorides of the alkaline-earth metals and magnesium, since they can be replaced by the alkali chloride; the chloride is the important component (Erie Tigdo and Arthur Schleede, Ber. 1923, 56, [B.] 674; Chem. Soc. Abstr. 1924, ii. 242). It has been proposed to use this property of zinc sulphide in the construction of an actinometer and for photometric purposes (Henry, Compt. rend. 1899, 128, 94). The phosphorescent sulphide glows when exposed to X- or to Becquerel rays; to the α -radiation from radium (Chem. News, 1903, 157; Becquerel, Compt. rend. 1904, 137, 629; Bamstead, Phil. Mag. 1908, [vi.] 15, 432), and under the influence of ozonised oxygen (Schenck and Mihr, Ber. 1904, 37, 3464). When zinc sulphide is heated with manganese nitrate and a number of other substances at 1200°, the product exhibits triboluminescence (Karl, Compt. rend. 1907, 144, 841).

According to J. Schmidt (Ber. 1922, 55, 3988) a highly phosphorescent zinc

be made by taking equal weights of pure zinc sulphate and sodium acetate, dissolving in water, and treating the hot solution with hydrogen sulphide until precipitation is complete. The zinc sulphide is washed by decantation, dried on the water-bath, and the product (200 grms.) uniformly moistened with a solution of magnesium chloride (20 grms.), calcium chloride (10 grms.), strontium chloride (10 grms.) and crystalline barium chloride (10 grms.), to which 0.04 gm. of ammonium tungstate dissolved in 10 c.c. of water has been added. The mixture with the zinc sulphide is evaporated to dryness on the water-bath with occasional stirring. The product is slowly heated to redness in a crucible for an hour and maintained at this temperature for 30–40 mins., after which it is allowed to cool in the furnace. The soluble salts are removed by water and the residual zinc sulphide is dried on the water-bath. It exhibits a strong green fluorescence. (J. Soc. Chem. Ind. 1923, 94 A).

The following account of the preparation of a highly phosphorescent zinc sulphide is taken from Sci. Amer. May, 1923, through Amer. Jour. Pharm. July, 1923, 568:—

A new process has been devised for making zinc sulphide, a compound which is used for many purposes for which phosphorescent salts are utilised. Equal weights of pure zinc sulphate and sodium acetate are dissolved in hot water; a stream of hydrogen sulphide is allowed to flow through the solution, which is kept hot, until precipitation is complete. After the zinc sulphide has settled, the liquid is syphoned off, the sulphide washed with hot water by decantation, filtered out, washed thoroughly again, and then dried on a water-bath. About 200 parts of the sulphide thus obtained is uniformly moistened with a solution containing 20 parts of magnesium chloride, 10 parts of calcium chloride, 10 parts of strontium chloride, and 10 parts of crystallised barium chloride, all being dissolved in 22 parts of water. Before this solution is added to the zinc sulphide, it is mixed with 10 parts of a solution of ammonium tungstate, which contains 0.004 gm. of the salt per c.c. The mixture of the prepared chloride solution and the zinc sulphide is evaporated to dryness on the water-bath with constant agitation, and the dried mass is then transferred to a crucible and heated in a gas-muffle furnace. The heat should be applied gradually, so that it requires about one hour for the crucible to become red-hot, at which temperature it should be maintained for 30–40 mins., and then allowed to cool to room temperature in the oven. The soluble salts are removed by decantation and washing with water. The washed sulphide is then dried on the water-bath (Pharm. Journ. Sept. 1923). A. A. Guntz (Compt. rend. 1923, 177, 479–482) has made a study of the phosphorescence of mixed crystals of zinc and cadmium sulphides. The phosphorescence of zinc sulphide changes in colour from green-blue to red with increasing quantities of cadmium sulphide. With 12 p.c., 20 p.c., and 30 p.c. of the latter substance, the phosphorescence is, respectively, lemon-yellow, orange, and red. The orange phosphorescence induced by the addition of traces of manganese to zinc sulphide is neither vigorous nor persistent, whereas cadmium sulphide produces no effect unless

present in fairly large quantities, and does not diminish the vigour or the duration of phosphorescence, the colour change being due to absorption of green light and not to phosphorogenic action (J. Soc. Chem. Ind. 1923, 42, 974 A).

A triboluminescent product may be prepared by heating to bright redness a dried mixture of 7 parts zinc carbonate and 3 parts of flowers of sulphur, previously made into a paste with water to which a small quantity of manganese sulphate is added. The resulting stonelike mass emits sparks of a yellowish light when scratched with a knife blade (Andrews, Trans. Amer. Electrochem. Soc. 1910, 18, 279; see also Tomaschek, Ann. Physik, 1921, [iv.] 65, 189, who has described the phosphorescence phenomena of zinc sulphide containing respectively, as phosphorogens, manganese, copper, bismuth, lead, silver, uranium, nickel, and cobalt).

Zinc sulphide may be obtained in a colloidal form by allowing it to remain in contact with water (Donnini, Gazz. chim. ital. 1894, 24, i. 219; Hausmann, Zeitsch. anorg. Chem. 1904, 40, 110); or by allowing a mixture of zinc sulphate, glycerol, and ammonium sulphide to stand for 3 days (Muller, Chem. Zeit. 1904, 28, 357), and in other ways.

Zinc sulphide, or a mixture of zinc sulphide and oxide, is used as a pigment. Griffiths' 'patent zinc white' is obtained by the addition of a soluble sulphide to zinc chloride or sulphate solution, drying the precipitate, and calcining it. It is raked out whilst hot into cold water, and levigated (J. Soc. Chem. Ind. 1885, 563).

A light-proof and weather-proof pigment may be obtained by precipitating zinc as a hydrated sulphide from an alkaline solution. The precipitate is then dehydrated at 300° until $\text{ZnS} : \text{H}_2\text{O} = 5 : 1$ (U.S. Pat. 884874, 1908; see also Griffiths' Eng. Pat. 750, 1883; Knight, Eng. Pat. 16220, 1884; J. B. Spence, Eng. Pats. 13462, 1885; 14128, 1885; 27420, 1907; Fr. Pat. 373027, 1906; Cowley, Chem. News, 1891, 63, 88; J. Soc. Chem. Ind. 1910, 99, 166).

A mixture of zinc sulphide and barium sulphate with some zinc oxide is known as *lithopone* or *zincolith*. It is obtained by precipitating hot concentrated zinc sulphate solution with barium sulphide. Rather less than 1 p.c. freshly-precipitated magnesium hydroxide and common salt are added and the precipitate is then washed, dried, crushed, mixed with 3 p.c. ammonium chloride, and heated. The mass, while still hot, is thrown into cold water, after which it is again dried and ground (Leyfert, Zeitsch. angew. Chem. 1902, 15, 802). It comes into commerce in different grades: yellow seal contains 11–18 p.c. ZnS, blue seal 22–30 p.c. ZnS, and green seal, 32–34 p.c. ZnS (Fr. Pats. 335115, 1903; 335358; U.S. Pat. 740072, 1903; Eng. Pats. 1836, 1837, 3768, 3769, 6521, 1903; D. R. PP. 199493, 202420, 163455, 167772, 202253, 202709; Riederer, J. Soc. Chem. Ind. 1909, 403).

Lithopone has the disadvantage of occasionally turning grey when exposed to light and moisture, due, it is supposed, to the reduction of the zinc sulphide to metal. On exposure to air in the dark the white colour is restored, presumably by oxidation. Various methods of protecting

the zinc sulphide have been employed and some have been patented. The presence of from 3 to 5 p.c. of zinc oxide acting as a film round the sulphide renders the colour more stable. On boiling the lithopone so protected with a concentrated solution of zinc chloride, the zinc sulphide again becomes sensitive to light (cf. O'Brien, *J. Phys. Chem.* 1915, 19, 113). A microscopical examination of lithopone shows that the particles of barium sulphate are coated with zinc sulphide (Gardner, *J. Ind. Eng. Chem.* 1916, 8, 794). Or the effect of light on zinc sulphide, see also P. Lenard, *Ann. Physik.* 1922, 68, 7 and 8, pp. 553-573; cf. Maus and Kempf, *Zeitsch. angew. Chem.* 1923, 36, 203.

Zinc carbonate ZnCO_3 occurs native as *smithsonite*, *calamine*, or *zinc spar*. It can be formed artificially by adding zinc sulphate solution to a solution of sodium hydrogen carbonate (Kraut, *Zeitsch. anorg. Chem.* 1896, 13, 1; *Eng. Pat.* 6752, 1902; *Fr. Pats.* 325587, 1902; 329079, 1903; 315888, 1901; *J. Soc. Chem. Ind.* 1902, 1457; *ibid.* 1903, 214, 752, 1007; Feist, *Arch. Pharm.* 1909, 247, 439). When the normal carbonate is employed, basic zinc carbonates are formed, the proportion of zinc oxide varying with the temperature and dilution of the solutions. The *zinci carbonas* of the British Pharmacopoeia has the approximate composition $\text{ZnCO}_3 \cdot (\text{ZnO})_2 \cdot 3\text{H}_2\text{O}$. At a red heat it loses carbon dioxide and forms zinc oxide.

According to Barbier basic zinc carbonate can be effectively employed as a pigment instead of white lead (*Fr. Pat.* 339151, 1903). It is prepared for this purpose by the electrolysis of a calcium carbonate solution with zinc as anode and carbon as cathode.

Zinc carbonate is a mild astringent to the skin, and is employed in dusting powders and lotion with, or instead of, zinc oxide.

According to Mikusch (*Zeitsch. anorg. Chem.* 1908, 56, 365) the only basic carbonate of zinc which exists in $5\text{ZnO} \cdot 2\text{CO}_2 \cdot 4\text{H}_2\text{O}$. All the others that have been described are solid solutions of zinc oxide and carbonate.

Zinc trithiocarbonate ammonia $\text{CS}_2\text{Zn}(\text{NH}_3)_2$ (Hofmann, *Zeitsch. anorg. Chem.* 1897, 14, 263); and **dihydroxylamine carbonate**



(Goldschmidt and Syngros, *ibid.* 1894, 5, 129) have been described.

Zinc cyanide $\text{Zn}(\text{CN})_2$ is prepared by precipitating zinc acetate with aqueous hydrocyanic acid or by heating zinc-dust with an organic substance containing nitrogen (Aufschläger, *Monatsh.* 1892, 13, 268). It is a white powder insoluble in alcohol and water, and has been used in the manufacture of alkali cyanides (D. R. P. 132294; *Chem. Zentr.* 1902, ii. 80). It forms double salts such as $\text{M}_2\text{Zn}(\text{CN})_4$ and $\text{M}_2\text{Zn}(\text{CN})_6$ (Berthelot, *Ann. Chim.* 1899, 17, [vii.] 458; Sharwood, *J. Amer. Chem. Soc.* 1903, 25, 570; see also Miller and Danziger, *ibid.* 1902, 24, 823; Fischer and Cuntze, *Chem. Zeit.* 1902, 26, 872). Herz (*J. Amer. Chem. Soc.* 1914, 35, 912) was unable to confirm the existence of $\text{NaZn}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$. It also combines with ammonia (Varet, *Compt. rend.* 1887, 105, 1070; *ibid.* 1888, 106, 1080; *Ann. Chim.* 1897, [vii.] 10, 5).

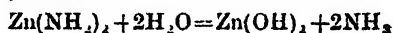
Zinc nitrate is formed by dissolving zinc in

nitric acid. It is said to crystallise with 2, 3, 4, 6, and 9 molecules of water (Funk, *Zeitsch. anorg. Chem.* 1899, 20, 400; Vasilieff, *J. Russ. Phys. Chem. Soc.* 1909, 41, 744, 748). When heated for some time at 100° it forms basic salts (Athanasescu, *Bull. Soc. chim.* 1896, [iii.] 15, 1078; Terrell, *ibid.* 7, 553; Riban, *Compt. rend.* 1892, 114, 1357). It also forms double salts (Urbain and Lacombe, *ibid.* 1903, 137, 568). It can be obtained anhydrous as a pasty substance which crystallises on cooling by heating the hydrated salt in the vapour of nitric anhydride.

Zinc nitrite forms fine unstable needles (Matuschek, *J. Soc. Chem. Ind.* 1902, 705), and also gives double salts (Rosenheim and Oppenheim, *Zeitsch. anorg. Chem.* 1901, 28, 171; cf. Ray, *Chem. Soc. Trans.* 1917, 111, 159).

Zinc nitride Zn_3N_2 is formed by heating zincamide to dull redness, or zinc in a current of ammonia at 600° (White and Kirschbraun, *J. Amer. Chem. Soc.* 1906, 28, 2343). It is a green powder which becomes incandescent when moistened with water. A nitride may also be obtained by passing ammonia free from oxygen and moisture over zinc-dust (previously washed with a solution of ammonia and ammonium chloride, alcohol, and ether, and dried in a vacuum) for thirty minutes at 650° , the product being cooled to at least 200° before exposure to the air (Bentley and Stern, *Science*, 1921, 53, 143).

Zincamide or **zinc diamine** $\text{Zn}(\text{NH}_2)_2$ is a white amorphous powder readily decomposed by water, thus:



It is formed by the action of dry ammonia on zinc ethyl (Frankland, *Phil. Mag.* [iv.] 15, 149). A number of zincamine compounds have been prepared, the number of ammonia molecules depending upon the nature of the associated zinc salt and the temperature (cf. Ephraim and Bolle, *Ber.* 1915, 48, 638).

Zinc hydroxylamine $\text{Zn}(\text{O-NH}_2)_2 \cdot 3\text{NH}_3 \cdot \text{OH}$ is prepared by the action of anhydrous hydroxylamine on finely-divided pure zinc and treating the product with absolute alcohol. It forms glistening crystals which detonate and evolve ammonia when heated rapidly (Ebner and Schott, *J. pr. Chem.* 1908, [ii.] 78, 289).

Basic Zinc azoimide $\text{N}_2\text{ZnOH}(\text{?})$, see Curtius and Rissom, *J. pr. Chem.* 1898, [ii.] 58, 261.

Zinc azide is a white sandy powder, very hygroscopic and readily hydrolysed, and not more explosive than the alkaline earth azides. Obtained by shaking together finely divided zinc carbonate with an ethereal solution of azoimide until a portion of the solid is completely soluble in water (Wöhler and Martin, *Ber.* 1917, 50, 586).

Zinc borate or **hydroxyborate** $\text{Zn}_2(\text{B}_4\text{O}_7)_2(\text{OH})_2$ is prepared by precipitating an aqueous solution of zinc sulphate (500 grms. salt to 5-10 litres water) by the gradual addition, with constant stirring, of 443.6 grms. of borax solution, and 309 grms. 15 p.c. sodium hydroxide solution. The precipitate is then washed and dried (Holdermann, *Arch. Pharm.* 1904, 242, 567; see also Ouvrard, *Compt. rend.* 1900, 130, 335; Chastelier, *ibid.* 1891, 113, 1034; Borchers, *Zeitsch. anorg. Chem.* 1910, 68, 269). It is employed in the preparation of zinc powder for wounds.

Zinc perborate is obtained by the action of sodium peroxide or its hydrate and boric acid, or sodium perborate on a zinc salt or from basic acid and zinc peroxide hydrate. It is a white amorphous powder applicable to dermatology (D. R. PP. 165278, 165279).

Zinc boracite $6\text{ZnO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{ZnI}_2$ is formed by passing a stream of carbon dioxide laden with iodine over a heated mixture of zinc and zinc borate (Allaire, Compt. rend. 1898, 127, 555).

Zinc phosphide Zn_3P_2 is obtained as a crystal line friable mass with metallic lustre, by heating zinc in phosphorus vapour in an atmosphere of dry hydrogen; or by passing a mixture of hydrogen phosphide and nitrogen over zinc heated to redness. It is insoluble in water and in alcohol, soluble in acids with evolution of hydrogen phosphide. Zinc phosphide possesses all the properties of free phosphorus, but is very stable and is used in medicine in place of the latter.

Johibois (Compt. rend. 1908, 147, 801) has also prepared the phosphide ZnP_2 (see also Rensault, *ibid.* 1873, 76, 283). For zinc phosphates and other compounds of zinc and phosphorus, see Bansa, *Zeitsch. anorg. Chem.* 1894, 6, 128, 143; Schwarz, *ibid.* 9, 249; Schulten, *Bull. Soc. chim. [iii.]* 2, 300; Ferrand, *ibid.* 1895, [iii.] 13, 115; Compt. rend. 1896, 12: 621, 886; Friedel, *ibid.* 1894, 119, 260.

Some natural zinc phosphates, viz. *hopewellite* $\text{Zn}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$; *parahopewellite*, same formula and *tarbuttite* $\text{Zn}_3\text{P}_2\text{O}_8 \cdot \text{Zn}(\text{OH})_2$, are described by Spencer (Min. Mag. 1908, 15, 1); *spencerite* $\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ is a basic zinc phosphate, like tarbuttite with water of crystallization, found in British Columbia; *hibbenite* $2\text{Zn}_3(\text{PO}_4)_2 \cdot \text{Zn}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ forms orthorhombic crystals of sp. gr. 3.213.

Zinc permanganate $\text{Zn}(\text{MnO}_4)_2 \cdot 6\text{H}_2\text{O}$ may be prepared by adding a concentrated solution of zinc sulphate to a similar solution of barium permanganate so long as barium sulphate is precipitated. The solution is filtered, and the filtrate evaporated to crystallization at a low temperature, or *in vacuo* over sulphuric acid, and the crystals finally dried at about 40° .

Zinc permanganate forms crystalline granules of a violet-brown colour, and is very soluble in water. In very dilute solutions it has been used successfully in the treatment of urethritis. It has no irritating action, but, like the potassium salt, it should never be compounded with alcohol, glycerol, sugar, or dry or fluid vegetable extracts as there may be danger of explosion owing to the readiness with which it is reduced and evolves oxygen (Merck, *J. Soc. Chem. Ind.* 1890, 409; Klobb, *Bull. Soc. chim. [iii.]* 9, 17).

Zinc orthosilicate Zn_2SiO_4 occurs native as *Willemite*. *Silicious calamine*, used to some extent as an ore of zinc, is a hydrated orthosilicate $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$. It is found in unmetamorphically-terminated rhombic prisms, and, like tourmaline, boracite, sugar, and other hemimorphic crystals, it is pyroelectric—that is, on warming, one end becomes positively, the other negatively, electrified.

Amorphous zinc silicate is prepared by precipitating a solution of zinc sulphate with sodium silicate. When heated with boric acid for 10 days at a high temperature it forms a white crystalline powder of ZnSiO_3 insoluble in acids

and isomorphous with the mineral *enstatite* (Traube, *Ber.* 1893, 26, 2735).

For some double zinc silicates, see Wyrnoff, *Bull. Soc. Franç. Min.* 1896, 19, 219; Wolff, *Zeitsch. Krist. Min.* 1900, 33, 147; Duboin, *Compt. rend.* 1905, 141, 254.

Zinc selenide ZnSe is formed by the direct union of its elements. It has a brilliant yellow colour, $D_{20}^{25} 5.29$, and does not fuse up to 1100° (Chikashige and Kurosawa, *Mom. Coll. Sci. Kyoto*, 1917, 2, 245; see also Fonze-Diacon, *Compt. rend.* 1900, 130, 832). Decomposes on drying (Moser and Atynski, *Monatsh.* 1925, 45, 235).

Zinc chromate v. Chromium.

Zinc also forms *arsenates*, *thioarsenates*, and *arsenites* (Reichard, *Ber.* 1894, 21, 1019; *ibid.* 1893, 31, 2163; Lefèvre, *Compt. rend.* 1890, 110, 405; Preis, *Annalen*, 1890, 257, 178; Avery, *J. Amer. Chem. Soc.* 1906, 28, 1155); *antimonates* and *thioantimonates* (Sanderens, *Bull. Soc. chim.* 1899, [iii.] 21, 47; Pouget, *Ann. Chim.* 1899, [vii.] 18, 508); *tellurates* (Guthrie, *Zeitsch. anorg. Chem.* 1902, 31, 340); *plumbates* (Hochmel, *Arch. Pharm.* 1896, 234, 397); *ferrocyanides* (Stone and Ingen, *J. Amer. Chem. Soc.* 1897, 19, 542; Miller and Matthews, *ibid.* 547), and other compounds.

ORGANIC COMPOUNDS OF ZINC

Zinc acetate $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ is prepared by neutralising acetic acid with zinc carbonate or oxide. It forms thin, soft, white, glistening translucent plates, or monoclinic crystals of pearly lustre soluble in water and in alcohol (Ley, *Zeitsch. physikal. Chem.* 1899, 30, 243). It closely resembles the sulphate in its action and uses.

Zinc oleate (*shoemaker's zinc oleate*) is prepared by dissolving 32 grms. of hard soap shavings in 180 c.c. of distilled water, heating if necessary, 64 grms. of zinc sulphate are dissolved in 64 c.c. of boiling water and added to the former solution, after stirring, the oleate is separated, washed with hot water until free from sulphate, cooled, dried, and powdered (Naylor, *Pharm. J.* 1901, 66, 392). It is used in medicine as a mild astringent ointment and as an absorbent dusting powder to retard perspiration.

Zinc stearate is formed by the interaction of zinc acetate and sodium stearate. It is a fine white, tasteless powder, used for similar purposes as the oleate.

Zinc valerate $\text{Zn}(\text{C}_4\text{H}_7\text{O}_2)_2$ is prepared by mixing zinc sulphate with sodium valerate. It forms white, lustrous, pearly scales, or a white powder having the odour of valeric acid and a sweet, astringent metallic taste. It is employed in medicine.

Zinc oxalate, **propionate**, **tartrate**, **sallylate** and **lactate** have also been prepared. The last of these has been recommended for use mordanting cotton and other vegetable fibre (Eng. Pat. 372, 1896; *J. Soc. Chem. Ind.* 1890).

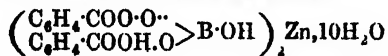
Zinc sulphanilate $(\text{NH}_4\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot \text{Zn}_2\text{Cl}_2$ is sold under the trade name of 'nizin,' a non-irritant antiseptic.

For the preparation of *zinc tannate*, Villon, *Bull. Soc. chim.* 1890, [iii.] 3, 784.

Zinc antipyrine salicylate is formed when a dilute solution of sodium salicylate and antipyrine is mixed with a solution of zinc chloride or sulphate. It forms colourless needles, m.p. 75°–76° (decomp.), sparingly soluble in cold, and more so in warm, water, alcohol, and ether (Schuyten, Chem. Zentr. 1898, ii. 704).

Zinc boropierate (*Chrysyl*) is obtained by the saturation of boropieric acid (prepared by boiling together 349 grms. picric acid, 62 grms. boric acid, and about 4 grms. of water) with 8 grms. of zinc oxide. It is a yellow powder used as a medicinal antiseptic (Monteil, J. Soc. Chem. Ind. 1908, 354).

Zinc boro-diortho-hydroxybenzoate



m.p. 100° (decomp.), is obtained by mixing 1 part boric acid with 1 of zinc carbonate, or 3 of salicylic acid, and adding the mixture in small portions to 10 times the weight of water at 65°. The mixture is agitated until no more carbon dioxide is evolved, when it is filtered and allowed to crystallise (Fr. Pat. 4116, 1910; J. Soc. Chem. Ind. 1910, 976).

Zinc compounds of 2-hydroxynaphthalene sulphonic acid-1-azo-β-naphthols have been prepared by treating 1-amino-2-naphthol sulphonic acids in concentrated aqueous solution, or in suspension, with alkali nitrite and an equivalent amount of zinc sulphate. The product so obtained is then made to react with a concentrated alkali solution of β-naphthol. The products dye wool in acid solution, bluish-red to violet shades, which turn bluish-black on subsequent treatment with a dichromate (U.S. Pat. 807442, 1905).

Basic zinc formaldehyde hydrosulphite is formed by adding 1 molecule of zinc to a mixture of 2 molecules of sulphurous acid and 2 of formaldehyde and then reducing the mixture by another molecule of zinc (U.S. Pat. 814032, 8124, 1906; J. Soc. Chem. Ind. 1906, 311, 217).

By the interaction of zinc-dust, sulphur dioxide, and aqueous formaldehyde, a difficultly soluble *zinc formaldehyde sulphoxylate*, or a readily soluble *zinc formaldehyde hydrosulphite* is formed, according to the conditions of the experiment (Eng. Pat. 81, 1906; J. Soc. Chem. Ind. 1906, 260; see also *ibid.* 1908, 1058; Becker, *ibid.* 1910, 43, 856; Fromm and Palma, *ibid.* 1906, 39, 3317; D. R. PP. 214041, 172217).

Zinc indigo white $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Zn}$ (?) is produced by the action of zinc chloride on calcium indigo white; of zinc oxide on indigo white in boiling naphthalene, and of zinc dust on indigo white in boiling naphthalene. It crystallises in lustrous leaflets (Binz, J. pr. Chem. 1901, ii. 63, 497).

Zinc gelatose is obtained by dissolving gelatose (formed by the action of superheated steam on gelatin) in dilute alcohol, adding a solution of a zinc salt and precipitating with alcohol. It is an amorphous powder, soluble in water, but insoluble in ether, benzene, and chloroform. It is said to be a valuable astringent without any irritating action on the mucous membrane (U.S. Pat. 698604, 1902).

Zinc chlorophyll is obtained by the action of zinc hydroxide and carbon dioxide on an extract

resembles chlorophyll in properties. When treated with alkalis it yields a substance closely analogous with alkachlorophyll, but containing zinc instead of magnesium (Marchlewski, Biochem. Zeitsch. 1909, 16, 3).

Zinc p-haemoglobin $\text{C}_{75}\text{H}_{113}\text{Zn}_2\text{S}_2\text{FeO}_{12}$ formed by shaking blood with zinc-dust or by the action of zinc salts on crystalline blood pigment, is a non-toxic compound, which has been recommended for use in the treatment of chlorosis (Grahe, Chem. Zentr. 1894, i. 636).

Zinc chloride forms stable double salts with diazo or tetrazo compounds of amino-azo or diamino-azo bodies which can be employed in dyeing (Eng. Pat. 1645; J. Soc. Chem. Ind. 1897, 40).

The diazo solution is prepared in aluminium or enamelled iron vessels, the requisite amount of zinc chloride is then added gradually with continual stirring. The double salt is formed as a voluminous precipitate, which, after settling, is filtered. When mixed with cold tragacanth thickening these double salts may be preserved unchanged for several days.

The goods prepared with sodium β-naphthol, to which sodium acetate is added, are printed with this paste, and then passed through a weak hydrochloric acid bath, washed, and soaped. The most satisfactory results have been obtained with α-naphthylamine hydrochloride, which yields a bright cardinal of a yellowish tone (Smirnoff and Rosenthal, Färber-Zeit. 7, 442).

Zinc chloride also forms double compounds, with fatty acids, with aliphatic compounds having a basic character, with aromatic bases containing one benzene nucleus, and with such compounds as piperidine, pyridine, and picoline (Lachowicz and Bandrowski, Monatsh. 1888, 9, 510; Bose, Amer. Chem. J. 1898, 20, 246; Bömer, Zeitsch. Nahr. Genussm. 1898, [viii.] 541).

The *zinc alkyl compounds* are formed, for the most part, by the action of the required alkyl iodide on zinc (Frankland and Duppa, Annalen, 1864, 130, 118; Gladstone and Tribe, Chem. Soc. Trans. 1879, 569; Fileti and Cantalupo, Gazz. chim. ital. 22, ii. 387; Ipatieff, J. pr. Chem. 1896, [ii.] 53, 257; Simonowitsch, Chem. Zentr. 1899, i. 1066; Worobéeff, *ibid.* 1907; Böhm, *ibid.* 1907; Ragosin, J. Russ. Phys. Chem. Soc. 1892, 24, 549; Lachman, Amer. Chem. J. 1900, 24, 31; J. Amer. Chem. Soc. 1901, 23, 897; Granichstädten and Werner, Monatsh. 1901, 32, 315; Haase, Ber. 1893, 26, 1052; Meyer, Chem. News, 1925, 131, 1).

Iocitsch (J. Russ. Phys. Chem. Soc. 1902, 34), by treatment of zinc and iodine with ether in a reflux apparatus, obtains a transparent ethereal solution of zinc ethyl iodide, which is identical in properties with the Grignard reagent, does not inflame in the air, and can be safely poured from vessel to vessel. Similar solutions of zinc methyl, isopropyl, amyl and allyl iodides can be obtained.

Zinc methyl is a colourless liquid, b.p. 46°, m.p. –40°, sp.gr. 1.386 at 10.5°, inflammable in air and decomposed by water. For its preparation, see Renshaw and Greenlaw, J. Amer. Chem. Soc. 1920, 42, 1472.

Zinc ethyl is a colourless liquid, b.p. 118°, m.p. –28°, sp.gr. 1.182 at 18°; it has similar properties to the methyl compound.

ZINC.

The zinc alkyl compounds are employed in the synthesis of many organic compounds (Grigorovitch and Pawloff, *J. Russ. Phys. Chem. Soc.* 1891, 23, 159; Bewad, *ibid.* 1900, 32, 420; Tichwinsky, *ibid.* 1903, 35, 155; Gwosdoff, *ibid.* 1907, 39, 1232; Lechman, *Amer. Chem. J.* 1896, 18, 372; Bamberger and Tichwinsky, *Ber.* 1902, 35, 4179; Menschikoff, *J. pr. Chem.* [ii.] 36, 347; Bewad, *ibid.* 1907, [ii.] 76, 62; Saytzeff, *ibid.* 98; Blaise and Maire, *Ann. Chim.* 1908, [viii.] 15, 556; *Compt. rend.* 1907, 145, 73; *ibid.* 1909, 148, 489; Blaise, *ibid.* 1907, 145, 1285; Blaise and Herman, *ibid.* 1908, 146, 479; Delacre, *Bull. Soc. chim.* [iii.] 48, 754; Wagner, *ibid.* [ii.] 42, 330).

Zinc ethoxide $\text{Zn}(\text{OEt})_2$, is formed by the action of zinc methyl on ethyl alcohol in an atmosphere of carbon dioxide, or, better, nitrogen or hydrogen. It is a white powder which cannot be distilled, is insoluble in ordinary solvents and readily absorbs moisture from the air. Zinc isobutyl oxide is prepared similarly by employing the corresponding alcohol (Tolkatscheff, *J. Russ. Phys. Chem. Soc.* 1901, 33, 469).

Zinc thiocyanate combines with pyridine to form an insoluble compound $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2][(\text{CNS})_2]$. This compound is formed by stirring pyridine into a solution of a zinc salt mixed with a concentrated solution of ammonium thiocyanate. The formation takes place preferably in neutral solution or a slight excess of pyridine: with great excess of pyridine the precipitate redissolves. This reaction may be used for the detection of zinc, one part of zinc in 200,000 parts of water may thus be recognised (G. Spacu, *Bul. Soc. Stiinte Cluj*, 1922, 1, 348-351; from *Chem. Zentr.* 1923, ii. 508, 1052).

Other zinc organic compounds have been described by Moitessier (*Bull. Soc. chim.* 1899, ii. 21, 336); Werner (*Zeitsch. anorg. Chem.* 1899, 21, 201); Rosenheim and Meyer (*ibid.* 1906, 49, 13); Grossmann and Schuck (*ibid.* 50, 1, 21); Ebler and Schott (*J. pr. Chem.* 1909, [ii.] 79, 72); also in D. R. P. 86148.

For methods of detecting and estimating zinc *v. ANALYSIS*.

Zinc, analysis of. The following methods are in use in the laboratories of the more important producers and consumers of zinc in the United States. Spellers are classified as A, high grade; B, intermediate; C, brass special; and D, prime western, the last a low grade used chiefly for galvanising.

Sampling.—A number of slabs should be sawn in half, and the saw-dust used as the sample. Fine drillings may be used. In neither case should a lubricant be used, and the drillings must be freed from iron by magnets.

Lead.—For the estimation of lead electrolytically, the sample (8.643 grms.) is covered with water in a 400 c.c. beaker, and 30 c.c. of nitric acid are then added gradually. The factor 8.643 differs from the theoretical factor (8.66) slightly, because lead dioxide cannot be dried completely. When action is complete, the solution is boiled to expel nitrous fumes, transferred to a 200 c.c. electrolytic beaker, diluted to 125 c.c. and electrolysed with a 5 ampere. Deposition is complete in 15 minutes. To insure complete de-

position, the covers and beaker are rinsed down with sufficient water to raise the level of the liquid 0.5 inch, and electrolysis continued for 15 minutes. The newly-exposed surface should remain bright. The anode is washed three or four times with distilled water, once with alcohol, and dried at 210°C. for 30 minutes. The number of decigrams of lead dioxide corresponds directly to the percentage of lead. The electrodes are cylinders of 20 mesh (per lineal cm.) platinum gauze. The anodes are 30 mm. in diameter and 30 mm. high, the cathodes the same height, but only 12 mm. in diameter. Both have stems of stout wire 10 cm. long.

In the absence of electrolytic appliances, lead is estimated as follows: The drillings (25, 15, 10, or 5 grms., according to grade) are treated with 300, 180, 120, or 60 c.c. (according to weight of drillings) of 'lead acid'—that is to say, dilute sulphuric acid saturated with lead sulphate, prepared by mixing 300 c.c. of concentrated acid with 1800 c.c. of water, and adding to the hot solution 300 c.c. of water in which 1 gm. of lead acetate has been dissolved. The 'lead acid' thus prepared is allowed to settle several days and then filtered. After all but 1 gm. of zinc has dissolved the solution is filtered, the undissolved residue washed with 'lead acid,' then washed back into the beaker and dissolved in a small quantity of hot dilute (1:1) nitric acid. The resulting solution is evaporated with 40 c.c. 'lead acid' until fumes arise. When cool, 35 c.c. of water are added, boiled, the first filtrate containing most of the zinc and a trace of lead is added, and the mixture left overnight. The lead sulphate is filtered on a Gooch crucible, washed with 'lead acid,' then with dilute (1:1) alcohol, and finally with strong alcohol. The Gooch crucible is placed in a porcelain crucible and heated for five minutes.

Iron.—The zinc (25 grms.) is dissolved in 125 c.c. nitric acid. The solution is boiled, diluted to 300 c.c., ammonium chloride (10 grms.) is added, and ammonia in sufficient amount to redissolve the zinc hydroxide. The mixture is boiled and filtered through a 11 cm. paper, which is washed with dilute ammonia and hot water. The ferric hydroxide is dissolved in hot dilute (1:4) sulphuric acid, the solution passed through a Jones reductor, which is washed with 150 c.c. of dilute sulphuric acid and 100 c.c. of water, the reduced solution being finally titrated with $\frac{N}{100}$ permanganate. Using

such dilute permanganate as this, it is essential to run a control with the same amounts of acid and water.

Cadmium.—The drillings (25 grms.) are covered with 250 c.c. water and 55 c.c. hydrochloric acid and left overnight. More acid is added 2 c.c. at a time, with an interval between each addition, so as to dissolve all but about 2 grms. of zinc with a minimum use of acid, about 60 c.c. in all usually sufficing. A piece of the undissolved zinc is transferred to a filter, the liquid is filtered, and the undissolved matter is washed with water, rejecting filtrate and washings. The undissolved matter is dissolved in nitric acid, and the solution evaporated with 20 c.c. of dilute (1:1) sulphuric acid until fumes arise. The residue is taken up with 100 c.c. of water, the mixture boiled and allowed to stand

overnight. The lead sulphate is filtered off and discarded. The filtrate is diluted to 400 c.c., 10 grms. ammonium chloride are added, and the solution saturated with hydrogen sulphide (1 hour). It is sometimes necessary to add a drop or two of ammonia to start the precipitation of cadmium sulphide. The impure cadmium sulphide is filtered off on a Gooch crucible and dissolved in 60 c.c. (more if necessary) of dilute (1:5) sulphuric acid by boiling for 30 minutes. The solution is filtered from asbestos and lead sulphide, diluted to 300 c.c. and cadmium reprecipitated as sulphide in presence of 5 grms. ammonium chloride. When much cadmium is present, a third precipitation may be necessary. The precipitate is dissolved in hot dilute (1:3) hydrochloric acid in a platinum dish, the solution evaporated with sulphuric acid to fuming, diluted, any filter fibres destroyed by addition of nitric acid and heating, which is continued to dryness and finally to 500°-600° or to dull redness, the cadmium being weighed as sulphate. (From a Report of a sub-committee on Methods of Analysis of Non-ferrous Alloys of the American Chemical Society, Abstract in Analyst, 1915, 369.)

Another method for the determination of cadmium in spelter and zinc ores is as follows: Ten grms. of spelter are dissolved in dilute nitric acid, and ammonia is added to remove iron, etc. From the filtrate a sulphide concentrate containing the cadmium is obtained by adding sodium sulphide until the precipitate becomes white; this is collected and dissolved by heating with 15 c.c. of sulphuric acid (1:1) until fumes are evolved. After dilution and removal of the lead sulphate, the filtrate is treated with sulphuric acid until it contains 20 p.c., then saturated with hydrogen sulphide to remove the bulk of the copper. The filtrate is diluted to 250 c.c. and again saturated with hydrogen sulphide. The cadmium sulphide is collected, washed free from zinc salts, and dissolved in nitric acid; the solution is evaporated to complete dryness with 1 c.c. of sulphuric acid (1:1), and the residue is heated to redness and weighed; it consists of cadmium sulphate plus a small quantity of copper oxide. The amount of the latter is determined iodometrically and deducted. In the case of ores the sample is dissolved in hydrochloric acid and the acidity of the filtered solution is adjusted to 1 p.c. A concentrate containing all the cadmium is then obtained by passing hydrogen sulphide into the liquid until precipitation of white zinc sulphide commences. The assay is finished as before (C. E. Barrs, J. Soc. Chem. Ind. 1924, 43, 77 T.; B. 520; see also Luff, Zeitsch. anal. Chem. 1924, 65, 97).

Zinc, technical analysis of. Ericson (Eighth Inter. Cong. App. Chem. 1912, vol. i. 183; Analyst, 1912, 521) gives the following method of analysing commercial zinc: The spelter (20 grms.) is covered with 100 c.c. water and 50 c.c. dilute (1:3) sulphuric acid, and allowed to stand overnight. The lead, cadmium, and undissolved zinc are then filtered off, washed with hot water, returned to the beaker, and dissolved in 10 c.c. of nitric acid. The solution is boiled until brown fumes cease to be evolved, and is then diluted and filtered from any trace of tin or antimony oxide. If these are absent,

as is usually the case, the solution is diluted to at least 100 c.c. and 30 c.c. of ammonia and 5 to 10 grms. ammonium persulphate are added, and the solution boiled for 5 minutes. After 10 minutes, the lead peroxide is filtered off on a double filter (11 cm.) and washed four times with hot 10 p.c. ammonia and five times with hot water. The precipitate is washed back into the beaker and treated with a measured volume of hydrogen peroxide solution of known strength until dissolved. After addition of 15 c.c. of dilute nitric acid (sp.gr. 1.2) and 75 to 100 c.c. water, the excess of hydrogen peroxide is determined by titration with permanganate. If 1 c.c. of the permanganate corresponds to 1 mgrm. of iron, it should theoretically correspond to 1.85 mgrm. of lead; but experience shows that the factor 1.92 should be employed. Using this factor, the results check well with results obtained by the gravimetric chromate method, and the method is recommended for spelter containing 1 p.c. or less lead.

The ammoniacal filtrate from the lead peroxide is boiled until nearly neutral and a white precipitate appears. About 40 c.c. of dilute (1:3) sulphuric acid is then added, and boiling continued for 10 minutes. After diluting to 200 c.c. the solution is saturated with hydrogen sulphide, with occasional additions of water. The precipitate is collected on a double filter, washed and redissolved on the filter in a slight excess of hot dilute hydrochloric acid. Any copper present remains on the filter as sulphide and may be ignited and weighed as oxide. The solution of cadmium (and zinc) chloride is nearly neutralised with ammonia, and about 8 grms. of trichloroacetic acid (*cf.* Fox, J. Chem. Soc. 1907, 91, 964) dissolved in water is added—or more if necessary—to dissolve the cadmium sulphide which separates on neutralisation. The solution is diluted to 200 c.c. and the cadmium reprecipitated by hydrogen sulphide. The cadmium sulphide is filtered off, and converted into sulphate or phosphate.

Gravimetric method for the estimation of zinc.—An excess of ammonium thiocyanate, either solid or in concentrated solution, is added to a neutral solution of a zinc salt. Pyridine is then added with agitation (3 drops to each 0.19 of zinc sulphate) until present in excess. The precipitate, which has the composition



is collected and washed with an aqueous solution containing 0.3 p.c. of ammonium thiocyanate, 0.2 p.c. of ammonium sulphate, and 0.2 p.c. of pyridine. The precipitate is dried, heated over a Techs burner, and weighed as zinc oxide. The results are in good agreement with those obtained electrolytically (G. Spacu, Bul. Soc. Stiinta Cluj, 1923, 1, 361-364; from Chem. Zentr. 1923, ii. 508; J. Chem. Soc. 1923, 580).

Determination by means of cyanamide.—Ammonium acetate is added to a neutral solution of a zinc salt. Dilute ammonia is added till the precipitate redissolves, excess of cyanamide added, and the zinc cyanamide filtered, washed, heated to redness and weighed as zinc oxide (Markwald and Gebhardt, Zeitsch. anorg. Chem. 1925, 147, 42).

For the estimation of fluorine in zinc blende, see L. da Rocha-Schmidt and K. Kruger (Zeitsch.

anal. Chem. 1923, 63, 29; Analyst. 1923, 48, 628).

For the estimation of calcium in spelter and zinc ores, see C. E. Barrs (J. Soc. Chem. Ind. 1924, 43, 35).

The use of powdered magnesium is recommended for the precipitation of copper and lead in hydrochloric acid solution; to ensure complete separation of zinc which may be present, the precipitated metals should be boiled with hydrochloric acid and reprecipitated with magnesium. The zinc in the filtrate from the copper lead precipitate may be titrated directly with potassium ferrocyanide solution, since even large quantities of magnesium chloride do not interfere with the titration. If aluminium is used for the precipitation of the copper and lead it is necessary to remove the aluminium salts before the zinc is titrated. If the zinc solution contains not less than 7 c.c. of concentrated hydrochloric acid per 250 c.c. the presence of lead does not affect the titration of the zinc with ferrocyanide solution (E. G. R. Ardagh and G. R. Bongard, Ind. Eng. Chem. 1924, 16, 300, Analyst. 1924, 49, 249).

Zinc may be separated from iron by means of ammonia and ammonium chloride in one precipitation when the following procedure is adopted. The solution, which may contain as much as 0.2 gm. of zinc and 0.4 gm. of iron, is treated with a few drops of hydrochloric acid and evaporated to a volume of about 5 c.c., while this liquid residue is still warm 5 grms. of ammonium chloride are stirred into it and 10 c.c. of concentrated ammonia are added. The mixture is then diluted with 25 c.c. of water, the precipitate collected on a filter and washed with about 100 c.c. of ammoniacal ammonium chloride solution (5 grms. of ammonium chloride and 5 c.c. of concentrated ammonia per 100 c.c.). The filtrate is acidified with hydrochloric acid, diluted to 250 c.c., and the zinc titrated with standardised potassium ferrocyanide solution (22 grms. of ferrocyanide and 10 grms. of sodium thiosulphate per litre), uranium nitrate solution is used as indicator. The same method may be employed for the separation of zinc from aluminium, but the aluminium hydroxide requires rather more washing than does the ferric hydroxide (E. G. R. Ardagh and G. R. Bongard, Ind. Eng. Chem. 1924, 16, 297, Analyst. 1924, 49, 249).

The presence of aluminium in the solution does not affect the blank determination in the usual potassium ferrocyanide titration of zinc, but the results obtained for zinc in the presence of aluminium are high under the usual conditions of the titration. Magnesium chloride does not interfere with the titration of zinc by potassium ferrocyanide, even when present in large quantities, and powdered magnesium may be used with advantage to precipitate copper and lead in hydrochloric acid solution. In order to separate the zinc completely from the precipitated metals, the latter must be filtered off, boiled with concentrated hydrochloric acid, and reprecipitated with magnesium. The magnesium used should be as free as possible from iron, and care must be taken that no copper goes back into solution. Correct results for zinc by titration with potassium ferrocyanide can be secured in the presence of lead, provided

that 7-10 c.c. of concentrated hydrochloric acid are present in 250 c.c. of the solution (E. G. R. Ardagh and G. R. Bongard, Ind. Eng. Chem. 1924, 16, 300; J. Soc. Chem. Ind. 1924, 43, B. 386).

Importance of zinc in the nutrition of animals.—According to Bertrand and Benson (Bull. Soc. chim. Biol. 1924, 6, 203), it is impossible to remove all traces of zinc from natural food materials without also removing vitamin B, with which the zinc appeared to be associated. A synthetic food, based on the composition of wheat, containing potato starch, casein, cellulose, lactose, calcium lactate, calcium chloride, and other salts was used. Mice receiving the synthetic food with the addition of an amount of zinc as sulphate equivalent to that present in a normal diet of wheat lived for periods 25-50 p.c. longer than those receiving the synthetic food alone. Analysis of the bodies after death showed that, in the absence of any supply of zinc in the food, the amount present at the beginning is retained throughout life, whilst, if zinc be given, the original amount present is about doubled (J. Soc. Chem. Ind. 1924, 43, B. 572).

The world's production of zinc.—In 1913 the total output of zinc in the world was 981,000 tons, a figure which fell to 445,000 tons in 1921, rising to 722,000 tons in 1922, and over 864,000 tons in 1923. Of the 1923 production the United States produced the largest quantity, namely, 481,000 tons, Belgium following with 138,000 tons (J. Soc. Chem. Ind. 1924, 43, 725).

ZINC BLENDE, BLENDE, or SPHALERITE. Zinc sulphide ZnS , crystallised in the cubic system with tetrahedral hemihedrism. The name blende is an old mining term, from the German blenden, to blind or deceive, because the mineral was frequently confused with galena, hence also the terms *galena inanis*, *pseudo galena*, and *mock lead*. With a qualifying prefix it has been applied to a variety of minerals¹ which possess in common a more or less metallic lustre often combined with a certain degree of translucency. It is therefore necessary to distinguish the present mineral as zinc blende. The name *sphalerite*, introduced by E. F. Glocker in 1847, has the same meaning, from *σφαλερός*, *deceptive*.

Crystals are of frequent occurrence, but, as a rule, the faces are much rounded and the form is further obscured by twinning. An important crystallographic character is the presence of perfect cleavages in six directions parallel to the faces of the rhombic dodecahedron, adjacent cleavages being inclined to one another at angles of 120° or 90° . Massive material with coarse or fine granular texture and usually a crystalline fracture, due to the cleavage, is more common. Compact material with a shelly concentric structure and reniform surface ('liver blende') also occurs. When pure and free from iron the mineral is white or pale yellowish; more often, however, the colour is dark brown to black ('black jack') with a

¹ E.g. cadmium-blende (=greenockite), silver-blende (=pyrrargyrite and proustite), mercuric-blende (=cinnabar), copper-blende (=tennantite), manganese-blende (=alabandite), samarskite-blende (=gasthite), pitchblende, hornblende, &c. Analogous terms occurring in many old compound names of minerals are glance, pyrites (Ger. Eisen), and spar.

resinous, adamantine, or sub-metallic lustre. This darker coloured material when scratched with a knife (H. 3½-4) always yields a brown streak or powder, which readily distinguishes the mineral from galena; it is also much lighter (sp.gr. 3.0-4.1). The lighter coloured material is sometimes perfectly clear and transparent; e.g. the small, beautifully developed tetrahedral crystals found singly in cavities of the white crystalline dolomite at Binn in Valais, Switzerland; and the large, pale yellow cleavage masses from Pico de Europa in Santander, Spain. The latter contains only 0.16 p.c. Fe, and has sp.gr. 4.098, and refractive index n_D 2.369. Transparent crystals of a rich ruby-red colour ('ruby-blende') are found in Flintshire and elsewhere. Certain specimens of the massive mineral display a bright phosphorescence when scratched with a knife or struck with a pick.

The pure mineral contains 67 p.c. Zn, but usually this is partly replaced isomorphously by 1-2 p.c. of iron, which may range up to 26 p.c. A black ferrous zinc-blende from Marinato in Colombia, South America, containing 11-15 p.c. Fe, has been called *marmatite*. Cadmium is usually present in small amount (traces to about 0.5 p.c., but ranging up to 3.2 p.c.). Gallium and indium were discovered in zinc-blende; and these elements, as well as germanium and thallium, can be detected spectrographically in most samples of the mineral. Other metals occasionally found in small amounts are silver, mercury, copper, lead, manganese, and tin; but these are perhaps present as impurities. The stanniferous zinc-blende of Freiberg, Saxony, for example, encloses minute needles of cassiterite. The mineral dissolves in hydrochloric acid with evolution of hydrogen sulphide. At a temperature of 1020° it is transformed into the hexagonal modification wurtzite (*q.v.*). In zinc-blendes containing more iron the inversion temperature and the density are lower, whilst the refractive index is higher; e.g. for material from Breitenbrunn, Saxony, containing 17 p.c. Fe (sp.gr. 3.935, n_D 2.47), the inversion temperature is 880°. On the stability relations and artificial production of the two modifications of zinc sulphide, v. E. T. Allen and others (*Amer. J. Sci.* 1912, 34, 341; 1914, 38, 393).

Zinc-blende is the commonest ore of zinc, and by its alteration it gives rise to the secondary ores smithsonite and hemimorphite. It occurs in metalliferous veins, as bedded deposits, and as pockets in limestones; and is sporadically distributed through sedimentary rocks, sometimes replacing fossil shells. It has been observed on old mine timbers, having, no doubt, been formed by the reducing action of the organic matter on solutions of zinc sulphate produced by the oxidation of pre-existing zinc sulphide. In most instances zinc-blende occurs with galena, there often being a very intimate association of the two minerals. 'Huasciolite,' at one time believed to be a homogeneous mineral, is such a mixture. The mixed ores (e.g. those of Broken Hill in New South Wales) can be separated by an electro-magnetic process, since the small amount of iron present in the zinc-blende causes it to be slightly magnetic. In addition to its principal use as an ore of zinc, the mineral is also a source of sulphuric acid,

since sulphur dioxide is given off when the ore is roasted. The mineral is also used directly for the manufacture of zinc white (ZnO) and zinc-vitriol; in the former case the vapour of reduced zinc is oxidised in a current of warm air; and in the latter the ore, either before or after roasting, is treated with sulphuric acid. L. J. S.

Refraction and absorption of light by zinc-blende at temperatures up to 700°.—Measurements made of the refractive index and absorption of zinc-blende coloured slightly greenish-yellow for temperatures ranging from 80°-700°, and for wave-lengths between about 400 μ and 800 μ , indicated that in the visible spectrum the dispersion is normal and attributable principally to an oscillator with a frequency in the ultra-violet. The refractive index increases with temperature, and considerably more rapidly for light of short wave-length than for light of long wave-length. Thus for $\lambda = 436\mu$, the results show that the refractive index, n_λ at t° , is given by

$$n_\lambda = 2.4885(1 + 3.8695 \times 10^{-5}t + 17.9 \times 10^{-9}t^2)$$

Similarly, for $\lambda = 546\mu$,

$$n_\lambda = 2.3870(1 + 2.7508 \times 10^{-5}t + 11.1 \times 10^{-9}t^2)$$

and for $\lambda = 578\mu$,

$$n_\lambda = 2.3717(1 + 2.5826 \times 10^{-5}t + 9.5 \times 10^{-9}t^2)$$

The transparency of zinc-blende increases with increasing wave-length of the light transmitted and decreases rapidly as the temperature increases. A minimum transparency observed in the mean or extreme red region of the spectrum is attributable to an impurity present in the blende. With increasing temperature, the region of selective absorption is displaced from the ultra-violet towards the visible region of the spectrum (Maria Mell, *Zeitsch. physikal. Chem.* 1923, 16, 244-265; *J. Chem. Soc.* 1923, ii, 513).

The ignition temperature of zinc blende is lowered only to a small extent by increasing the oxygen content of the air; in pure oxygen this temperature is 25° below that in ordinary air. Other conditions being equal, the rate of oxidation of blende varies very nearly directly as the partial pressure of oxygen in the surrounding air, consequently the sulphur dioxide content of the roaster gas varies directly, and the time required for roasting inversely, as the oxygen content of the air supply. The amount of zinc sulphate formed at any temperature is greater with enriched air than with ordinary air. The addition of oxygen to the air supply of a furnace roasting zinc blende will increase its capacity, reduce the fuel consumption, and increase the proportion of sulphur dioxide in the gases, hence the capacity of the sulphuric acid plant will be increased and the cost of running is reduced (B. M. O'Harra, W. Kahlbaum, E. S. Wheeler, W. J. Darby, *Trans. Amer. Inst. Min. Met. Eng.* Mar. 1924; *J. Soc. Chem. Ind.* 1924, 43, B. 385).

ZINC-DUST is usually obtained as a by-product from zinc smelters, but it is also made by blowing gas against a stream of liquid zinc or by grinding. Such dusts contain varying amounts of impurities, some of which are undesirable for certain uses. Microscopic examination has shown that the grains of zinc-dust consist of metallic globules coated with crystals

of zinc oxide which prevent the globules from uniting.

The chief properties for which zinc-dust is used may be summarised as follows: (a) Reducing properties, as in the dye industry, for reducing nitro compounds to organic amines and in preparing sodium hydrosulphite for the reduction of vat colours; (b) the property of precipitating metals from their solutions, in purifying zinc-sulphate solutions for electrolysis or for the manufacture of lithopone; (c) the property of combining with dry oxygen only at a high temperature, and of giving with moist air a basic carbonate or with sea air an oxy-chloride which protects the metal from further alteration. These properties have led to application in painting iron objects, sherardising (i.e. immersing iron objects in zinc-dust at 300°C.), galvanising cast-iron and metallisation (i.e. deposition by projection of a layer of zinc on the surface of a metal) (Met. & Chem. Eng. 1923; J. Soc. Chem. Ind. 1923, 455).

Zinc-Dust (valuation of). Klemp has devised a process for the above purpose which depends on the power of zinc to reduce potassium iodate to potassium iodide in an alkaline solution. When the solution is afterwards acidified, iodine is liberated by the interaction of the iodic and hydriodic acids, and is distilled off from the mixture into potassium iodide solution, and titrated with thiosulphate. The details of the method are as follows:—

0.5–1 gm. of the well-mixed zinc-dust is weighed in a tube, and poured into a 200 c.c. stoppered flask, the tube being again weighed. For every 0.1 gm. of zinc present, 10 c.c. of a solution of alkali (containing 370 grms. of potassium hydroxide, or 300 grms. of sodium hydroxide per litre), and 3 c.c. of a solution of potassium iodate (containing 15.25 grms. of potassium iodate per 300 c.c.) are measured into a beaker, and then poured into the flask. Some glass beads are added, and the flask stoppered and shaken for 5 mins. in the cold, no advantage being gained by heating it. Its contents are then washed into a 250 or 500 c.c. flask, and made up to the mark with water. 100 c.c. are now pipetted into the retort of a Töpfer's apparatus (Zeitsch. anal. Chem. 26, 293), dilute sulphuric acid is added, and the apparatus filled with carbon dioxide. A solution of potassium iodide is placed in the receiver, and the retort heated, at first gently, and then more strongly till the contents are perfectly colourless. The stream of carbon dioxide is continued throughout the distillation, which generally occupies about 20 mins. The solution of iodine in potassium iodide is then transferred from the receiver into a flask, a standard solution of sodium thiosulphate added in slight excess, and the excess titrated back with weak standard iodine solution, starch being used as an indicator. After correcting for the excess, the quantity of zinc is calculated from the amount of thiosulphate used.

Klemp finds that the addition of powdered lead and iron to the zinc makes very little difference in the quantity of zinc found by this process, the results being a little lower in the presence of these metals.

The results by this method agree well with those obtained by Fresenius's method, but are

generally higher than those obtained by Drewson's and lower than those obtained by Töpfer's method (G. Klemp, Zeitsch. anal. Chem. 29, 253–266; J. Soc. Chem. Ind. 9, 968). For a volumetric method, depending on the amount of hydrogen evolved by the action of an acid on zinc-dust, v. *ibid.* 5, 145, 1886.

According to Edwards (Met. & Chem. Eng. 1919, 21, 1927) the hydrogen gas method is not on the whole suitable. The following process is recommended: 1 gm. of the zinc-dust is treated with 50 grms. of ferrous ammonium sulphate in 100 c.c. of water and constantly stirred. As soon as the zinc-dust is dissolved, 100 c.c. of sulphuric acid (1:10) is added and the solution is titrated with potassium permanganate.

ZINC FLOWERS. Zinc oxide produced by combustion; v. ZINC.

ZINC GREEN. Cobalt green, or Rinnmann's green; v. COBALT; also FIGMENTS. This term is also applied to a mixture of zinc yellow and Prussian blue.

ZINCITE. Native zinc oxide ZnO , crystallising in the hexagonal system. The crystals, which are of rare occurrence, possess the same degree of symmetry (hemimorphic-hemihedral) and very nearly the same angles as those of wurtzite (ZnS) (q.v.). The mineral is usually found as lamellar cleavage masses (there being a perfect basal cleavage), which are opaque to translucent and deep-red, rarely orange-yellow, in colour. The streak is orange yellow; sp.gr. 5.6. Manganous oxide (3–6 p.c.) replaces part of the zinc, and there is often a little ferric oxide present. Zincite is known only from the zinc mines at Franklin Furnace and Sterling Hill in Sussex Co., New Jersey, but it occurs there in some abundance, and is mined, together with franklinite and willemite, as an ore of zinc. Fragments of the mineral and of artificial crystallised zinc oxide have been used in the wave detectors of wireless telegraphy installations. White or yellowish crystals of hexagonal zinc oxide have often been observed in zinc furnaces, and sometimes in iron furnaces.

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ZINCKENITE. Lead sulphantimonite PbSb_2S_4 , crystallised in the orthorhombic system. The best crystals are of columnar habit, but their form is much obscured by twinning; these are known only from Wolfsberg in the Harz. Elsewhere the mineral is found as radiating aggregates of fine needles or compact fibrous masses; such material resembles stibnite in appearance, but differs from this in the absence of cleavage. The colour and streak are steel-grey, lustre metallic, opaque; sp.gr. 5.30–5.33; H. 3; soluble in hot hydrochloric acid with evolution of hydrogen sulphide. The mineral is not readily distinguished from the several other lead sulphantimonites of acicular habit (v. JAMESONITE and FEATHER-ORE). It occurs together with these and stibnite in metalliferous veins, and is no doubt often present in lead antimony ores, e.g. at Oruro, Bolivia. The name, which is sometimes spelt zinckenite, is after J. K. L. Zincken (1790–1862).

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ZINCOPYRIN. Trade name for phenyl-dimethyl-pyrazolone zinc chloride
($\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}$) $_2\text{ZnCl}_2$

first obtained by Schuyten. Shining scales, m.p. 156°. Readily soluble in water, alcohol, and chloroform. Used in the treatment of inoperable carcinoma of the uterus.

ZINC-SPAR. Syn. with calamine; v. **ZINC**.

ZINC-SPINEL v. **GAHNITE**.

ZINC-VITRIOL. *Zinc sulphate* v. **ZINC**; also **GOSLARITE**.

ZINC WHITE v. **ZINC**.

ZINC YELLOW, or *Buttercup yellow* and *Zinc chromate*, v. **CHROMIUM**.

ZINGERONE v. **GINGER**; **KETONES**.

ZINGIBEROL $C_{15}H_{26}O$, a sesquiterpene alcohol occurring in the essential oil of ginger, possessing the fragrance of ginger. B.p. 154°–157°/14.5 mm. (Brooks, J. Amer. Chem. Soc. 1916, 38, 430), v. **GINGER**.

ZINKENITE v. **ZINOKENITE**.

ZINNWALDITE v. **MICA**.

ZINOL v. **SYNTHETIC DRUGS**.

ZIRCON. Native zirconium silicate $ZrSiO_4$, crystallising in the tetragonal system and homeomorphous with cassiterite and rutile. A little ferric oxide (0–3 p.c.) and sometimes thorium are present. The mineral varies considerably in its characters and appearance; and further, several altered and hydrated forms are distinguished by special names (*malacon*, *cyrtolite*, *oerstedite*, &c.). The transparent gem-varieties show a wide range in colour; brownish-yellow and red specimens are known as *hyacinth* (or jacinth), and yellowish and green as *jargon* (or jargoon). Fine sky-blue stones are said to come from Siam. The colour can usually be changed by heat, and some brownish-yellow stones are completely decolorised. With their brilliant adamantine lustre, these artificially decolorised stones ('Matura diamonds,' from Matura in Ceylon) may be mistaken for diamond. The hardness is 7½. The mineral is remarkable in showing a wide range in sp.gr. (4.0–4.7), and in optical characters, and these sometimes undergo a marked change when the crystals are heated to redness. These differences and changes suggest the existence of three modifications of zircon, which may occur as intergrowths in the zoned crystals (L. J. Spencer, Min. Mag. 1904, 14, 48). Possibly the so-called zircons of lower density are really hafnium silicates rather than zirconium silicate. In sixteen zircons from various localities, G. Hevesy and V. T. Jantzen (Chem. Soc. Trans. 1923, 123, 3218) estimated HfO_2 1.3 to 6 p.c., but unfortunately there is no statement of the densities of the materials examined.

Zircon occurs as a primary constituent of many igneous rocks, but, as a rule, only as minute crystals. Being heavy, hard, and resistant to weathering agencies, it collects in the beds of streams. Most of the gem material is obtained from gem-gravels in Ceylon and Australia. Rough and opaque zircon has been collected in considerable quantity from decomposed pegmatite in Henderson and Buncombe counties, North Carolina, and in Brazil. Zircon-bearing pegmatites occur also in Virginia (T. L. Watson, Trans. Amer. Inst. Mining Engin. 1917, 55, 936); and near Ashland in Virginia there is an important development of zirconiferous sandstone, containing 13–30 p.c. zircon as crystals and grains with an average diameter of 0.5 mm. Zircon is employed as a source of

zirconia (ZrO_2 , 67.2 p.c.), used in incandescent gas-lighting and in electric arc-lamps, and as a highly refractory material for lining furnaces and for chemical ware. A minor use is as an abrasive for grinding mother-of-pearl. Zircon, used in the natural crystalline form, does not melt at 2126°. At 1800°, some dissociation occurs, dense white fumes of silicon dioxide being formed at 1900°. The residue melts at about 2600°. Zirkite (that is, zircon containing excess of silica and some ferric oxide) does not melt at 1950° (C. Matignon, Compt. rend. 1923, 177, 1290; Chem. Soc. Abstr. 1924, 126, ii, 48).

References.—T. L. Watson and F. L. Heas, Zirconiferous Sandstone near Ashland, Virginia, with a summary of the occurrence, properties, and uses of zircon in general, Univ. of Virginia, Sci. Ser. 1912, 1, 267; W. T. Schaller, Zirconium Minerals, Min. Res. U.S. Geol. Survey, for 1916, 1917, ii, 377. L. J. S.

ZIRCONIUM. Sym. Zr. At.wt. 91.76 (Venable and Bell); 91.22 (Hönigschmid, Zintl, and Gonzales, Chem. Soc. Abstr. 1925, 128, ii, 174); 91.3 (Hevesy, Nature, 1925, 115, 335). Zirconia, an oxide of this metal, was identified in 1789 by Klaproth in the zircon of Ceylon, and this observation was confirmed by Guyton and Vauquelin.

It is the main constituent in zircon and malacon, which are found as accessory minerals in many metamorphic and igneous rocks (granites, syenites, elaeolite-syenites, basalts, amphibolites), and in baddeleyite (brazilite) in Ceylon, the Urals, Norway, and Australia. Large deposits of zirconia earth have been found in the Caldas region, about 130 miles north of São Paulo City, Brazil, and cover a mountainous plateau about 30 miles long and 15 miles wide (Meyer, Brazilian Review, 1916). The deposits are worked by the Foote Mineral Co., of Philadelphia (cf. Fletcher, Min. Mag. 1893, 10, 148; Hussak and Reiting, Zeitsch. Krist. 1903, 37, 567; Wodekind, Zeitsch. angew. Chem. 1908, 21, 2270; Ber. 1910, 43, 290). Brazilian zirconia deposits are feebly radioactive, and on heating evolve a gas containing argon and helium (Zeitsch. Elektrochem. 1908, 14, 585; Ann. Chim. 1898, [vii.] 13, 433; Chem. Soc. Trans. 1906, 89, 1568; 1908, 93, 350). The following minerals contain a high percentage of zirconium: *zirkelite* (zirconium titanate with thorium and rare earths), *eudialyte* (*eucolite*), *elpidite*, *catapleite* (zirconium double silicates of sodium and calcium), *polymignite* (Norway, a complex zircon-silicate, with titanium and tantalum oxides, columbium oxide, thorium, and the rare earths). Zirconium is a frequent constituent of rare-earth minerals (v. **CERITE EARTHS**), and is found also in *pitchblende*, *columbite*, and *tantalite*. *Baddeleyite* (q.v.) (82–94 p.c. ZrO_2) from Brazil, and *zircon* ($ZrSiO_4$) from monazite sands, &c. are the chief sources of zirconia. For methods of their analysis, see Powell and Schoeller, Analyst, 1919, 397; Chem. Soc. Trans. 1921, 120, 1927; Lundell and Knowles, J. Amer. Chem. Soc. 1920, 42, 1439; Analyst, 1920, 45, 342; Thompson, Trans. Ceram. Soc. 1919–20, 19, 153.

Separation and purification of zirconia.

1. *Fusion with sodium carbonate or hydroxide.*—The native silicate (zircon), disintegrated by heating and dropping into water, is treated

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with hydrochloric acid to remove metallic impurities (iron, &c.) and is fused with sodium carbonate or hydroxide (4 parts) containing 10 p.c. of sodium fluoride. When extracted with water the fused mass leaves an insoluble crystalline precipitate of sodium zirconate, which is dissolved in hydrochloric or sulphuric acid, and the zirconium hydroxide precipitated by ammonia (Monatsh. 1885, 6, 531; Chem. Soc. Trans. 1889, 58, 705; Amer. Chem. J. 1892, 5, 551; Marden and Rich, J. Ind. Eng. Chem. 1920, 12, 651; cf. Jackson and Shaw, J. Amer. Chem. Soc. 1922, 44, 2712; Wenger and Müller, Chem. Soc. Abstr. 1925, 128, ii, 1207).

2. *Decomposition with hydrofluoric or sulphuric acid, or their acid salts.*—Zircon is exposed to the vapour of hydrogen fluoride or heated with potassium hydrogen fluoride; in the latter case, the product, when boiled with hydrofluoric acid, leaves a deposit of potassium silicofluoride, whilst the more soluble potassium zirconofluoride crystallises out on concentrating the solution (J. 1859, 677; Ann. Chim. 1860, [iii.] 60, 257). Zircon can also be decomposed with hot concentrated sulphuric acid, or with fused potassium hydrogen sulphate (Ber. 1870, 3, 58; Annalen, 1876, 181, 232). When the ore is fused with KHSO_4 , the fused mass may be extracted with water and the metals precipitated as hydroxides and redissolved in concentrated hydrochloric acid. From the strongly acid solution zirconium is precipitated as phosphat $\text{Zr}(\text{HPO}_4)_2$. This is washed by decantation with hydrochloric acid and water and then dissolved in hydrofluoric acid. From this solution the zirconium is precipitated as hydroxide (de Boer, Zeitsch. anorg. Chem. 1925, 144, 190). Zirconium salts may also be purified by precipitation from boiling hydrochloric acid solution by sodium arsenate. The precipitate $\text{Zr}_3(\text{AsO}_4)_4$ affords a means for separating zirconium from hafnium, cerium, and thorium (Moser and Lessing, Monatsh. 1924, 45, 323).

3. *Reduction with carbon or calcium carbide.*—Crude zirconium carbide obtained by heating an intimate mixture of zircon and carbon in the electric furnace is heated in chlorine, and the resulting chloride dissolved in concentrated hydrochloric acid; the crystalline oxychloride, which separates from this solution, is decomposed by ammonia. Or a mixture of zircon, calcium oxide, and carbon is heated in the electric furnace (1030 amperes, 50 volts for 7 mins.; the product, when extracted with water and dilute hydrochloric acid, is decomposed by chlorine at 300° , yielding zirconium chloride (Compt. rend. 1893, 116, 1428; 1896, 122, 65; Zeitsch. anorg. Chem. 1902, 33, 81; Ber. 1903, 35, 3929; Chem. Zeit. 1907, 31, 654). Zircon may be mixed with 25 p.c. of carbon and treated with a stream of chlorine at 1000° – 1200° . From the mixture of chlorides thus formed zirconium oxychloride is obtained by crystallisation from aqueous solution. Heating this in air yields zirconium oxide.

4. *Other methods of purification.*—Zirconia is freed from silica by heating with potassium hydrogen fluoride when the latter oxide is eliminated as volatile silicon fluoride. Crude zirconia is rendered soluble by heating with strong sulphuric acid or by fusion with sodium hydroxide. Treatment of the product

with warm water leads to the separation of crystalline basic sulphate (Ber. 1904, 37, 2024; cf. Zeitsch. anorg. Chem. 1905, 45, 155; Rosster and Sanders, J. Soc. Chem. Ind. 1921, 40, 701). Zirconia is freed from iron by crystallising the oxychloride from strong hydrochloric acid (Chem. Soc. Trans. 1889, 58, 705; Amer. Chem. J. 1891, 5, 551; J. Amer. Chem. Soc. 1894, 16, 469). Ferruginous zirconium hydroxide, when dissolved in hydrochloric acid and boiled with sodium thiosulphate, gives the pure hydroxide mixed with sulphur. The addition of ammonia and ammonium sulphide to an iron and zirconium solution precipitates zirconium hydroxide, and ferrous sulphide, the latter being dissolved out with sulphurous acid. In the presence of tartaric acid the foregoing solution yields ferrous sulphide alone on adding ammonium sulphide; the concentrated filtrate, when mixed with excess of hydrogen peroxide, furnishes pure hydrated zirconium peroxide (Zeitsch. anorg. Chem. 1902, 33, 81). Brazilian zirconia earth (74.94 p.c. ZrO_2) is dissolved in mineral acid, and the iron and titanium removed from the dilute solution with ammonia and ammonium carbonate, the liquid being warmed until it gives no coloration with sulphuric acid and hydrogen peroxide. The acidified filtrate is boiled to expel carbon dioxide and the zirconium hydroxide precipitated with ammonia. The mineral may also be heated with magnesium in an atmosphere of hydrogen; the product extracted successively with ammonium chloride, hydrochloric acid, and potassium hydroxide to remove magnesium, iron, and silicon; the residue is heated in hydrogen, and then in chlorine or bromine, when zirconium chloride or bromide sublimes (Wedekind, Ber. 1910, 43, 290).

Zirconium is isolated only with difficulty owing to the readiness with which it combines with oxygen, nitrogen, carbon, silicon, &c. When reduced with carbon in the electric furnace zirconia yields zirconium containing either oxide or carbide, depending on the proportion of the reagents (Troost, Compt. rend. 1893, 116, 1227; Moissan, *ibid.* 1222; Greenwood, Chem. Soc. Trans. 1908, 93, 1843). The metal (97.7 p.c.) may be obtained by heating an intimate mixture of zirconium oxide and metallic calcium or aluminium in an exhausted iron tube, heated until reduction begins and the ignited mass extracted with water and dilute acids out of contact with air (Wedekind, Annalen, 1913, 395, 149; cf. Marden and Rich, J. Ind. Eng. Chem. 1920, 12, 651; Bureau of Mines, Bull. 186, 1921). A thick layer of pure zirconium is deposited upon a heated tungsten filament when the vapour of zirconium iodide unadmixed with other gases is passed over the filament (van Arkel and de Boer, Zeitsch. anorg. Chem. 1925, 148, 345). Boron or silicon reacts with zirconia in the electric furnace, but the product is contaminated with boride Zr_3B_4 or silicide. Amorphous zirconium (95–96 p.c. Zr) is obtained by heating potassium zirconofluoride with sodium under fused potassium chloride in closed iron vessels, the product being extracted with alcohol and then with hydrochloric acid. It is pyrophoric and behaves like a colloidal gel, retaining water with great tenacity. With acids it easily passes into a hydrosol (Wedekind and Lewis)

Lely and Hamburger (Zeitsch. anorg. Chem. 1914, 87, 209) obtained the element in a compact ductile form by heating the chloride with sodium in an exhausted steel bomb (see also Cooper, Trans. Amer. Electrochem. Soc. 1923, 209). By reducing the double fluoride with aluminium at the temperature of melting iron impure metallic zirconium (98 p.c.) is produced, but in the electric furnace an alloy of this element and aluminium is formed. Reduction of the double fluoride with magnesium in the electric furnace gives crystalline zirconium (94 p.c.), but sometimes contaminated with nitride. The product, containing 97-98 p.c. of zirconium, is pressed into rods, and then used as the terminals of an electric arc operating in hydrogen under diminished pressure; fusion takes place, and 99.8 p.c. zirconium is obtained. This resembles white cast iron, and has a hardness 7-8, sp.gr. 6.40 at 18°, sp.ht. 0.004, and heat of combustion (1 gm.) = 1958.7 cal., m.p. 1530° (Burgess), 1700° (Guertier and Puani). The amorphous variety, which is a black powder, and a bad conductor of electricity, is readily oxidisable, whereas the crystalline modification yields zirconia only at white heat. Zirconium is attacked by hydrogen fluoride, and at red heat by hydrogen chloride or chlorine, but is not appreciably affected by sulphuric, hydrochloric, or nitric acid; it is oxidised by fused potassium hydroxide or nitrate (Zeitsch. anorg. Chem. 1905, 45, 385; 1910, 65, 245; Zeitsch. Elektrochem. 1904, 10, 331; Annalen, 1910, 371, 367). An alloy of zirconium 65 p.c., iron 26 p.c., aluminium 7.7 p.c., and titanium 0.12 p.c., is highly resistant to acids, and not liable to oxidation. Ferro-zirconium has been used for the production of hard steel for armour plates and bullet-proof sheets. Zirconium carbide is hard enough to cut quartz, and might replace the diamond for glass-cutting.

The hot-rolling properties of steel containing 0.075 p.c.-0.32 p.c. S were observed in relation to the minimum zirconium content required to prevent red-shortness. Zirconium in steel reacted quantitatively with sulphur in the ratio corresponding with the formation of ZrS_2 , no excess being necessary as is required when manganese is used alone as a desulphurising agent. Zirconium also militates against the effect of iron sulphide and increases the capacity of manganese to combine with sulphur. Like manganese sulphide, zirconium sulphide is plastic at rolling temperatures and is visible on etching the metal as grey inclusions elongated by the mechanical treatment received. The normal sulphide, ZrS_2 , is soluble in hydrochloric acid (1:1), but if more zirconium than corresponds with this ratio is present in the steel, the sulphur is not evolved as hydrogen sulphide upon treatment with the acid, and it is suggested that the excess zirconium is partitioned between the metal and the normal disulphide, the latter forming possibly an insoluble zirconium-zirconium sulphide solid solution, the proportion of sulphur rendered insoluble being 10 p.c. of the zirconium in excess of that required to form the normal disulphide (A. L. Field, Trans. Inst. Min. Met. Eng. Feb. 1924; J. Soc. Chem. Ind. 1923, 1026 A.; 1924, 43, B. 470).

Zirconia (Zirconium dioxide) ZrO_2 occurs native as baddeleyite (q.v.) in monoclinic forms,

not isomorphous with cassiterite or rutile. When crystallised from borax a quadratic form of zirconia is produced isomorphous with rutile. Ignition of zirconium hydroxide, sulphate, oxalate, or nitrate yields the dioxide as a hard white powder. The density varies with the mode of preparation, unfused specimens having sp.gr. 5.4824 at 18.5°, whilst fused rods vary from 5.48 to 5.89. Zirconia melts at $2653^\circ \pm 10^\circ$ (3000°, Podszus) (Ruff and Lauschke, Zeitsch. anorg. Chem. 1916, 97, 73), and may be vaporised in the electric furnace (360 ampères, 70 volts). The vapour condenses to a fine powder which scratches glass. Its hardness is 6.5, between that of quartz and corundum. The sp.ht. of zirconia is 0.1076; it is a bad conductor of heat, and has a linear coefficient of expansion = 0.0000084, near to that of fused quartz (Nilson and Petterson, Compt. rend. 1880, 91, 232; Moissan, *ibid.* 1893, 116, 1222; Lehman, Dissert. Techn. Hochsch. München. 1910; Zeitsch. anorg. Chem. 1909, 65, 178). For its production from zirkite, see under ZIRKITE.

The solubility of zirconia in mineral acids depends on the temperature of ignition; after slight ignition it dissolves readily, but after strong ignition it becomes practically insoluble, although it is attacked by hydrofluoric and concentrated sulphuric acids. It resists fused cyanides and alkalis, but is easily attacked by fusion with potassium acid sulphate and fluorides.

When heated in the oxy-coal-gas flame zirconia becomes brilliantly incandescent, so that it may replace for certain special purposes the lime of the Drummond light, and it has been thus employed by Lannemann and others in spectroscopy and microphotography. It has received an important technical application in the Nernst lamp in which the incandescent body is composed chiefly of zirconia (85 p.c.), together with oxides (15 p.c.) of the yttrium series. This material conducts only at high temperatures, so that it requires to be first heated before the electric current can be transmitted.

Strongly ignited zirconia is very stable towards acids and alkalis, and as it is not fractured by sudden changes of temperature, it may be employed for crucibles in which platinum and quartz can be melted. Refractory vessels have also been made from zirconia mixed with 10 p.c. of magnesia or clay, phosphoric acid being employed as a binding material (Zeitsch. anorg. Chem. 1909, 65, 178).

Zirconia crucibles are moulded from the plastic mass made by kneading together gelatinous zirconium hydroxide and artificial or purified native zirconia, a little starch being added to keep the mass firm while drying. After 2 days the crucibles are gently heated at 50°-100°, and the temperature then raised gradually to 2000°-2300°. These crucibles are not affected by fused alkalis or alkaline bisulphates (Bayer, Zeitsch. angew. Chem. 1910, 23, 488; Ruff and Lauschke, *l.c.*; Podszus, Zeitsch. angew. Chem. 1917, 30, i. 17; Andley, Trans. Ceram. Soc. 1916-17, 16, 121; Rodd, J. Soc. Chem. Ind. 1918, 213 R).

Zirconia is a very good insulator, and mixed with good conducting material it is employed for electrical heating purposes, and may be used to prevent disintegration of the iridium in the

iridium furnace. It has found application as a substitute for bismuth prior to the use of Röntgen rays for medical purposes, and has been recommended as a non-irritant powder for covering the surface of wounds.

It is a good catalyst for the preparation of aliphatic esters by passing the mixed vapours of acids and alcohols over the oxide at 270°–290°.

The effect of additions of zirconia to a typical commercial ground coat enamel (borax 32, felspar 29, quartz 19, soda ash 9, sodium nitrate 5, fluorspar 4.7, cobalt oxide 0.8, manganese oxide 0.4 pts.) and to a base white enamel (borax 25.5, felspar 25, quartz 21, soda ash 3.5, sodium nitrate 3.0, cryolite 14.0, antimony oxide 3.0, zinc oxide 5.0 pts.) on the resistance of the enamel to impact, thermal shock, and acid attack, and on the opacity has been determined by Wolfram. All additions of zirconia made the enamel more viscous and thus increased the time of burning. The addition of zirconia to the smelter batches increased the resistance of the enamel to impact. Increased substitutions of zirconia for tin oxide in the mill increased the resistance to thermal shock, but increasing the amount of zirconia in the smelter batch decreased the resistance to thermal shock. The addition of zirconia to the smelter batch did not increase the resistance to attack by acid, but the substitution of zirconia for tin oxide in the mill gave a slightly increased resistance. Zirconia can be used as a satisfactory substitute for tin oxide in the mill additions as an opacifier (H. G. Wolfram, J. Amer. Ceram. Soc. 1924, 7, 1; J. Soc. Chem. Ind. 1924, 43, B. 218).

Zirconium hydroxide behaves as an amphoteric hydroxide, its compounds with the alkalis undergoing considerable hydrolysis in aqueous solution. The zirconates are produced either by adding zirconium salts (e.g. nitrate) to concentrated alkali solution, or by fusing zirconia with the alkaline hydroxides or oxides. The substances obtained by the wet process are probably adsorption products rather than definite chemical compounds, for prolonged washing gradually removes the alkali from the colloidal mass. The fusion process leads to *metazirconates* CaZrO_3 , Na_2ZrO_3 , and Li_2ZrO_3 , but even these products vary somewhat in composition. Other types, such as $\text{Li}_2\text{Zr}_2\text{O}_5$, have been described. When zircon (zirconium silicate) is fused with alkalis the crystalline silicozirconates are obtained, e.g. $\text{K}_2\text{O}(\text{SiO}_2, \text{ZrO}_2)$ and $\text{CaO}(\text{SiO}_2, \text{ZrO}_2)$, the latter being isomorphous with titanite (Ouvrard, Compt. rend. 1891, 112, 1444; 113, 80).

A zirconium hydroxide of the composition $\text{Zr}_2\text{O}_3(\text{OH})_4$, corresponding to the 5:4 basic zirconium chloride (v. *infra*), is obtained by adding ammonia to an aqueous solution of that compound; it appears to be chemically distinct from the normal hydroxide (Rodd, *loc.*).

Colloidal insoluble zirconium hydroxide (hydrogel) is produced by boiling solutions of zirconium oxychloride (Ruer, Zeitsch. anorg. Chem. 1905, 43, 282; van Benumelen, *ibid.* 1906, 49, 125). The hydrogel modification is prepared by adding ammonia to aqueous zirconium nitrate or by dissolving freshly-precipitated zirconium hydroxide in this solution (Müller, *ibid.* 1907, 52, 316).

There is no certain evidence of the existence

of a zirconium monoxide. The black powder assumed to be the monoxide is a mixture of metallic zirconium and the dioxide.

Zirconium peroxide is produced as a gelatinous precipitate by adding ammonia to aqueous zirconium sulphate containing hydrogen peroxide; or by the electrolysis of an alkaline sodium chloride solution in which zirconium hydroxide is suspended. The product is probably $\text{Zr}(\text{OH})_2 \cdot \text{O}_2 \cdot \text{H}_2\text{O}$, a hydrated form of ZrO_2 (Pissarjewski, Zeitsch. anorg. Chem. 1899, 25, 378; 1900, 31, 359; v. Bailey, Chem. Soc. Trans. 1886, 49, 481; 1889, 58, 705).

The alkali *perzirconates* $\text{Na}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ and $\text{K}_4\text{Zr}_2\text{O}_{11} \cdot 9\text{H}_2\text{O}$ are precipitated by alcohol, from cold aqueous alkaline solutions of the hydrated peroxide and hydrogen peroxide.

Zirconium hydride ZrH_2 , black powder, produced from metallic zirconium and hydrogen at red heat, burns in oxygen under ordinary pressure to the sesquioxide Zr_2O_3 , and in the compressed gas to zirconia. According to Schwarz and Konrad (Ber. 1921, 54, [B.] 2122), 10 gaseous hydride exists.

Zirconium fluoride ZrF_4 , anhydrous, sp.gr. 4.4333 at 16°, sparingly soluble in cold water, hydrolysed on warming, prepared by heating zirconia with ammonium hydrogen fluoride. The hydrate $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$, triclinic crystals, obtained by dissolving zirconia in hydrofluoric acid, is probably a hydrate of acid zirconyl fluoride $\text{ZrOF}_2 \cdot 2\text{HF} \cdot 2\text{H}_2\text{O}$.

Zirconofluorides. These double fluorides are of interest on account of their employment in the preparation of zirconium compounds and in the isolation of the element, and also because they illustrate the family relationship between zirconium and the other elements (silicon, titanium, and tin) of the fourth periodic group. Moreover, the existence of these well-defined crystallisable double salts distinguishes zirconium from the rare earth metals. They are produced by dissolving zirconium fluoride or oxide together with a metallic oxide or carbonate in aqueous hydrogen fluoride. The zirconofluorides corresponding with the general formula R_2ZrF_6 are the most stable, although other forms exist (Maignac, Compt. rend. 1860, 50, 952; Wells and Foote, Zeitsch. anorg. Chem. 1896, 10, 434; Amer. J. Sci. 1897, (iv.) 3, 466).

Potassium zirconofluoride K_2ZrF_6 , rhombic prisms, is the most important compound of this series; 100 parts of water dissolve 0.78 part of the salt at 2°, and 25.0 parts at 100°.

Zirconium tetrachloride ZrCl_4 can only be obtained pure by dry processes owing to its great tendency to undergo partial hydrolysis. It may be formed:

(i.) By the action of chlorine and sulphur chloride on heated zircon (Maignon and Bourron, Compt. rend. 1904, 138, 631). The chlorides of silicon and titanium are also produced in this process, but are readily separated owing to their greater volatility.

(ii.) The interaction at 300° of zirconium carbide, and chlorine (Wedekind, Zeitsch. anorg. Chem. 1902, 33, 81).

(iii.) Sublimation in chlorine of the product obtained by heating zirconia and phosphorus pentachloride in sealed tubes at 190° (Smith and Harris, J. Amer. Chem. Soc. 1896, 17, 448; v. Venable, *ibid.* 1894, 16, 469; Annalen, 1887,

239, 253; Compt. rend. 1885, 61, 109; 1872, 75, 1819; 1887, 104, 113; Ber. 1887, 20, 688).

The anhydrous chloride is a white crystalline sublimate of sp.gr. 2.803 fuming in moist air, reacting energetically with water, and combining with 1-8 molecules of dry ammonia (J. Amer. Chem. Soc. 1898, 20, 815, 839, 843; Ber. 1905, 38, 2611). It forms additive compounds with phosphorus pentachloride and sulphur tetrachloride, and double chlorides $B_2H_4 \cdot ZrCl_4$ with alcoholic pyridine



and quinoline hydrochlorides (Ber. 1905, 38, 812). For its reaction with methane and acetylene, see Venable and Deitz (Chem. Soc. Abst. 1923, ii. 170).

When zirconium tetrachloride is heated at about 250°C. with aluminium powder and a small quantity of aluminium chloride, in absence of air, it is reduced to zirconium trichloride, a brown, microcrystalline substance, which could not be obtained free from aluminium chloride. Zirconium trichloride is rapidly oxidised by air and decomposes water with evolution of hydrogen and formation of $ZrOCl_2$. When the trichloride is heated at about 330°C. it decomposes into tetrachloride and the dichloride $ZrCl_2$. The latter is a black, amorphous substance, which is almost insoluble in air free water, but is slowly oxidised in damp air. When heated above 600 C. the dichloride decomposes into the tetrachloride and zirconium (O. Ruff and R. Wallstein, Zeitsch. anorg. Chem. 1923, 128, 96-116; J. Soc. Chem. Ind. 1923, 42, 1220 A.)

Zirconium trichloride, obtained as a brown, microcrystalline solid, d^{20}_4 3.0, and the black dichloride formed by its dissociation at 330° generally resemble the titanium compounds (O. Ruff and R. Wallstein, Zeitsch. anorg. Chem. 1923, 128, 96).

Zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, colourless tetragonal prisms, the most characteristic product of hydrolysis of the tetrachloride, is somewhat sparingly soluble in concentrated hydrochloric acid, and is on this account utilised in the separation of zirconium. The addition of ether to an alcoholic solution of this oxy-salt produces a precipitation of metazirconium chloride $Zr_2O_3Cl_2$, corresponding with metastannic chloride. It is practically insoluble in strong hydrochloric or nitric acid, dissolves in water to an opalescent colloidal solution, and this liquid on dialysis furnishes metazirconic acid (J. pr. Chem. 1875, [ii.] 2, 219; Ber. 1907, 40, 803; Zeitsch. anorg. Chem. 1904, 42, 87; 1905, 43, 803; 48, 456; Compt. rend. 1912, 154, 1234). For zirconium chlorate, perchlorate, and iodates, see Venable and Smithey (J. Amer. Chem. Soc. 1919, 47, 1722).

A 5 : 4 basic zirconium chloride



has been described by Rödd (Chem. Soc. Trans. 1917, 111, 398), it gives a white curdy precipitate with any soluble sulphate. Zirconium oxychloride is very readily hydrolysed, forming complexes of the type $zZr(OH)_yZrOCl_z$, which react with the hydrochloric acid to form complex acids of the types $Zr(OH)_xCl_yH_z$, and $Zr(OH)_xCl_yH_z$ (Adolf and Pauli, Kolloid. Zeitsch. 1921, 20, 173).

Zirconium bromide $ZrBr_4$, crystalline white powder, and zirconium iodide ZrI_4 , yellowish-brown powder, are prepared by passing over heated zirconium or its carbide a stream of bromine vapour or hydrogen iodide respectively (Ber. 1904, 37, 1135; 1905, 38, 2611). The corresponding oxy-salts $ZrOBr_2 \cdot 8H_2O$ and $ZrOI_2 \cdot 8H_2O$ are produced by hydrolysis.

Zirconium carbide ZrC , hard metallic mass, scratching quartz but not ruby, is obtained by heating an intimate mixture of zirconia and carbon in the electric furnace (Moissan and Lengfeld, Compt. rend. 1896, 122, 651). A mixture of calcium carbonate, carbon, and zircon gives a similar result after extracting the fused mass with water and dilute hydrochloric acid. The carbide is also produced by heating native zirconia with carbon, using a current of 600 ampères (Wedekind, Ber. 1902, 35, 3929; Chem. Zeit. 1907, 31, 654). Zirconium carbide melts at 3400°-3500° Abs. (Friederich, Chem. Soc. Abstr. 1925, ii. 128, 374). It is an excellent conductor of electricity. A mixture of 90 parts with 10 parts of ruthenium made into filaments has been suggested for use in incandescent lamps. When heated in nitrogen the carbide furnishes zirconium nitride Zr_3N_4 . This nitride may also be obtained by heating the tetra-ammonia derivative of zirconium chloride $ZrCl_4 \cdot 4NH_3$ at 350° (Bruère and Chauvenet, Compt. rend. 1918, 167, 201). The nitride Zr_3N_4 is obtained by heating the metal in nitrogen at 1050°, D^{18}_4 0.75.

The extreme hardness of zirconium carbide renders it suitable as a polishing material and for cutting glass.

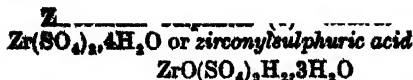
Zirconium silicide $ZrSi_2$, iron-grey rhombic crystals, sp.gr. 4.88 at 22°, is prepared by the aluminothermic process (200 parts aluminium, 250 parts sulphur, 180 parts sand, and 40 parts potassium zirconofluoride covered with a thin layer of magnesium as priming). It is not attacked by acids except hydrofluoric acid, and is only decomposed by caustic potash at moderately high temperatures (Compt. rend. 1906, 143, 224; v. Ber. 1902, 35, 3929). A colloidal variety of zirconium silicide has been observed (Zeitsch. Chem. Ind. Kolloide, 1910, 7, 249).

Zirconium silicate may be used in the preparation of opaque glazes and enamels in place of tin oxide.

Zirconium phosphate $ZrP_2O_7 \cdot 2H_2O$. Prepared by adding a solution of Na_2HPO_4 in 6N-hydrochloric acid to zirconium oxychloride in hydrochloric acid (Hevesy and Kimura, Zeitsch. angew. Chem. 1925, 38, 774). Zirconium phosphate is dissolved by hydrofluoric, oxalic, phosphoric, and conc. sulphuric acids (De Boer and van Arkel, Zeitsch. anorg. Chem. 1925, 144, 190; 148, 84).

Zirconium phosphite $Zr(PO_3)_2 \cdot H_2O$ is readily obtained by precipitation.

Zirconium hypophosphite $Zr(OPH_2O)_2 \cdot H_2O$ is obtained by adding hypophosphorous acid to a solution of zirconium nitrate until the precipitate has redissolved and then adding alcohol. It forms colourless, highly refracting crystals, which become deep violet on exposure to light (Häuser and Herzfeld, Zeitsch. anorg. Chem. 1913, 84, 92).



rhombic crystals from sulphuric acid solution. It is isomorphous with uranium sulphate $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and with cerium sulphate (Fernandes, Atti R. Accad. Lincei, 1925, [vi.], 2, 182; Gazz. chim. Ital., 1925, 55, 290) differs considerably in its properties from the oxychloride. The zirconium present is not precipitated as oxalate by oxalic acid or its soluble salts, and the precipitation which occurs with the aqueous chloride is prevented by the addition to this solution of sulphuric acid or an alkali sulphate. In hydrochloric acid solutions of the chloride the zirconium ion passes to the cathode on electrolysis, but in solutions of the sulphate the zirconium passes to the anode in the complex anion $(\text{ZrOSO}_4 \cdot \text{SO}_4)^{2-}$ (v. Hauser, Zeitsch. anorg. Chem. 1905, 45, 185; 1907, 53, 74; 54, 190; J. pr. Chem. 1907, [ii.] 76, 363; Ruer, Zeitsch. anorg. Chem. 1904, 42, 87; 1905, 46, 449).

(2) *Basic sulphates* (i.) 4 : 3 *Basic sulphate* $\text{Zr}_4(\text{SO}_4)_3(\text{OH})_{10} \cdot 10\text{H}_2\text{O}$, microscopic birefringent needles, separates at 39.5° from a solution of 10.2 molecules of $\text{Zr}(\text{SO}_4)_2$ in 1000 molecules of water. When dried at 300° the anhydrous compound $4\text{ZrO}_2 \cdot 3\text{SO}_3$ is obtained (Ber. 1904, 37, 2024; Zeitsch. anorg. Chem. 1910, 67, 369; Hauser and Herzfeld, Zeitsch. anorg. Chem. 1919, 106, 1).

(ii.) 2 : 3-*Basic sulphate*



is obtained in a crystalline form by boiling concentrated solutions of zirconium sulphate; in cold water it gradually changes into the preceding basic salt.

(iii.) 5 : 2-*Basic sulphate* $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$ or $\text{Zr}_5\text{O}_8(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$ is obtained by adding sulphuric acid or ammonium sulphate to the 5 : 4-basic chloride (Rodd, l.c.; cf. Rossiter and Sanders, J. Soc. Chem. Ind. 1921, 40, 70 T).

(3) *Acid sulphate* $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, monoclinal prisms or needles, is a very hygroscopic salt produced by adding strong sulphuric acid to an aqueous solution of zirconylsulphuric acid (Zeitsch. anorg. Chem. 1907, 54, 196).

(4) *Complex sulphates*. These are of two types $\text{Zr}_2\text{O}_3(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ and $\text{Zr}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$, where R is an alkali metal; the former are produced by adding an alkali sulphate to a solution of zirconium oxide in aqueous alkali disulphate and the latter by dissolving zirconium hydroxide in a boiling saturated solution of alkali disulphate (Ber. 1907, 40, 803, 810).

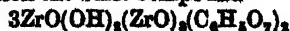
Combinations of normal zirconyl sulphate with alkali sulphates have been described by Chauvenet and Gueylard (Compt. rend. 1918, 167, 24; cf. Hauser and Herzfeld, l.c.).

Zirconium nitrate. Aqueous solutions of zirconium hydroxide in nitric acid yield on evaporation *basic nitrates* $\text{Zr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zr}_2\text{O}_3(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ (Chauvenet and Nicolle, Compt. rend. 1918, 166, 821).

Zirconium nitride, m.p. 2530° D 6-93, is prepared by heating the oxide with carbon in nitrogen at 1900° (Z. Physik. 1925, 21, 813).

Normal zirconyl citrate $(\text{ZrO})_2(\text{C}_6\text{H}_5\text{O}_7)_2$ may be prepared by adding a dilute solution of

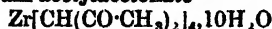
acid to a freshly prepared solution of zirconyl chloride. If the zirconyl chloride is boiled before precipitation the basic compound



is formed (Venable and Lineberry, J. Amer. Chem. Soc. 1922, 44, 1708).

Zirconium oxalate is a basic salt $\text{ZrO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ or $4\text{H}_2\text{O}$, white powder, hydrolysed by water. By saturating aqueous oxalic acid with zirconium hydroxide an *acid oxalate* $\text{Zr}(\text{OH})(\text{C}_2\text{O}_4)_2 \cdot 7\text{H}_2\text{O}$ is obtained in large prisms. Double oxalates are produced by dissolving zirconium hydroxide in solutions of the alkali hydrogen oxalates (Mandl, Zeitsch. anorg. Chem. 1903, 37, 252; v. Venable and Baskerville, J. Amer. Chem. Soc. 1897, 19, 12).

Zirconium acetylacetonate



crystallises from an aqueous solution of zirconium nitrate and acetylacetone to which sodium carbonate is cautiously added; it is dehydrated by repeated crystallisation from absolute alcohol when it separates in needles.

Zirconium tetrachloride reacts with benzoylacetone in dry ether to form $(\text{CHAcBz})_2\text{ZrCl}_2$, m.p. 232°-231°, or in boiling benzene to form $(\text{CHAcBz})_2\text{ZrCl}_2$, m.p. 129° (Morgan and Bowden, Chem. Soc. J. 1924, 125, 1252; Dilthey, J. pr. Chem. 1925, ii. 111, 147).

Hafnium. *Cultum*. Associated with zirconium and found in many common zirconium minerals to the extent of from 1 to 30 p.c. of their zirconium content, especially the zircons and zirconium minerals like alvite, cyrtolith, naegeite, and malakon, is the element *hafnium*, discovered by G. von Hevesy and Cooter by using Moseley's method of X-ray spectroscopy. The zirconium extracted from alakon contains 21 p.c. of hafnium, and a specimen of cyrtolith from Rockport contained 10 p.c. hafnium. The methods of separating hafnium from zirconium are based partly on the different solubilities or vapour pressures of the corresponding compounds, partly on the difference in their basicity. The solubilities of the double fluorides $(\text{NH}_4)_2\text{RF}_6$, $(\text{NH}_4)_2\text{RF}_6$, and K_2RF_6 of zirconium and of hafnium have been determined by Hevesy, Christiansen, and Berglund (Zeitsch. anorg. Chem. 1925, 144, 69).

The most practical method of separation is the crystallisation of the double fluorides of potassium or ammonium. The mineral is melted with KFHF and the K_2ZrF_6 extracted with boiling water, in which this compound is soluble to the extent of 25 p.c. cent. On cooling down the greater part of the salt crystallises out. The zirconium double fluoride being less soluble (2.6 p.c. at 20°) than the hafnium double fluoride (nearly 3 p.c. at 20°), the latter accumulates in the mother liquor. Still more convenient is the crystallisation of the highly soluble $(\text{NH}_4)_2\text{ZrF}_6$, soluble at 20° to the extent of 26 p.c. The ammonium double fluoride of hafnium crystallises in beautiful prismatic (pseudo-hexagonal) crystals. The next suitable method of separation is the crystallisation of the ammonium zircon oxalate. A soluble zirconium salt, like the stilphate, is precipitated with ammonia, the hydroxide dissolved in an excess of oxalic acid and neutralised with ammonia. By crystallising the oxalate formed, hafnium accumulates in the mother liquor.

G. Hevesy and V. T. Jantzen have given detailed accounts (*Chem. News*, 1923, 127, 353, see also De Boer and van Arkel, *Zeitsch. anorg. Chem.* 1924, 141, 284) of the preparation of ammonium zirconium fluoride and ammonium hafnium fluoride from alvite, and of the separation of hafnium from this mineral by the double fluoride method, employing the ammonium double fluorides (*Abstracts*, 1923, ii, 570). For the separation of zirconium and hafnium by fusing the ores with hydrofluoric acid and potassium fluoride, see also Fr. Pats. 568971, 569016; *Chem. Soc. Abstr.* 1925, 128, ii, 62, 63).

Less satisfactory is the result of the crystallisation of the complex sulphate, like the ammonium salt of zirconium and sulphuric acid. The hafnium concentrates here also in the mother liquor (see also Marquis and Urbain, *Compt. rend.* 1925, 180, 1377).

Hafnium phosphate $\text{HfH}_2\text{P}_2\text{O}_7$ is less soluble in hydrochloric acid than zirconium phosphate, and a separation of the two may be carried out in concentrated acid (von Hevesy and Kimur, *Zeitsch. angew. Chem.* 1925, 38, 774; *J. Amer. Chem. Soc.* 47, 2540).

To purify zirconium from iron and other impurities it is often converted into the oxychloride. By repeatedly crystallising this compound from hydrochloric acid pure zirconium is retained. Hafnium oxychloride is less soluble than zirconium oxychloride; thus while purifying zirconium from iron, its hafnium content is raised at the same time. For example, starting from 100 grs. ZrOCl_2 containing 1 p.c. hafnium, the 30 grs. oxychloride residue obtained after 10 successive crystallisations contained a little over 2 p.c. hafnium.

Hafnium is more basic than zirconium, and accordingly when precipitating a solution of a zirconium salt with ammonia the first precipitate contains less hafnium than the successive ones.

For example, when precipitating one half of an oxychloride solution containing 1 p.c. hafnium with dilute ammonia, the precipitate contains only 0.8 p.c., whilst the hafnium content of the solution is increased to 1.2 p.c. This difference can be somewhat increased by the presence of large amounts of ammonium chloride in the solution. By boiling a solution of zirconium and hafnium with sodium thiosulphate, zirconium being more strongly hydrolysed, the first precipitate contains a larger amount of zirconium than the successive ones. From a solution of zirconium sulphate, diluted about 1:40, a basic zirconium compound precipitates on standing a few days at 39.5°. Also with this process, like many similar ones, the precipitate contains slightly more zirconium than the solution.

The difference in the basicity is also shown on heating the neutral sulphate of zirconium or hafnium; whereas the first mentioned compound begins to decompose above 400°, the decomposition temperature of $\text{Hf(SO}_4)_2$ lies about 100° higher.

On dissolving the oxychloride in alcohol and precipitating with ether a higher basic compound $\text{Zr}_2\text{O}_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ is formed, which is found to be less soluble than the corresponding hafnium compound. This difference in the solubilities was repeatedly used by V. T. Jantzen

and von Hevesy to purify concentrated hafnium preparations from zirconium.

In some cases, including the phosphate, salicylate, the hafnium compounds were found to be less soluble than the corresponding zirconium compounds.

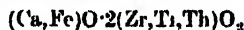
Like zirconium tetrachloride, hafnium tetrachloride also volatilises appreciably at about 250°, and the first distillate contains somewhat more zirconium than hafnium.

Though hafnium is to be placed in the periodic table between zirconium and thorium where formerly cerium was placed, its chemical properties are not intermediate between those of zirconium and thorium, but much nearer to the former element. It is of interest to note that in several cases the solubility of the hafnium compound is greater than the solubility of the corresponding zirconium compound and thorium compound. Thus the solubility of the hafnium double fluoride is much greater than that of the thorium double fluoride and somewhat greater than the solubility of the zirconium double fluoride (G. von Hevesy, *Brit. Assoc. Reports, Liverpool Meeting*, 1923). A preliminary determination employing hafnium containing from 5 to 6 p.c. of zirconium indicated that the atomic weight of hafnium is between 178.4 and 180.2.

The atomic weights of the zirconium of the rare earth fractions of a number of zirconium minerals have been determined. The zirconium fractions of the different minerals (purified through the oxychloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, which does not cause removal of hafnium) gave atomic weights varying from 90.3 to 95.0, as determined from the conversion of sulphate into oxide. The higher atomic weights corresponding with a higher hafnium content, were obtained with minerals of higher rare earth (yttrium metals, atomic weight 96-93) content (E. Urbain and G. Urbain, *Compt. rend.* 1924, 178, 268; *Chem. Soc. Abstr.* 1924, 126, ii, 194).

The density of hafnium dioxide at 20° is 9.67, while that of zirconium dioxide is 5.73. This difference may be used in determining the percentage of hafnium dioxide in zirconia (Hevesy and Berglund, *Chem. Soc. Trans.* 1924, 125, 2372).

ZIRKELITE. Zirconate, titanate, and thorate of calcium, iron, &c.



crystallised in the rhombohedral system. Analyses show ZrO_2 , 30.73-52.80, ThO_2 , 0.23-20.44, UO_2 , 1.4-14 replacing thoria, Ce_2O_3 , &c. up to 3.61, Y_2O_3 up to 1.08 p.c. The mineral is black or brownish-black, opaque, and with a resinous to sub-metallic lustre; sp.gr. 4.70-5.22, H. 5½; slowly decomposed by hydrochloric acid, but readily by hydrofluoric acid. Crystals are small, and their form is usually obscured by twinning. Crystals of octahedral habit are found with baddeleyite in the rock jacupirangite (a magnetite-pyroxenite) at the Jacupiranga iron mine in São Paulo, Brazil. Grains and crystals are found in the gem-gravels at several places in Sabaragamuwa province, Ceylon. L. J. S.

ZIRKITE or BADDELEYITE.

Zirkite is an impure zirconium dioxide containing silica, iron, and titanium as the chief

Properties. It is not suitable as a refractory, since its melting-point lies between 1200° and 2000°, whilst that of zirconium oxide is 2950°-3000°. The mineral may be converted into a substance sufficiently refractory for most purposes by heating a mixture of the ore with coke in an arc furnace, the amount of carbon being such that it will combine with the silicon alone. Such treatment removes 90-95 p.c. of the silicon; if, however, the amount of coke is in excess of that stated, the removal of the silicon is less complete, owing to the formation of stable double carbides of zirconium and silicon. When the silicon has been removed the iron is removed by treatment with chlorine. Zirconium carbide is exceedingly refractory, being infusible in a 40-50 kw. arc, but its use is restricted as it is oxidised at high temperatures (Thompson, J. Phys. Chem. 1922, 26, 812, J. Soc. Chem. Ind.

In order to prepare zirconium oxide, zirkite is digested at 275°-310°C. with concentrated sulphuric acid (sp.gr. 1.84) in the proportion of 2 parts of acid to 1 part of ... About 57 p.c. of the zirconia content of the ore passes into solution; the remainder is combined with silica and insoluble under these conditions. The product is diluted with about 20 times its volume of water and the insoluble portion filtered off. The solution of the basic sulphate is then treated with calcium carbonate or chloride, or a mixture of carbonate and chloride, in such a quantity as is necessary to reduce the sulphuric acid content to a value equal to one-half the zirconium dioxide content. The calcium sulphate is filtered off, the filtrate considerably diluted (about 50 times), and the precipitate filtered off, washed and strongly heated. The result is not so good with calcium chloride alone as with calcium carbonate, but the product in the former case is whiter and more granular (Bain and Gollop, Canad. Chem. and Met. 1922, 7, 35; J. Soc. Chem. Ind. 1923, 42, 351 A.). For methods of improving the refractory qualities of zirkite by eliminating the associated impurities, the chief of which are silicon, iron, and titanium. The melting-point of the raw ore varies from 1200°-2000°, while that of the pure oxide is 2950°-3000°. The method for purification found most satisfactory is based on the fact that zirconium carbide is stable at temperatures above the decomposition point of silicon carbide (J. G. Thompson, J. Phys. Chem. 1922, 26, 812).

A rock-forming mineral of the

epidote group, consisting of basic calcium aluminium silicate $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \cdot \text{SiO}_2$, or $\text{Ca}_2(\text{AlOH})_4(\text{SiO}_3)_2$, crystallised in the orthorhombic system. Crystals are prismatic in habit and have a perfect cleavage parallel to the brachypinacoid; but the mineral is more often found as columnar or compact granular masses of a dull greyish colour. Sp.gr. 3.3, H. 6; decomposed by hydrochloric acid after being previously heated. It occurs as a constituent of crystalline schists. An interesting variety, known as *thulite*, is found as rose-pink granular masses at Lerviken near Trondhjem, and intermixed with sky-blue vesuvianite ('cyprius') at Souland, Telemark, Norway. This polishes well and is occasionally used as an ornamental stone. A rock also sometimes used for small ornaments in the prettily coloured eclogite from Sau Alp in Carinthia, and the Fichtel in Bavaria; this consists of emerald-green blende ('smaragdite'), reddish garnet, and bluish-grey zoisite. L. J. S.

ZOOMARIC ACID ($\text{C}_{18}\text{H}_{30}\text{O}_2$), an acid discovered by Bull in cod liver oil, and found in the oils and fats of most marine animals.

ZORGITE. Selenide of lead and copper ($\text{Pb,Cu}_2\text{Se}$), containing Se 29-34 p.c. It is a massive granular mineral with a lead-grey colour and metallic lustre. Sp.gr. 7-7.5, H. 2½. It is found together with other selenides at Zorge and several other localities in the Harz, and at Cacheuta in Mendoza, Argentina. L. J. S.

ZYCLOFORM *p*-Aminobenzoic isobutyl ester.

ZYGADENINE. A crystalline alkaloid ($\text{C}_{13}\text{H}_{15}\text{NO}_3$) found in the leaves of *zygadenus intermedius*. Shining needles from benzene; rhombic crystals from alcohol, m.p. 200°-201°. Very soluble in chloroform, sparingly soluble in ether. Specific rotation in chloroform -48.2°. An acid solution precipitates Mayer's reagent, gives a crystalline chloroaurate. With conc. sulphuric acid, an orange colour changing to cherry-red. In physiological action resembles veratrine (Henry, Hepner and Loy, J. Amer. Chem. Soc. 1913, 35, 258).

ZYMASE *v.* FERMENTATION.

ZYMIN *v.* SYNTHETIC DRUGS.

ZYMURGY. A term used to denote that section of applied chemistry which treats of the scientific principles of those arts in which fermentation is employed—e.g. preparation of yeast, vinegar, wine, beer, alcohol.

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A DICTIONARY
OF
APPLIED CHEMISTRY

VOL. VII

A DICTIONARY
OF
APPLIED CHEMISTRY

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ASSISTED BY EMINENT CONTRIBUTORS

REVISED AND ENLARGED EDITION

VOL. VII.

WITH AN INDEX TO THE WHOLE WORK BY
FRANCES M. G. MICKLETHWAIT

WITH ILLUSTRATIONS.

LONGMANS, GREEN AND CO. LTD.

CALCUTTA, BOMBAY AND MADRAS

1927

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Amer. Min.</i>	American Mineralogist.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst.</i>	The Analyst.
<i>Annalen</i>	Annalen der Chemie (Justus Liebig).
<i>Ann. Appl. Biol.</i>	Annals of Applied Biology.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Falsif.</i>	Annales des Falsifications.
<i>Ann. Inst. Pasteur.</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik.</i>	Annalen der Physik.
<i>Ann. Physique.</i>	Annales de Physique.
<i>Ann. Report.</i>	Annual Reports of the Chemical Society.
<i>Annali Chim. Appl.</i>	Annali di Chimica Applicata.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arch. exp. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Astrophys. J.</i>	Astrophysical Journal.
<i>Atti R. Accad. Lincei.</i>	Atti della Reale Accademia dei Lincei.
<i>Bentl. a. Trim.</i>	Bentley and Trimen. Medicinal Plants.
<i>Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
<i>Bio-Chem. J.</i>	The Bio-Chemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Brewers J.</i>	Brewer's Journal.
<i>Brit. Assoc. Rep.</i>	Report of the British Association for the Advancement of Science.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Asso. Chim. Suor.</i>	Bulletin de l'Association des Chimistes de Sucrierie et de Distillerie.
<i>Bull. Imp. Inst.</i>	Bulletin of the Imperial Institute.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. Biol.</i>	Bulletin de la Société de chimie Biologique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Chem. and Met. Eng.</i>	Chemical and Metallurgical Engineering.
<i>Chem. Ind.</i>	Chemische Industrie.
<i>Chem. News.</i>	Chemical News.
<i>Chem. Soc. Abstr.</i>	Chemical Society of London. Abstracts.
<i>Chem. Soc. Proc.</i>	Journal of the Chemical Society of London. Proceedings.
<i>Chem. Soc. Trans.</i>	Journal of the Chemical Society of London. Transactions.
<i>Chem. Umschau.</i>	Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse, und Harze.
<i>Chem. Weekblad.</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dingl. poly. J.</i>	Dingler's polytechnisches Journal.
<i>D. R. P.</i>	Deutsches Reichs-Patent.
<i>Färber-Zeit.</i>	Färber-Zeitung.
<i>Flück. a. Hanb.</i>	Flückiger and Hanbury. Pharmacographia.
<i>Frdl.</i>	Friedländer's Fortschritte der Teerfarbenfabrikation.
<i>Gazz. Chim. Ital.</i>	Gazzetta Chimica Italiana.
<i>Helv. Chim. Acta J.</i>	Helvetica Chimica Acta.
<i>Jahrb. Min.</i>	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
<i>Japan J. Phys.</i>	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
	Japanese Journal of Physics.

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<i>J. Agric. Res.</i>	Journal of Agricultural Research.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Bact.</i>	Journal of Bacteriology.
<i>J. Bd. Agric.</i>	Journal of the Board of Agriculture.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Chem. Soc. Japan</i>	Journal of the Chemical Society of Japan.
<i>J. Chim. Phys.</i>	Journal de Chimie Physique.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i>	Journal of General Physiology.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Inst. Brewing</i>	Journal of the Institute of Brewing.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Soc. Japan</i>	Journal of the Pharmaceutical Society of Japan.
<i>J. Phys. Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Soc. Dyers.</i>	Journal of the Society of Dyers and Colourists.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Kolloid Zeitsch.</i>	Kolloid-Zeitschrift.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Met. & Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Zeil.</i>	Pharmaceutische Zeitung.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society.
<i>Phot. J.</i>	Photographic Journal.
<i>Physikal. Z.</i>	Physikalische Zeitschrift.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i>	Proceedings of the Physical Society of London.
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Rec. trav. chim.</i>	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Sci. Abstr.</i>	Science Abstracts.
<i>Sci. Proc. R. Dublin Soc.</i>	Scientific Proceedings of the Royal Dublin Society.
<i>Sitz.</i>	Sitzungsberichte der K. Akademie zu Wien.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i>	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Swiss Pat.</i>	Swiss Patent.
<i>T.</i>	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>U.S. Pat.</i>	United States Patent.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Krist.</i>	Zeitschrift für Kristallographie.
<i>Zeitsch. Krist. Min.</i>	Zeitschrift für Kristallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i>	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. Physik.</i>	Zeitschrift für Physik.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Z. Elektrochem.</i>	Zeitschrift für Electrochemie.
<i>Z. ges. Brauw.</i>	Zeitschrift für das gesamte Brauwesen.

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OTTO N. WITT, Geh. Prof. Dr. (the late), *The Polytechnic, Charlottenburg, Berlin.* [TRIMETHYLENE COLOURING MATTERS, revised with supplement by ARTHUR E. EVEREST, q.v.]

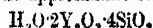
SYDNEY YOUNG, D.Sc., F.R.S., F.I.C., *Professor of Chemistry, Trinity College, Dublin.* [THERMOMETERS.]

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A DICTIONARY OF APPLIED CHEMISTRY.

THALENITE. Silicate of yttrium (Y_2O_3 , 53.64 p.c.) with the approximate formula



Several other constituents are present in small amount, including 1.4-2.5 p.c. of gas (nitrogen and helium) liberated when the mineral is heated or treated with acids. It is yellow to flesh-red and translucent with a greasy lustre; sp.gr. 4.11-4.23; H. 6½; readily decomposed by dilute hydrochloric acid with separation of gelatinous silica. Monoclinic crystals and massive material occur with fluorocrite, gadolinite, and allanite in quartz at Osterby in Sweden.

L. J. S.

THALLIUM, sym. Tl., at.wt. 204.0, was discovered spectroscopically by Crookes in 1861 (Chem. News, 1861, 3, 193) in a seleniferous deposit from a sulphuric acid manufactory. It occurs in many iron and copper pyrites, in some micas, in zinc blendes, in the minerals *marcasite*, *hematite*, *crookesite* ($CuTlAg_2Se$, *lorundite* ($TlAsS_4$), *urbaitite* $TlAs_2SbS_6$, and in various other iron and manganese ores (Igelström, Z. Krist. Min. 1895, 25, 94; Antipoff, J. Russ. Phys. Chem. Soc. 1896, 28, 384; Hartley and Ramage, Chem. Soc. Trans. 1897, 533). It also occurs in small quantities in various mineral springs, and has been found in volcanic exhalations.

Its presence has been observed in crude zinc (Kosmann) and in platinum and its ores (H. N. Warren, Chem. News, 1887, 55, 241).

Thallium is prepared from fine dust by boiling it with dilute sulphuric acid and precipitating the chloride or iodide by treatment with hydrochloric or hydriodic acid, after which the metal can be obtained by electrolytic deposition, by the action of potassium cyanide or by electrolysis (Bunsen, Phil. Mag. 1865, [iv.] 20, 168; Foerster, Zeitsch. anorg. Chem. 1897, 15, 71). Traces of lead, tin, copper, and aluminium occur as impurities in commercial thallium (Pollock, Sci. Proc. Roy. Dublin Soc. 1899, 11, 338).

Thallium is a bluish-white, lead-like, crystalline, extremely soft metal, malleable, but of

low tenacity. It exists in two modifications, the transition temperature being 226° (235.3° , Richards and Smyth). Its sp.gr. is 11.85, its m.p. 303° (Potrenko; Zeitsch. anorg. Chem. 1906, 50, 133), its b.p. in vacuum 818° (Krafft and Knocke, Ber. 1909, 42, 202); at ordinary pressure $1515 \pm 2^\circ$ (Isaac and Tammann, *ibid.* 1907, 55, 58); but its b.p. should be 1462° at 760 mm. It gives a monatomic vapour. For its absorption spectrum, see W. Grotrian, Zeits. f. Physik. 1923, 12, 218-231; Narayan, Gannaiya and Rao, Proc. Roy. Soc., 1914, A., 100, 596. It commences to volatilise at 174° in *vacuo*. At a high temperature it may be distilled in a current of hydrogen. When heated it burns with a beautiful green flame, and its flame spectrum is characterised by a single green line. The heat of solution of thallium in thallium amalgams of 0.0-11.17 p.c. thallium has been determined by Theodore W. Richards and Charles P. Smyth by the adiabatic method (J. Amer. Chem. Soc. 1923, 45, 1435-1460). The following values of the heat of solution in joules at 20° of 1 gram-atom of thallium in amalgams of the composition stated are recorded: 0.92 p.c., 2706; 2.49 p.c., 2265; 3.81 p.c., 1917; 5.21 p.c., 1590; 6.89 p.c., 1975; 8.76 p.c., 486; 10.43 p.c., 45; 11.81 p.c., 234. These values are compared with those obtained by Richards and Daniels for concentrated amalgams, and found to be consistent with them (A. 1920, ii. 34). A short extrapolation of the composition-heat of solution curve above 0.92 p.c. gives a value for the heat of solution of thallium in an infinite quantity of mercury of 2970 joules, a value which is in fair agreement with 3220 joules, the value obtained by Lewis and Randall (Chem. Soc. Abstr. 1921, ii. 241) by calculation from the E.M.F. measurements of Richards and Daniels (*loc.*) of thallium amalgam concentration cells (Abstr. J. Chem. Soc. 1923, 123, 124, ii. 536).

The temperature of transformation of α - into β -thallium was found by Asahara (Chem. Soc. Abstr. 1925, ii. 463, 645) to be 232° .

Thallium oxidises before the blowpipe. It dissolves readily in dilute nitric and sulphuric

THALLIUM.

acids, but more slowly in hydrochloric acid, and at a red heat decomposes water.

Thallium and its salts are very poisonous (Curci, Chem. Zentr. 1895, ii. 999; Swain and Bateman, J. Biol. Chem. 1910, 7, 137). Thallium forms alloys with a large number of metals, and an amalgam with mercury, which has been proved to be useful in thermometry (McIntosh and Johnson, J. Amer. Chem. Soc. 1912, 34, 910; Pavlovitch, J. Russ. Phys. Chem. Soc. 1915, 47, 29; Hildebrand and Eastman, J. Amer. Chem. Soc. 1915, 37, 2452). The existence of a solid compound Tl_2Hg has been established by Richards and Daniels (J. Amer. Chem. Soc. 1919, 41, 1732), who have studied the electro- and thermo-chemical behaviour, densities and freezing points of thallium amalgams (cf. Richards and Smyth, J. Amer. Chem. Soc. 1922, 44, 524). For references to alloys, see Masumi Chikashigé (Zeitsch. anorg. Chem. 1912, 78, 68); Kurnakov, Shemtschushin, and Tararin (J. Russ. Phys. Chem. Soc. 1913, 45, 300); Rolla (Gazz. chim. ital. 1915, 45, i. 185; Di Capua, Chem. Soc. Abstr. 1925, ii. 787). For the electric resistance of thallium in the temperature field of liquid helium, see H. K. Onnes and W. Tynj (K. Akad. Amsterdam, Proc. 25, 1923, 9 and 10, pp. 443-450, Comm. No. 160A, from the Phys. Lab. Leiden).

Compounds.—Thallium forms two series of compounds—

(1) **Thallic** (TlX_3) compounds in which the metal is trivalent, corresponding to its position in the aluminium group. Like the compounds of aluminium, the thallic salts undergo hydrolysis in aqueous solution and form complex salts more readily than the corresponding thallous compounds (Spencer and Abegg, Zeitsch. anorg. Chem. 1905, 44, 379). Metallic thallium reduces the thallic salts to the thallous condition. They are also reduced by hydroxylamine in acid or alkaline solutions, by acid solutions of ferrous sulphate, by sodium arsenite solution and, on boiling, with finely divided copper (Berry, Chem. Soc. Trans. 1922, 394). In the absence of oxidising agents, even in the presence of thallous salts, thallic salts give the blue coloration of indophenols when α -naphthol and dimethyl-*p*-phenylene-diamine are added to an alkaline solution of the salt (Marigo, Gazz. chim. ital. 1907, 37, i. 55).

(2) **Thallous** (TlX) compounds in which thallium is monovalent. The thallous salts closely resemble the salts of the alkali metals; thus the hydroxide and carbonate are readily soluble and give an alkaline aqueous solution. Many of the thallous salts, like the sulphate, phosphate, &c., are isomorphous with the corresponding potassium salts and give double salts with platinum chloride Tl_2PtCl_6 . The alums $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and other double sulphates are also closely analogous to the corresponding potassium salts. The thallous halides and sulphides, on the other hand, resemble the corresponding lead and silver salts. Thallous salts react with a clear aqueous solution of antimony chloride and potassium iodide, giving a characteristic voluminous orange precipitate of the compound $3Tl_2SbI_3$ (Eppraim, Zeitsch. anorg. Chem. 1908, 58, 353).

Thermal studies of the systems formed by thallous nitrate with mercuric chloride, bromide,

and iodide show that no double decomposition occurs, but the following compounds are formed: $TlNO_3 \cdot HgCl_2$, m.p. 202.5° ; $2TlNO_3 \cdot HgCl_2$, m.p. 195° ; $TlNO_3 \cdot HgBr_2$, m.p. 152° (A. G. Bergmann, T. A. Hepke, and F. M. Isakén, J. Russ. Phys. Chem. Soc. 1922, 54, 466; see also J. Russ. Phys. Chem. 1922, 54, 200).

Oxides.—Thallium trioxide (thallic oxide) Tl_2O_3 is formed when an alkaline solution of a thallous salt is treated with 3-5 p.c. solution of hydrogen peroxide. When the precipitation is made in the cold, the oxide is brown, is readily soluble in acids, and has sp.gr. 9.65 at 21° , but when the solutions are hot, the oxide is black, is sparingly soluble in acids, and has the sp.gr. 10.19 at 22° . The brown oxide is partly reduced when boiled with water, but the black oxide remains unchanged. At 100° the brown slowly changes into the black variety, and at 520° this change is complete within 24 hours (Rabe, Zeitsch. anorg. Chem. 1900, 48, 427; *ibid.* 50, 158; *ibid.* 1907, 55, 130). Thallic oxide may also be made by acting upon thallous sulphate with an alkaline solution of potassium ferricyanide (cf. Berry, Chem. Soc. Trans. 1922, 394). The crystalline oxide obtained by heating the nitrate has sp.gr. 9.97 (Thomas, Compt. rend. 1904, 138, 1697; see also Fortini, Gazz. chim. ital. 1905, 35, ii. 450). Thallous hydroxide is readily obtained in good yellow, micro-crystalline powder by adding to thallous ethoxide in the cold an equal volume of water, and drying the precipitate on porous plates out of contact with air. A determination of the heat of hydration of thallous oxide by finding the difference in the heat of solution of the oxide and hydroxide in dilute hydrofluoric acid gave a value 3.117 cal., compared with 3.231 cal. found by Thomsen. The heat of hydration is therefore very far removed from that of the oxides of the alkali metals, but thallous hydroxide is nevertheless an equally powerful base, and towards feeble acids, phenols, &c., shows even stronger basic properties than the alkali hydroxides. It can be estimated acidimetrically using phenolphthalein as indicator (R. de Forcrand, Compt. rend. 1923, 176, 873-876; J. Chem. Soc. 1923, 124, ii. 420).

The oxide dissolves in concentrated hydrochloric acid without evolution of chlorine, forming thallic chloride.

Thallium monoxide (thallous oxide) Tl_2O is obtained by shaking fine turnings of the metal with cold water in a current of oxygen or by heating the corresponding hydroxide at 150° - 200° in nitrogen. It is a black powder, m.p. 300° , readily dissolving in water with formation of the hydroxide $TlOH$, which crystallises with 2 molecules of water in yellow needles. The hydroxide is darkened by light, turns turmeric brown, and finally destroys the colouring matter.

With phenolphthalein, thallous hydroxide gives a yellow colour which is slowly discharged by moderately concentrated aqueous solutions, especially on warming. It dissolves in tin to form a deep purple liquid, the colour of which on warming with slight excess of the reagent changes to yellow, due to the formation of a salt of isatic acid. Thallous salts are generally isomorphous with the salts of the alkali metals (Thorpe, J. 1876, i. 859).

Thallous salts of mono- and di-basic normal

aliphatic acids have been prepared. The *valerate* described by Kuhlmann (Annalen, 1863, 126, 78) is prepared by adding thallous hydroxide solution to valeric acid until the reaction is faintly alkaline to litmus, evaporating the solvent, and recrystallising the residue from benzene. The salt, m.p. 145°-147°, is very soluble in water, ethyl alcohol, or hot benzene, readily soluble in amyl alcohol, and sparingly soluble in boiling ether, hot light petroleum, or cold benzene. It is not readily thrown out of solution in ethyl alcohol by addition of ether.

The *palmitate*, prepared by adding 33 p.c. thallous hydroxide solution to a hot alcoholic solution of palmitic acid until the reaction is neutral to litmus, crystallises from alcohol in feathery aggregates. It is readily soluble in hot alcohol, insoluble in ether, and soluble in water, the solution being opalescent when dilute. On shaking a warm dilute aqueous solution a froth forms on the surface, which disappears on cooling, and is not formed on shaking the cold solution. It softens on heating at 116°-118°, but does not melt completely at 170°.

The *oleate*, is prepared by adding the theoretical amount of thallous hydroxide solution to oleic acid, dissolved in alcohol, and evaporating the solution to dryness in a vacuum desiccator. The residual soap separates from ethereal solution in white needles, which are soft and can easily be bent. On drying they cohere to a solid, soap-like mass. The salt is also soluble in perfectly dry ether free from alcohol. It forms an opalescent solution and, on shaking, a froth permanent in the cold (distinction from the palmitate). It forms a jelly below the main bulk of the solution, the volume of the jelly being many times greater than that of the oleate left undissolved.

The normal *adipate* is prepared by accurately neutralising adipic acid with aqueous thallous hydroxide solution, using phenolphthalein as indicator. The solution is evaporated to small bulk and the crude adipate precipitated with ethyl alcohol. The salt is dissolved in ethylene glycol, in which it is very soluble, and butyl alcohol added with continued heating until a faint cloudiness is apparent in the boiling mixture; on cooling, the salt separates out in crystalline leaflets.

The normal *pimelate* is obtained by neutralising an aqueous solution of pimelic acid with thallous hydroxide solution, using phenolphthalein as indicator and evaporating the solution to dryness. It is much more soluble in water than the normal adipate, and is almost insoluble in ethyl alcohol, but can be recrystallised from amyl alcohol, in which at the boiling-point it is sparingly soluble, separating on cooling in long needles. The acid *pimelate* is readily soluble in water, almost insoluble in ethyl alcohol, and crystallises from amyl alcohol in prisms.

Thallous salt of ethyl acetonedicarboxylate.—Minute needles, melting at 125° (decomp.), readily soluble in cold ethyl or methyl iodide, thallous iodide being deposited on standing or on heating. This property is shared by thallous acetylacetonate (Kurzwil, Ber. 1910, 43, 1078; Morgan and Moss, J. 1914, 105, 195).

Thallous salts of fumaric, maleic, succinic and

tartaric acids, and also of cresol, resorcinol, guaiacol, naphthol and vanillin are described by Christie and Menzies (J. Chem. Soc. 1925, 127, 2308).

Qualitative reactions of aqueous thallous hydroxide solutions with sugars.—In concentrated aqueous solution, fructose, glucose, and xylose give with thallous hydroxide solution in the cold yellow precipitates which, on heating, become reddish-yellow, and finally very dark; under suitable conditions mirrors are formed. With dilute solutions no precipitates are formed with glucose and fructose, but the same colour changes are observed on heating, and again on heating thallium mirrors are formed, provided only the thallous hydroxide is present in sufficient excess. Sucrose and mannitol can be boiled with 10 p.c. thallous hydroxide solution without change other than the appearance of a faint yellow colour, but after hydrolysis of sucrose with dilute sulphuric acid mirrors are formed on subsequent heating with thallous hydroxide solution. The formation of mirrors is favoured by addition of ammonium or sodium hydroxide. Good results are obtained by heating a mixture of N-glucose and thallous hydroxide with addition of 4 or 5 drops of N-sodium hydroxide solution in a clean test-tube for 2 minutes in a water-bath. The mirrors obtained can readily be removed from the glass by boiling with tap-water, but are permanent for some weeks under cold air-free distilled water. On adding tetra-methyl-γ-fructose to thallous hydroxide solution, a brown colour is developed in the cold, a small amount of a dark flocculent precipitate being also formed; on boiling this brown colour becomes darker and the precipitate dissolves. No mirror is formed. A standard solution of thallous hydroxide may be used for the titration particularly of organic acids. The thallous salts of organic acids are considerably less soluble than those of the alkali metals, are readily crystallised, and hence can be used as a convenient means of isolation and purification (Menzies and Wilkins, Chem. Soc. Trans. 1924, 125, 1148).

The *oxide* (TiO)₂, probably Tl₂O₃.Tl₂O, is prepared by adding 175-200 grms. of 20 p.c. potassium hydroxide to 15 grms. of a 10 p.c. aqueous solution of thallous sulphate. The solution is filtered, cooled to -15°, and 3.5 grms. of a 3 p.c. solution of hydrogen peroxide is added with constant shaking. The oxide forms a bluish-black, lustrous precipitate, is quickly decomposed into thallous oxide and thallous hydroxide by cold water and by dilute acids. It readily absorbs carbon dioxide, and, unlike thallous salts, is oxidised by a current of oxygen at ordinary temperature to thallous oxide (Rabe, Zeitsch. anorg. Chem. 1908, 58, 23).

When a mixture of thallous sulphate and oxalic acid is electrolysed at the ordinary temperature with a current of 3-4 volts and 0.15-0.2 ampère, the oxide Tl₂O₃ or Tl₂O₃.Tl₂O, is deposited on the anode. When the deposit is dissolved in dilute hydrochloric acid, chlorine is evolved and a yellow salt TlCl₃.3TlCl is formed (Gallo and Cenni, Atti R. Accad. Lincei, 1906, [v.] 17, 276).

The following complex salts of copper and thallium are described by G. Cannori (Gazz. chim. Ital. 1922, 52, ii. 208), viz.: Tl₂Cu₂(SO₄)₂.8H₂O

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blue crystals; $\text{Ti}_2\text{Cu}(\text{SO}_4)_2$, a yellow powder; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Cu_2SO_4 , Ti_2SO_4 , cinnabar-like crystals soluble in aqueous ammonia to a blue solution; $\text{Ti}_2\text{Cu}(\text{S}_2\text{O}_8)_2$, a yellow, microcrystalline powder (Chem. Soc. Abstr. 1923, 124, ii. 74).

For the halogen and mixed halogen compounds of thallium, see Wells and Penfield (Zeitsch. anorg. Chem. 1894, 6, 312); Meyer (*ibid.* 1900, 24, 321; *ibid.* 1902, 32, 72); Thomas (Compt. rend. 1900, 131, 892, 1208; *ibid.* 1901, 132, 80, 1487; *ibid.* 1902, 133, 735; *ibid.* 1902, 134, 545; *ibid.* 1903, 135, 1051; *ibid.* 1906, 142, 838; *ibid.* 1907, 143, 282; Ann. Chim. 1907, [viii.] 11, 204); Cushman (Amer. Chem. J. 1900, 24, 222; *ibid.* 1901, 26, 505); Maitland and Abegg (Zeitsch. anorg. Chem. 1906, 49, 341); Stolzenberg and Huth (Zeitsch. physikal. Chem. 1910, 71, 641). Thallium halides form double salts with many other metals (Meyer, *l.c.*; Thomas, *l.c.*; Pratt, Zeitsch. anorg. Chem. 1895, 9, 19; Wells and Foote, Amer. J. Sci. 1897, 3, 466; Ephraim and Heymann, Ber. 1909, 42, 4456; Ephraim and Bartczko, Zeitsch. anorg. Chem. 1909, 61, 238; Gewecke, Annalen, 1909, 366, 217; Delépine, Compt. rend. 1909, 149, 1072; Gewecke, Zeitsch. anorg. Chem. 1912, 75, 272; Sandonini, Atti R. Accad. Lincei. 1913, [v.] 22, ii. 20; Scarpa, *ibid.* 1912, [v.] 21, ii. 719; Lunde, Chem. Soc. Abstr. 1925, ii. 941; Randall and Vanselow, *ibid.* 1925, ii. 33). Thallous chloride darkens on exposure to light and becomes blackish-brown, due to the formation of a photo-thallous chloride and thallous-thallic chloride (*cf.* Renz, Helv. Chim. Acta, 1919, 2, 704). When thallium is dissolved in hot dilute hydrofluoric acid, H_2TlF_6 is obtained crystallising in white prisms. On heating it evolves hydrofluoric acid; its aqueous solution is acid, but does not attack glass, the fluorine ion being masked. It forms two types of salts, KHTlF_6 and K_2TlF_6 (Barlot, Compt. rend. 1920, 171, 1143).

Thallic sulphide Ti_2S_3 is formed when the metal is fused with excess of sulphur. It is black and above 12° is plastic, but below 12° it is hard and brittle. When sulphuretted hydrogen is passed into a solution of a thallous salt, thallous sulphide Ti_2S is formed as a black precipitate, which can be obtained in a crystalline form (Staněk, Zeitsch. anorg. Chem. 1898, 17, 117; see also Loczka, Chem. Zentr. 1898, i. 657; Hawley, J. Amer. Chem. Soc. 1907, 29, 1011). According to Pélabon, (Compt. rend. 1907, 145, 118) the sulphides Ti_2S_7 , Ti_2S_8 also exist (see Hofmann and Hochtlen, Ber. 1903, 36, 3090). Double sulphides with copper and tin are also known (Bruner and Zawadzki, Bull. Acad. Sci. Cracow, 1909, 312; Hawley, J. Phys. Chem. 1906, 10, 654).

Thallium sulphates and their double salts are described by Stortenbeker (Rec. trav. chim. 1902, 21, 87); Kohn (Zeitsch. anorg. Chem. 1908, 59, 111); Piccini and Fortini (*ibid.* 1902, 31, 451); Locke (Amer. Chem. J. 1902, 27, 280); Marshall (Proc. Roy. Soc. Edin. 1902, 24, 306); Meyer and Goldschmidt (Ber. 1903, 36, 238). Many double salts of thallic and thallous sulphates have been described, but according to Benrath and Espenschied (Zeitsch. anorg. Chem. 1922, 121, 361), only two exist, viz. $\text{Ti}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3$ and $5\text{Ti}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3$, all others being regarded as mixtures of these. For

the reduction of thallic sulphate in presence of ferrous sulphate, see Berry (Chem. Soc. Trans. 1923, 123, 1109).

The solubility of thallic oxide, the basic sulphate, $\text{Ti}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and the acid sulphate, $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, has been determined in sulphuric acid of various concentrations from 10 p.c. to 90 p.c. at various temperatures and the stability diagram constructed. It is shown that no other thallic sulphate exists under the above-named conditions, and that the other thallic sulphates described in the literature are mixtures, the formation of which is due to the slowness of the change from one salt to another. The transition point of the two sulphates mentioned above lies at about 40° . The corresponding selenates have also been investigated, and are found to be very similar to the sulphates; the main point of difference between them is that the transition point lies at 45° (Julius Meyer, Rec. trav. chim. 1921, 43, 614-619; J. Chem. Soc. 1923, 123, 124, ii. 637).

Thallium sulphite is a white granular crystalline powder (Seubert and Elten, Zeitsch. anorg. Chem. 1892, 2, 434; *ibid.* 1893, 4, 44).

Thallium selenides Ti_2Se and TiSe_2 are known. The existence of a third Ti_2Se_3 (Pélabon), or Ti_2Se_4 (Murakami) is doubtful.

Thallium telluride is described by Brukl (Monatsh. 1924, 45, 471, Chem. Soc. Abstr. 1925, ii. 895).

Thallium nitrates are described by Wells and Beardsley (Amer. Chem. J. 1901, 26, 257); Meyer (*l.c.*); Thomas (Compt. rend. 1904, 138, 1697); van Eyk (Zeitsch. physikal. Chem. 1906, 51, 721).

Thallium mercurous nitrate, m.p. 76° , sp.gr. 5.3, gives a clear mobile solution miscible with water and not reacting with sulphides. It forms a useful liquid for the separation of mineral sulphides (Retgers, Jahrb. Min. 1896, ii. 183).

Thallium nitrite forms double salts with cobalt and other metals (Przibylla, Zeitsch. anorg. Chem. 1898, 18, 448; Cunningham and Perkin, Chem. Soc. Trans. 1909, 1569; Tanatar and Petroff, J. Russ. Phys. Chem. Soc. 1910, 42, 94).

For nitrous-nitric complexes of thallium, v. Gazz. chim. ital. 1919, 40, ii. 217.

Thallous tetraborate $\text{Ti}_2\text{B}_4\text{O}_{10}$, hexaborate $\text{Ti}_2\text{B}_6\text{O}_{18}$, $3\text{H}_2\text{O}$, octaborate $\text{Ti}_2\text{B}_8\text{O}_{22} \cdot 4\text{H}_2\text{O}$, decaborate $\text{Ti}_2\text{B}_{10}\text{O}_{26} \cdot 8\text{H}_2\text{O}$, dodecaborate $\text{Ti}_2\text{B}_{12}\text{O}_{28} \cdot 7\text{H}_2\text{O}$, have also been prepared. Thallous perborate is also known.

Thallium azoimide or nitride TiN , remains unchanged when heated to 340° , but explodes when heated more strongly or when struck (Curtius and Rigson, J. pr. Chem. 1898, [ii.] 58, 261; also Dennis and Doan, J. Amer. Chem. Soc. 1896, 18, 970; Franklin, J. Phys. Chem. 1912, 16, 682).

Thallium oxalate $\text{HTl}(\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ is prepared by treating the freshly precipitated hydroxide at 25° with a large excess of a cold saturated solution of oxalic acid. When suspended in absolute alcohol, cooled to 0° , and treated with dry ammonia, the compound $\text{Ti}(\text{CO}_2)_2 \cdot \text{NH}_3(\text{NH}_3)_2$ is formed; at a higher temperature the compound $\text{Ti}(\text{CO}_2)_2 \cdot \text{NH}_3$ separates. The pyridine salt $\text{Ti}(\text{CO}_2)_2 \cdot \text{HC}_5\text{H}_5\text{N}$ and the salt $\text{Ti}(\text{CO}_2)_2 \cdot (\text{NH}_3)_2$, as well as other oxalates $\text{Ti}(\text{CO}_2)_2 \cdot (\text{C}_6\text{H}_5)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Ti}_2(\text{CO}_2)_4 \cdot 3\text{H}_2\text{O}$

have also been obtained (Rabe and Steinmetz, Ber. 1902, 35, 4447).

Thallous alkyl oxides (Chem. Soc. Abstr. 1923, i, 84).

Thallous carbonate, nitrite, and cyanide are also known.

Thallous chromate is practically insoluble in dilute alcohol and may be employed for the quantitative separation and estimation of thallium (see Cuttica and Canneri, Gazz. chim. ital. 1921, 51, 2189).

Thallous persulfate, see Gius (Gazz. chim. ital. 1924, 54, 204; Chem. Soc. Abstr. 1924, 126, i, 770).

For a number of other thallium salts, see Georgis, Gazz. chim. ital. 1894, 24, ii, 474; Stavenhagen, J. pr. Chem. 1895, [ii] 51, 1; Joly, Compt. rend. 1894, 118, 649; Mauro, Real. Accad. Lincei, 1893, ii, 382; Hofmann, Zeitsch. anorg. Chem. 1896, 12, 55; Piccini, *ibid.* 1897, 13, 441; Piccini and Marino, *ibid.* 1901, 27, 62; Marino, *ibid.* 1909, 62, 173; Glauser, *ibid.* 1910, 66, 437; Dennis and Doan, *l.c.*; Wyrouboff, Bull. Franc. Min. 1899, 19, 219; Hawley, J. Amer. Chem. Soc. 1907, 29, 300; Kurowski, Ber. 1910, 43, 1078; Buchtala, J. pr. Chem. 1913, [ii] 88, 771; Franklin, J. Amer. Chem. Soc. 1915, 37, 2279; Benrath, Zeitsch. anorg. Chem. 1915, 93, 161; for photochemical reactions of compounds of thallium, see Benrath, Zeitsch. wiss. Photochem. 1915, 14, 217; Renz, Helv. Chim. Acta, 1919, 2, 704; 1921, 4950; 1923, 1161; Goddard, Chem. Soc. Trans. 1921, 672; 1922, 36, 256, 482.

Thallium dimethyl fluoride TlMe_2F and the corresponding thallium diethyl fluoride and thallium diphenyl fluoride and similar compounds are described by Krause and von Grosse, Ber. 1925, 58 [B], 272, 1933; Chem. Soc. Abstr. 1925, i, 378, 1252.

For the constitution of aqueous solutions of thallium salts, see Drucker, Zeitsch. Electrochem. 1922, 28, 463-467.

Thallium may be determined by the electrolytic deposition of thallic oxide as follows: A solution containing 0.1-0.5 gm. of thallous nitrate and 0.1 gm. of free nitric acid is placed in a roughened platinum dish, diluted to 100 c.c., and either 10 c.c. of absolute alcohol or 5-10 c.c. of rectified acetone added. The dish is made the anode in the electrolysis, and the cathode is a disc of iridio-platinum of 12 sq. cm., which is rotated at 300 revs. per minute. The electrolysis is carried out at 60°-62°, directly from a single accumulator. After 10 hours the voltage is raised to 2.5-3.0 volts and a current of 0.05 amp. passed for a short time. The deposit, which is firm, is washed with water and dried at 160°-170°, preferably in an electrically heated oven; in any case reducing gases must not come into contact with the deposit. When dry the dish is cooled in a desiccator and weighed rapidly, since the deposit is somewhat hygroscopic. The method is good, the results being accurate to within ± 0.2 p.c. (W. Dieterle, Zeitsch. Elektrochem. 1923, 29, 493; J. Soc. Chem. Ind. 1924, 43, B, 79).

THALLOCHLORE. A name given by Knop and Schnedermann to the green colouring matter of lichens (Annalen, 56, 147).

THAPSIC ACID $\text{C}_{14}\text{H}_{18}\text{O}_4$. Obtained from the dried roots of *Thapsia geryanica* (Linn.)

(Canzoneri, Gazz. chim. ital. 18, 514; 24, ii, 437); m.p. 123°-124°. The anhydride melts at 71°.

Thapsic acid is identical with tetradecane dicarboxylic acid obtained by the electrolysis of potassium ethyl azelate (Carmichael, Chem. Soc. Trans. 1922, 121, 2545).

THAUMASITE. Hydrated silicate, carbonate, and sulphate of calcium, crystallised in the hexagonal system. This mineral is of interest in containing three acid radicles, and the existence of such a compound, which has not been prepared artificially, may possibly have some bearing on the setting of plasters. The formula is $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$. Since $13\text{H}_2\text{O}$ is expelled at 150°, and the remainder in four stages below a red-heat, corresponding to four hydroxyl groups, the formula may be written $[(\text{CaOH})\text{CO}_2][(\text{CaOH})\text{SO}_4][(\text{CaOH})\text{HSiO}_4 \cdot 13\text{H}_2\text{O}]$. The mineral forms snow-white, alabaster-like masses or loose aggregates of small transparent hexagonal prisms. It is very light, sp.gr. 1.88; H. 3½; readily decomposed by dilute hydrochloric acid, and slightly soluble in water. It is known from two mines in Sweden, and has been found in considerable quantity with pectolite ($\text{HNaCa}_2(\text{SiO}_3)_2$) and apophyllite in cavities in basalt at West Paterson in New Jersey. Another occurrence is as a filling of small fissures in metamorphosed dolomitic limestone in Beaver Co., Utah.

Wilkeite is a similar complex combination of calcium salts, but containing in addition phosphate and a surplus of oxide, the formula being $3\text{Ca}_3(\text{PO}_4)_2 \cdot 3\text{Ca}_2\text{SiO}_4 \cdot 3\text{CaSO}_4 \cdot \text{CaO}$. The hexagonal crystals have characters near those of apatite, sp.gr. 3.234. They are pink in colour and are found embedded in the blue calcite of a contact-metamorphic limestone at Crestmore in Riverside Co., California.

L. J. S.

THEBAINE v. OPTUM.

THEINE or *Caffeine* v. **CAFFEINE.** For the extraction of caffeine by various solvents, see H. E. Watson, K. M. Sheth, and J. J. Sudborough, (J. Ind. Inst. Sci. 1922, 5, 177-207).

The fact that theine (caffeine) exists in the leaves of the coffee plant has long been known, but it is only since the war that they have been commercially exploited to produce this drug. The idea originated in Sumatra, where under the present system of cultivation coffee is frequently attacked by insects of the genus *coccus*. With the failure of the berry crop, the growers, seeking a substitute for the ordinary caffeine-containing product, collected the leaves from which pure theine was prepared. With the war the demand for theine so greatly expanded that the process of extracting it from the leaves was resorted to on an extensive scale by the Dutch factories, which purchased them by the ton from the native growers and pickers. So far, the process of preparation has been kept secret, but there is no gainsaying the purity of the product. On the western side of the island of Sumatra the producers, and, in fact, the general public, have long used an infusion of torrefied coffee leaves as a beverage, the berries themselves all being reserved for export. The use of the leaves for this purpose has grown to such an extent that

it is now looked upon as an absolute necessary of life.

During the past four years Germany has been importing enormous quantities of coffee leaves from Sumatra and utilising them in the same way; and in some parts of Germany the infusion from the leaves has quite taken the place of the berry, the price of which has been an obstacle to its ready sale. Careful research work has resulted in proof that the extract obtained from the leaves has undoubted nutritive properties. In addition, a vast number of analyses have been taken which furnish data practically guaranteeing its safety as an article of diet, with an entire absence of deleterious effects. With a little boiled rice and infusion of the coffee leaf a man will support the labours of the field in rice-planting for days and weeks successively up to the knees in mud, under a burning sun or drenching rains, which he could not do by the use of simple water, or by the aid of spirituous or fermented liquors. Planters in Sumatra had opportunity of observing for twenty years the comparative use of the coffee leaf in one class of natives, and of spirituous liquors in another, the native Sumatrans using the former, and the natives of British India (imported labour) the latter. Records show, while the former expose themselves with impunity for any period to every degree of heat, cold and wet, the latter can endure neither wet nor cold for even a short period without danger to their health. Although the coffee berry can only be produced in certain climates and on soils containing marked peculiarities, the plant itself will flourish in any tropical country where the soil is sufficiently fertile, and in consequence the field for production of the leaves is almost unlimited. As a means, therefore, of providing caffeine for general consumption, free from deleterious qualities, and yet containing great nutritive properties, the leaves appear to be eminently suitable.

Samples of the leaves grown in North Queensland have already been shipped to Hamburg, where they have been most favourably commented upon. The shipmen's withstood the long voyage well. They disclosed fairly regular fragments of shining leaves mixed with small pieces of stalk, all of deep brown colour. The odour is described as exceedingly fragrant and something like a mixture of tea and coffee. An infusion in boiling water produced a transparent, dark-amber to brown-coloured liquid, which, used in the same way as ordinary coffee, with the addition of milk and sugar, was pronounced by experts as excellent. The price of the leaves is only about one-half that of the berries for which they are proposed as a substitute (Pharm. J. 1924, 113, 59).

For the determination of theine in coffee, see Lucas (J. Soc. Chem. Ind. 1924, 43, B, 489).

THENARDITE. A mineral consisting of anhydrous sodium sulphate (Na_2SO_4), crystallised in the orthorhombic system. It is found as large crystals, 6 ins. or more in length, on the shores of salt, soda, and borax lakes in arid regions, and sometimes forms beds of considerable extent, together with glauberite, &c. Sp.gr. 2.68-2.69; H. 2-3. The water-clear crystals absorb water from a moist atmosphere and become cloudy. Localities are: Borax

Lake in San Bernardino Co., California; on the Rio Verde in Arizona; Rhodes Marsh in Nevada; Tarapaca and elsewhere in the Chilean nitrate deposits; Espartinas near Madrid; the oasis of Bilma in French Sudan; and the salt lakes north of the Caspian. It is of rare occurrence in the German abraum-salts and in the fumaroles of volcanoes. I. J. S.

THENARD'S BLUE. Cobalt blue v. PIGMENTS.

THEOBROMA CACAO v. COCOA.

THEOBROMIC ACID $\text{C}_{19}\text{H}_{39}\text{COOH}$ is obtained from cocoa butter and melts at 72° ; it is apparently identical with arachidic acid (q.v.).

THEOBROMINE v. CAFFEINE, Vol. I., 726. For the estimation of theobromine in cocoa and its products v. Wadsworth, Analyst, 1921, 32. The theobromine content of nibs from 21 different producing areas varied from 2.2 to 3.9 p.c. calculated on dry, fat-free material, the variation depending upon the variety of the bean and on the degree of fermentation, a process which considerably reduces the theobromine content. In the shell the theobromine varied from 0.19 to 2.89 p.c., the alkaloid being carried by the sweatings from nut to shell. No theobromine was lost from nibs or shells during roasting. In order to determine the amount of theobromine in cocoa, the cocoa is heated in a dry Kjeldahl digestion flask until the theobromine is sublimed and the cocoa completely carbonised. The theobromine is extracted with hot water, the solution filtered, and the filtrate evaporated to dryness of the water-bath. The residue is purified by extraction with absolute alcohol, treated with aqueous ammonia, and dissolved in chloroform. The chloroform solution is filtered and evaporated to dryness, the residue extracted three times with 3 c.c. of hot water, filtered, and the filtrate evaporated to dryness on a watch glass, dried at 100° - 105°C ., and weighed. The whole determination takes about 2½ hrs. The percentage of theobromine in various samples of commercial cocoa varied from 0.45 p.c. to 1.17 p.c. (T. Ugarte, J. Pharm. Chim. 1923, 27, 420-423; J. Soc. Chem. Ind. 1923, 42, 675A).

Theobromine may be distinguished from caffeine by the differences in the colorations produced when the respective bismutho-iodides are reduced by hydriodic acid. For the distribution of theobromine during the fermentation of cacao, see Knapp and Wadsworth (J. Soc. Chem. Ind. 1924, 43, 124 T).

THEOBROMOSE, THEOCIN, THEOLACTIN, THEOPHORIN, THEOPHYLLIN, v. SYNTHETIC DRUGS.

THEOCYCLEKE. Compound of theobromine and aspirin.

THEOFORM. A condensation product of theobromine and formic acid.

THEOPHYLLINE v. CAFFEINE.

THEOPHYSEM. Iodoethylallylthioxy-urea.

THEOSALIN. Trade name for an addition product of theobromine sodium, and sodium sulphosalicylate.

THERMAL PROPERTIES OF GASES. In J. Phys. Chem. Feb., 1924, 28, 97, Pickering reviews the constants of the more common gases

THERMIT PROCESS.

and gives the following values as the most probable:—

Gas	Critical Temperature °C. abs.	Critical Pressure atm.	Critical Density gr per c.c.
Acetylene	300.0 ?	10.6	0.231
Air	132.4	37.2	0.356
Allylene	401.0	—	0.31c
Ammonia	405.5	112.0	0.236
Argon	350.7	48.0	0.52
Butane (iso)	406.8 ?	36.5 ?	—
Butane (n)	426.3 ?	35.7 ?	—
Carbon dioxide	304.1	72.9	0.460
Carbon monoxide	134.4	34.6	0.311
Chlorine	417.0	76.0	0.573
Cyanogen	401.4	59.7	—
Ethane	305.2	48.8	0.21
Ethyl chloride	456.0 ?	54.0 ?	—
Ethylene	282.6	50.7	—
Helium	5.20	2.26	0.066
Hydrogen	33.18	12.8	0.0310
Hydrogen bromide	363.5	—	—
Hydrogen chloride	321.5	83.0 ?	—
Hydrogen iodide	423.9 ?	—	—
Hydrogen sulphide	373.5	89.0	—
Krypton	210.6	54.3 ?	—
Methane	190.6	45.7	0.162
Methyl chloride	416.2	65.9	0.37 ?
Neon	44.7	26.9	—
Nitric oxide	180.0 ?	71.0 ?	—
Nitrogen	126.0	33.5	0.3310
Nitrous oxide	309.6	71.7	0.45 ?
Oxygen ozone	268.0 ?	92.3 ?	—
Phosgene	456.0 ?	—	—
Propane	368.7	45.0	—
Propylene	364.5 ?	45.3 ?	—
Sulphur dioxide	430.3	77.7	0.52 ?
Xenon	289.7	58.2	1.155

(Sci. Abstr. 1924, 27, 531).

Determination of the normal boiling-points of oxygen, nitrogen, and hydrogen.—Henning and Heuse's (Zeits. f. Physik. 1924, 23 1, 105) final results reduced to the thermodynamic scale of temperature are:

Oxygen	—183.00±.02
Nitrogen	—195.81±.02
Hydrogen	—252.78±.02

Over the range —183° to —205° the variation of the boiling-point of oxygen with pressure is given by the equation

$$\log p_{mm} = -379.95/T - 0.0096219T + 1.75$$

$$\log T + 4.53939 \text{ (where } T = 273.20 + t)$$

and for nitrogen by

$$\log p_{mm} = -301.91/T - 0.0090272T + 1.75$$

$$\log T + 4.17643$$

The resistances of two Pt thermometers used over a period of twelve years in this work were again measured at these fixed-point temperatures. The values have remained practically constant, the greatest observed alteration only corresponding to a change of temperature of 0.02° (Sci. Abstr. 1924, 27, 645).

THERMIOL. Trade name for sodium phenylpropiolate.

THERMIT PROCESS. 'In a thermit reaction a metallic compound (e.g. an oxide) is reduced by one or several metals or metallic alloys in such a way that when the mixture is ignited at one place, the reaction continues to go on spontaneously with complete oxidation of the reducing element, a fluid slag being formed, whilst the reduced metal is obtained as a compact

uniform regulus; if the oxide is used in excess, the reduced metal is free, or practically free, from the element used as reducing agent' (H. Goldschmidt, Electrochem. and Metall. Ind. 1908, 6, 360).

In 1898 Goldschmidt (Stahl und Eisen, 1898, 18, 408; J. Soc. Chem. Ind. 1898, 17, 543, 584, 649; Zeitsch. für. Elektrochem. 1898, 4, 494; 1899, 6, 53) succeeded in reducing the oxides of chromium, manganese, iron, copper, titanium, boron, tungsten, molybdenum, nickel, cobalt, zirconium, vanadium, columbium, tantalum, cerium, thorium, barium, calcium, sodium, potassium, lead, and tin very conveniently by means of aluminium. Such reduction processes had been anticipated, owing to the fact that measured with respect to the same quantity of oxygen, aluminium has a greater heat of oxidation than almost any other metal. Earlier attempts to carry out such experiments had, however, proved very unsatisfactory; either the reactions would not begin, or they occurred with explosive violence. Goldschmidt overcame the difficulty by mixing the finely-divided oxide intimately with powdered or granulated aluminium, and starting the action at one point by raising its temperature sufficiently high. The reaction being once initiated, the enormous heat developed causes it to spread quickly throughout the entire mass, the time of reaction not varying appreciably with the quantity of material employed, and being about 30 seconds in the case of iron oxide and aluminium. To start the reaction at one spot, Goldschmidt placed a small heap of a mixture of powdered aluminium (or magnesium) and barium peroxide on top of the mixture to act as a fuse, and inserted therein a strip of magnesium ribbon. On lighting the latter, the fuse ignites, and the thermit reaction is started.

Owing to the heat developed in these reactions and the rapidity with which they occur, an enormous temperature is produced, second only to that of the electric arc. It has been estimated at 2600°–3000°, and direct observation with a Fery radiation pyrometer has shown that the temperature of a stream of steel produced from iron oxide and aluminium, as it was poured from the crucible, was 3200° (the melting-point of steel is approximately 1350°). At such temperatures the entire contents of the crucible remain liquid; the reduced metal sinks to the bottom, covered with a layer of molten alumina.

Other metals have been tried for the reduction of metallic oxides. Perkins (Faraday Soc. Trans. 1907, 3, 115, 179), and also Goldschmidt have tried calcium, but the reactions are too violent to be of much use, whilst the slag is difficultly fusible. Silicon (made in the electric furnace) has also been tried; but the reactions are too slow. The so-called mixed-metal, which consists essentially of cerium, has, however, been successfully employed in the preparation of pure vanadium, columbium, and tantalum (Muthmann, Weiss, and Riedelbauch, Annalen, 1907, 355, 58; Weiss and Aichel, *ibid.* 1904, 337, 370).

A number of mixtures may be used in place of aluminium, and some have been patented. A mixture of equal parts of calcium-thermit and silicon-thermit, so that the active elements,

calcium and silicon, are in the ratio of 2 to 1, is especially effective (Fr. Pat. 361197, 1905). It reacts like an ordinary aluminium-thermit, yielding a thin fluid having approximately the composition $4\text{CaO} \cdot 3\text{SiO}_2$, and melting at 1425° (Boudouard, Iron and Steel, 1905, 352). The active mixture may be prepared either by mixing or alloying calcium with silicon (v. Fr. Pat. 388638, 1908). A mixture of magnesium and silicon may also be used to replace aluminium, giving a reaction like ordinary thermit (Eng. Pat. 3089, 1906; Fr. Pat. 364313, 1906; U.S. Pat. 902871, 1908), whilst magnesium itself acts similarly to calcium in its reactions with metallic oxides. Magnesium-silicon thermit is best mixed in proportions which yield a slag of the composition $7\text{MgO} \cdot 4\text{SiO}_2$. A third mixture, viz. aluminium-thermit and calcium-thermit, gives very good results. The proportions may vary between wide limits, avoiding too large an excess of calcium, and the calcium aluminate slag is more fusible than alumina. A mixture containing 40 p.c. calcium-thermit produces a very fluid slag $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, and has a heat effect greater than that of aluminium-thermit (Fr. Pat. 361197, 1905; addn. Jan. 1906; U.S.A. Pat. 875345, 1907; 875666, 1907; 906009, 1908; Eng. Pat. 926, 1906). See also Watts and Breckenridge, Electrochem. & Metall. Ind. 1908, 6, 237; Weston and Ellis, Faraday Soc. Trans. 1907, 3, 170; 1908, 4, 60, 130; 1910, 6, 144; and Skinder, Chem. Zentr. 1909, i. 629.

Technical applications.—Although the thermit reaction (Goldschmidt's reaction only dates from 1898, it has acquired great technological importance, and the subject of 'aluminothermics' has been extensively developed.

Preparation of metals and alloys.—The following are obtained by reducing the requisite metallic oxides (or mixtures of oxides) with a slight deficit of aluminium; chromium, manganese, molybdenum, ferro-titanium, ferro-vanadium, ferro-boron, manganese-copper, manganese-zinc, manganese-tin, manganese-titanium, chromium-manganese. They are of great value in the iron and steel and other metallurgical industries; chromium, in particular, is largely employed in the manufacture of high-speed tool steel and armour plate. The metals and alloys produced are carbon-free. The crucibles in which the preparations are carried out must be lined with magnesia (Eng. Pat. 9610, 1905; Fr. Pat. 354597, 1906), one of the few oxides that aluminium is unable to reduce. The best method of procedure to ensure a maximum yield of chromium or manganese consists in mixing 1-4 p.c. of higher oxide with the bulk of lower oxide to be reduced to metal (Eng. Pat. 20004, 1905; Fr. Pat. 358071, 1905; U.S. Pat. 895628, 1908).

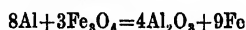
For experimental purposes, steel of any grade can be made by the thermit process, since the heat developed is sufficient to melt thoroughly small portions of even the most refractory metals. The thermit steel is free from carbon, but may be converted into high carbon steel by the addition of cast-iron shot.

The slag produced is also of commercial value. It may be employed in the preparation of aluminium, or used in place of natural corun-

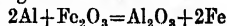
dum. It is especially valuable for use in the manufacture of pottery, for which purpose it is mixed with clay and burned (D. R. P. 160780, 1901). Corubin, an abrasive material for making emery wheels, emery cloth, &c., is prepared by crushing the slag obtained as by-product in the manufacture of chromium.

Welding iron and steel, and repairing broken steel castings.—The advantages of the thermit process for these applications are, that it is simple, rapid, requires no special skill, and enables repairs to be made *in situ*, when any other process would necessitate a dismantling of apparatus.

The mixture employed is composed of powdered aluminium and magnetic iron oxide, and when ignited yields half its weight of molten steel. Its registered trade name is 'thermit.' The reaction



indicates that approximately 3 parts of aluminium powder require 10 parts of magnetic oxide, and produce 7 parts of iron. Early literature on the subject gives the reaction as



but examination of thermit with a magnet will show that the magnetic oxide is now employed. It is added in the form of granulated rolling-mill scale.

The firing of a charge of thermit produces a pure mild steel of the following average composition—

Carbon	0.05-0.10
Manganese	0.08-0.10
Silicon	0.09-0.20
Sulphur	0.03-0.04
Phosphorus	0.04-0.05
Aluminium	0.07-0.18

Two methods of welding are in use, (a) the reaction serving merely as a source of heat (Eng. Pat. 19328, 1899), and (b) the steel produced by the reaction being utilised as well (Eng. Pat. 10859, 1901; 20894, 1900; U.S. Pat. 729573, 1903). In process (a) pure materials need not be used, and, if necessary, the thermit may be diluted with a cheap oxide, e.g. iron ore or sand, to lower the final temperature reached. This process is used in the butt-welding of pipes and bars. The ends are cut square, smoothed, and clamped together. A mould is then clamped round the junction. A charge of thermit is fired in an ordinary magnesia-lined crucible, allowed to stand half a minute so that slag and steel may separate (the volume of the molten slag is three times that of the iron produced), and then poured out so that the slag comes first. As the slag is poured in the mould on to the pipe, it forms a hard casing around the metal, and the liquid which follows distributes its heat uniformly through this casing to the metal. In about a minute the pipes have been raised to welding heat. The ends are then pressed tightly together by means of screws arranged in position beforehand. The mould is then removed, the slag collar carefully knocked off, and the red-hot joint allowed to cool. Process (b) has been largely employed in welding together tram and railway line sections. The ends are brought together and clamped accurately in position. A refractory clay mould is clamped

round the ends and the requisite charge of thermit fired in a crucible placed over the pouring gate of the mould. At the end of the reaction, the crucible is tapped from the bottom (see Fig. 1), and the liquid steel flows into the mould, passes upwards from the bottom of the mould, surrounds the base and web of the rail, with which it fuses on account of its enormously high temperature, and on cooling makes a solid steel joint.

The welding of rails is a typical instance of the application of process (b) above, which is also employed for all kinds of repairing work, e.g. mending broken engine frames, driving rods

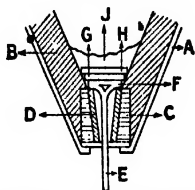


FIG. 1.—TAP-HOLE OF THERMIT CRUCIBLE.

A, iron casing; B, magnesia lining; C, hollow cylindrical magnesistone; D, conical magnesistone; E, iron tapping pin, with flattened end F; G, asbestos washer; H, iron washer; J, layer of sand.

and spokes, crank shafts, rudder and propeller shafts, stern-posts, &c., in fact, in the majority of cases where it is cheaper to repair than to replace. Where necessary, the fracture is opened out by drilling holes. A wax matrix is then built up over the break of the exact shape that the thermit steel collar to be fused into the casting is to have. Over this, in a sheet iron box, is constructed a mould, having a pouring gate, a preheating gate, and a large riser (Fig. 2). A gasoline torch, fed with compressed air, is then directed through the preheating gate. It melts out the wax, dries the mould, and heats

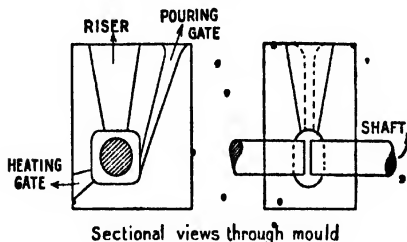


FIG. 2.

the junction to be repaired to a bright red heat. Meanwhile, the crucible containing the thermit is arranged over the pouring gate. The quantity of thermit required is given by the rule: take 32 times the weight of the wax used, or 18 times as many ounces of thermit powder as there are cubic inches of surplus space in the mould. The crucible (Fig. 1) is designed so as to be tapped from the bottom (Goldschmidt, Zeitsch. Elektrochem. 1901, 7, 935; Cohn, J. Gasbeleucht, 1901, 44). The gasoline torch is withdrawn when the junction is red hot, the preheating gate plugged with a sand core held in readiness, and the thermit fired without delay. After the reaction is over, and the molten liquid

has stood 30 seconds to allow the slag to rise, the crucible is tapped. The molten steel passes down the pouring gate, around the fractured joint, and up into the riser. The ends of the casting melt into the liquid steel, and on cooling one homogeneous mass is formed. The projecting collar of thermit steel around the joint is left on whenever possible.

The average tensile strength of a thermit steel joint is about 30 tons per square inch cross-section. If the projecting collar of thermit steel has to be planed off, and the tensile strength of the joint is less than that of the body of the casting, the weld may be made stronger by introducing nickel into the composition of the thermit; 1 p.c. of nickel increases the tensile strength of the weld about one-third. For a 1 p.c. alloy, 2 p.c. of nickel thermit may be added to the usual steel thermit, or 5 oz. of metallic nickel may be added to each 100 lbs. of thermit.

Thermit powder is supplied in 50 or 100 lb. drums. For use in repair work, about 2 p.c. of manganese and 5 p.c. of mild steel punchings are added. The former acts as a purifier of the steel produced; the latter serves to lower the final temperature of the reaction and so prevent the contents of the crucible from boiling over.

Use of thermit in foundry practice.—(a) The thermit reaction provides a ready means of introducing in an iron ladle a material which will stir up or pole the entire contents of the ladle, and at the same time produce an increase of temperature. For this purpose, the thermit is contained in cylindrical cans with a sleeve in the middle, suitable for passing on an iron rod. The can is held by the iron rod under the surface of the metal, where the reaction takes place. This procedure prevents the iron from becoming too dull to pour (U.S. Pat. 733957, 1903).

(b) A convenient means of purifying the iron in the ladle, by reducing the presence of harmful nitrogen in the molten metal, consists in holding a can of titanium-thermit under the surface as described in (a). This thermit is a mixture of pulverised aluminium and a titanium-iron oxide. The titanium set free in the reaction is sufficient to combine with the nitrogen in the ladle, titanium cyanonitride being produced. During this formation, the entire contents of the ladle are stirred up, to give the gases an opportunity of escaping. The iron is thereby rendered hotter and distinctly more fluid, and castings made from it are distinguished by their closeness of grain, being especially well adapted for withstanding pressure, e.g. cylinders, valves, &c.

(c) The enormous heat developed may be utilised to decrease the size of the risers of steel castings. The thermit, contained in suitable cans, is held in the neck of the riser, which is thus kept in the liquid state for a longer time than would otherwise be the case, thereby facilitating the proper feeding of the casting. The same principle is successfully applied to reduce the size of lost heads of steel ingots.

(d) In foundries where it is of importance to occasionally make a steel casting in a hurry, burning down the requisite quantity of thermit with an admixture of steel punchings affords by far the easiest method of procedure.

See also Hart's Welding (McGraw-Hill Book Co.).

THERMODIN. An acetyl derivative of *p*-ethoxy-phenylurethane. Used as an anti-pyretic.

THERMOMETERS. Changes of temperature are measured by the corresponding alterations produced in one or other of the physical properties of a substance. Thus the expansion of solids, liquids, and gases, the vapour pressures of liquids, the electrical resistance of metals, and other properties have been utilised for the determination of temperature.

In nearly every case the amount of change produced by a given rise or fall of temperature depends on the nature of the substance, and must therefore be carefully determined beforehand for the particular material employed.

There is, indeed, only one known method of measuring temperature which is theoretically perfect, that is to say, which is entirely independent of the nature of the substance; this method, proposed by Lord Kelvin, depends on the ratio of the work done by a reversible heat engine to the heat supplied to it, and the temperature, reckoned from absolute zero, may be defined as the reciprocal of Carnot's function. The method is not one, however, that is capable of practical application.

It has been found that within certain limits of temperature and pressure the expansion of all gases is very nearly the same for equal changes of temperature. Hence it is possible to devise a method of measuring temperature which, while practically independent of the nature of the (gaseous) substance employed, is at the same time fairly convenient for many purposes. It is important also to remark that the values given by an air or gas thermometer are in very close agreement with Lord Kelvin's thermo-dynamical temperatures.

The relation of the volume of a gas to its temperature and pressure may be stated simply as follows: The volume of a gas varies inversely as the pressure and directly as the absolute temperature, or $p = c/T$, where p is the pressure, v the volume, T the absolute temperature, and c a constant depending on the units chosen. If the volume remains constant the pressure varies directly as the absolute temperature, or $p = c'T$, while if the pressure is kept constant the volume varies directly as the absolute temperature, or $v = c''T$.

It is true that the co-efficients of expansion of different gases are not absolutely identical, and that the law holds good only within certain limits of temperature and pressure; but under pressures not greatly exceeding that of the atmosphere the deviations are extremely small in the case of nitrogen, hydrogen, helium, and some other gases, except at very low temperatures. Very accurate investigations of the properties of gases at extremely low temperatures have been carried out by Kamerlingh Onnes and his collaborators at Leiden, and their results show that the constant volume hydrogen thermometer gives nearly accurate results down to -250° and the helium thermometer to still lower temperatures.

An 'air' thermometer may be so constructed that (1) the pressure remains constant and the alteration of volume is measured; (2) the volume remains constant and the change of pressure is observed; (3) both pressure and volume are

allowed to alter, and both are measured. The air or other gas is contained in a bulb of glass, or for very high temperatures of some other material, connected by means of a capillary tube with a mercury or sulphuric acid manometer. The bulb is heated to the required temperature while the other parts of the apparatus remain at the temperature of the room. If the pressure be kept constant the gas will expand, and at high temperatures a considerable portion of it will pass into the cold part of the apparatus and must be measured at the ordinary temperature; it is therefore usually considered better to raise the pressure so as to keep the volume of gas as nearly constant as possible. The vessel containing the gas expands, however, when the temperature rises, and a correction on account of this expansion must be introduced.

There are also three sources of error which are difficult to estimate, but they may be almost entirely eliminated by taking suitable precautions. The first depends on the fact that at ordinary temperatures air condenses to a slight extent as a sort of film on the surface of glass, while at high temperatures this condensed air is converted into gas, so that the apparent expansion is a little greater than the real. If, however, the bulb, after thorough exhaustion at a high temperature, is filled with air from which all moisture and carbon dioxide have been removed, the error becomes practically negligible (Callendar, Phil. Trans. 178A, 161).

The second is due to slight changes of volume which a glass vessel is liable to undergo after being strongly heated and allowed to cool again. The magnitude of the possible error becomes extremely small, however, if the bulb is heated for some hours to at least the highest temperature which is to be registered, before its volume is determined. This point will be more fully discussed when dealing with mercurial thermometers. The third source of error is due to the deformation of the bulb or to leakage of gas through it when the temperature and the internal gaseous pressure are greatly raised. This difficulty has been overcome by Day and Clement (Amer. J. Sci. 26, 1908), who employed a platinum-iridium bulb containing nitrogen, by surrounding the bulb with nitrogen at the same pressure as that within the bulb. Further precautions are described by Day, Sosman and Allen, Carnegie Inst. of Washington, Geophys. Lab. 1; Day and Sosman, Amer. J. Sci. 33, 517; and Ezer Griffiths, Methods of Measuring Temperature, 1918.

Of the numerous forms of air thermometer which have been devised, the three shown in the diagrams may serve as examples. The first (Fig. 1) represents a form of instrument employed by Regnault in his classical researches. The bulb A of the thermometer is connected by a capillary tube (passing through a perforation in the screen B) with the mercury manometer mm' , a front view of which is shown in Fig. 2. By addition of mercury to the open limb m' , or by its removal by means of the stopcock s , the mercury in the limb of the manometer connected with the air thermometer may be always kept at the same height, so that there is no alteration of the volume of air except that due to the expansion of the bulb when heated.

The calculation of the temperature is based on the fact that the mass of air remains constant, although its temperature, its pressure, and, to a small extent, its volume undergo change. Let

V = volume of bulb A at 0° ;

v = volume of capillary tube, together with the small portion of the manometer above the mercury in m , also at 0° ;

α = coefficient of increase of pressure of dry air at constant volume;

κ = coefficient of expansion of glass;

D = mass of 1 c.c. of air at 0° and 76 cms. pressure;

P = observed pressure—that is to say, the barometric pressure, *plus* or *minus* the difference of level of the mercury in m and m' .

When the bulb is placed in melting ice, while the capillary tube and manometer are at the

Hydrogen	760 mm.	0.0036627
Helium	700 "	0.0036626
Nitrogen	760 "	0.0036714
Oxygen	663 "	0.003674

If the volume of air be allowed to vary, the limb m of the manometer must be graduated, and should be surrounded by cold water of known temperature. In this case the additional volume v' at the temperature of the water must be brought into the equation.

Sulphuric acid may be employed with advantage in place of mercury, since it moves more freely in a narrow tube, and, being lighter, allows of more delicate readings; or a small sulphuric acid gauge may be interposed between the thermometer and the mercury manometer. An apparatus which can be employed either as a constant volume or constant pressure manometer has been described by Callendar (l.c.)

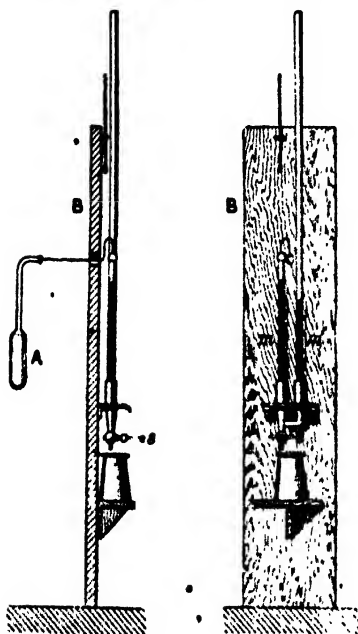


FIG. 1.

FIG. 2.

temperature t' of the room, the total mass of air will be

$$D.P. \left\{ V + \frac{v(1+\kappa t')}{1+\alpha t'} \right\}$$

When the bulb is heated to the unknown temperature x , the temperatures of the capillary tube and manometer being now t' the mass of air will be

$$D.P. \left\{ \frac{V(1+\kappa x)}{1+\alpha x} + \frac{v(1+\kappa t')}{1+\alpha t'} \right\}$$

Therefore

$$P \left\{ V + \frac{v(1+\kappa t')}{1+\alpha t'} \right\} = P' \left\{ \frac{V(1+\kappa x)}{1+\alpha x} + \frac{v(1+\kappa t')}{1+\alpha t'} \right\}$$

an equation in which everything is known but x

Values of α for several gases for the temperature range 0° to 100° are given below, p_0 being the initial pressure (at 0°).

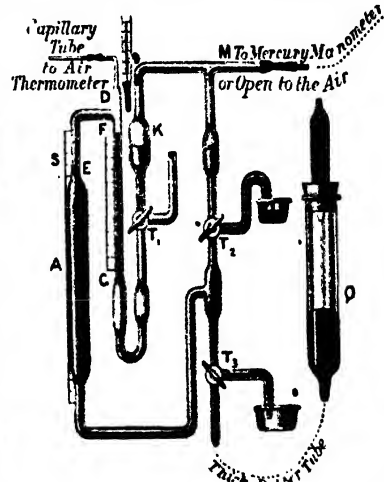


FIG. 3.

and more fully by Callendar and Griffiths (Phil. Trans. 1824, 119). It is represented in Fig. 3.

When the measurement is to be made at constant volume the mercury in A is brought up to the zero point, and the stopcocks T_1 and T_2 are closed. The level of the sulphuric acid in the gauge is then regulated by means of an ordinary mercury manometer, not shown in the diagram, and the pressure is the algebraical sum of the barometric pressure, that registered by the mercury manometer, and the slight difference in level, if any, of the sulphuric acid in the two limbs of the gauge FK , divided by the specific gravity of mercury compared with that of sulphuric acid.

If the pressure is to be kept constant, the tube A is first filled from the reservoir Q until the level of the mercury stands at some point in the tube nx , recorded by the scale s , the pressure of the air in the bulb being equal to that of the atmosphere, as shown by the sulphuric acid gauge. (In this case the tube x is not connected with the mercury manometer, but is open to the air.) When the bulb is heated, mercury is allowed to escape by the three-way tap T_2 into the weighed beaker, the tap being closed as soon as the sulphuric acid gauge indicates that the pressure is again equal to that of the

atmosphere. The increased volume is calculated from the weight of mercury expelled. The narrow tubes DE and FG are calibrated and provided with scales. For the advantages of the sulphuric acid gauge see also Bottomley (Phil. Mag. 1888 (Aug.), 149).

Callendar has (Nature, 1891, 45, 212) described a modified constant-pressure air thermometer which appears to possess marked advantages over those previously devised, and gives extremely accurate results. The pressure of the air in the thermometer is not adjusted to equality with that of the atmosphere, but always with the same constant pressure, obtained by connecting the outer limb of the sulphuric acid gauge to a glass bulb filled with air and kept in melting ice.

The effect of changes of temperature of the connecting tubes on the readings is entirely eliminated by the employment of compensating tubes of the same size, and thus the troublesome and somewhat uncertain correction hitherto necessary is obviated. The compensation is perfect when (1) the two sets of connecting tubes are of equal volume and at the same mean temperature; (2) the mass of air inclosed in the standard pressure-bulb is equal to that in the thermometric and mercury bulbs; (3) the pressures are adjusted to equality. Under these conditions, the temperature of the thermometer bulb (on the air-thermometer scale) is given by the simple equation $\theta_1 = V_1 \theta_0 / (V_0 - V_m)$, where V_1 is the volume of air in the thermometer bulb at θ_1 , V_0 and V_m are the volumes of air at 0° in the standard pressure bulb and the mercury reservoir (this being also surrounded by melting ice), and θ_0 is the temperature of melting ice on the air-thermometer scale.

For moderate ranges of temperature, and when extreme accuracy is not required, the apparatus may be greatly simplified, and may be so constructed that the temperatures are read directly on the sulphuric acid gauge; it is stated that such thermometers can be made to read to the tenth of a degree at 450° . This form of direct reading thermometer has been patented and is recommended for technical purposes.

Other forms of air thermometer have been described by Balfour Stewart, Phil. Trans. 153, 425; Codazza, Dingl. poly. J. 210, 255; Jolly, Pogg. Jubelband, p. 82; Mitscherlich, Annalen, 12, 146; Crafts, Ann. Chim. [v.] 14, 409; Andrews, Ber. 14, 2116; Pettersson, J. pr. Chem. [ii.] 25, 102; Caillaud, Compt. rend. 106, 1055; Berthelot, Ann. Chim. [iv.] 13, 144; Murray, J. Phys. Chem. 1897, i. 714; *v.* also Ezer Griffiths, *l.c.* A platinum bulb was recommended by Pouillet (Compt. rend. 3, 782), but it was pointed out by Becquerel (Ann. Chim. 58, 49) that at high temperatures air passes through the platinum. A porcelain bulb was employed by Weinhold (Pogg. Ann. 149, 188), by Deville and Troost (Ann. Chim. [iii.] 58, 265), and others. According to Holborn and Day (Wied. Ann. 68, 817; Amer. J. Sci. 8, 165; 10, 171), however, porcelain does not give satisfactory results at high temperatures. They recommend bulbs of Jena boro-silicate glass, No. 59^{III}, containing hydrogen for temperatures up to 500° , and bulbs of a platinum-iridium alloy (10 p.c. Ir) with pure nitrogen gas from 500° to 1300° . The Pt Ir bulbs

should be heated electrically or else protected from gaseous combustion products, which are liable to pass through the alloy. Holborn and Henning (Ann. d. Physik. 35, 4, 761) used Jena glass No. 59^{III} for nitrogen, hydrogen, and helium, and quartz for nitrogen. Day and Sosman (Amer. J. Sci. 1910, 20) have measured temperatures to 1550° . They describe special precautions required to obtain a uniform temperature about the bulb (*ibid.* 1912, 33, 517). Harker proposes to make bulbs of rare earths such as those used for Nernst filaments.

For very low temperatures, the glass bulbs should contain hydrogen or helium. A very complete account of the hydrogen thermometer in use at the cryogenic laboratory at Leiden is given by Kamerlingh Onnes and Clay (Comm. No. 95e), and of the helium thermometer by K. Onnes and Weber (Comm. No. 147b, 1915), and Cath and K. Onnes (Comm. 152a, 1918).

As regards the theory of the subject and the comparison of the temperatures registered by different gas thermometers with each other and with the thermodynamical scale, reference may be made to the following memoirs and papers: D. Berthelot, Sur les thermomètres à gas, Paris, 1903; Ann. d. poids et mesures, 1907, 13b, 3; Chappuis, Phil. Mag. 1900, 50, 433; 1902, 3, 234; Phil. Trans. 1900, 191, 37, 131; J. Phys. 1904, 3, 833; Ann. d. poids et mes. 1907, 13a, 3; Kamerlingh Onnes, Comm. 97a and b, 102b and d; Holborn, Ann. Physik. 1901, [vi.] 2, 242; Buckingham, Bureau of Standards, 1907, 3, 237; Phil. Mag. 1908, 15, 526; Rose-Innes, *ibid.* 1908, 14, 301; Kamerlingh Onnes and Holst, Comm. 141a; Report by Kamerlingh Onnes at Third International Congress of Refrigeration, 1913, section for Physics, Chemistry and Thermometry; Ezer Griffiths, *l.c.*; Cath and K. Onnes, Comm. No. 156a, 1922.

Air thermometers for technical purposes are generally provided with scales which are calibrated empirically by heating the bulbs to two or three known temperatures, so as to obtain a certain number of fixed points. The scales are then constructed by interpolation.

Thermometers of this class have been described by P. Schoon, D. R. P. 20345, 1882; Witz, Compt. rend. 91, 164; Beilby, J. Soc. Chem. Ind. 1885, 41; Coleman, *ibid.* 1885, 43; Heisch and Folkard, and by Bristol (Mech. Eng. 1900, 6, 916). They consist of a porcelain bulb, a copper capillary, and a pressure gauge constructed with two spiral tubes on the Bourdon principle. They can be constructed as recording instruments. The thermometer of Heisch and Folkard is very simple, and has been found by Hurter (J. Soc. Chem. Ind. 1886, 635) to give good results. The bulb A (Fig. 4) contains air under reduced pressure, and there is a vacuum over the mercury in the manometer M.

The mercurial thermometer.—For ordinary purposes the mercurial thermometer is the most convenient, for it may be made of any required size, is easily portable, and the bulb, if elongated, need not be wider or, indeed, so wide as the stem. The instrument consists of a spherical or cylindrical bulb fused to a capillary tube of suitable length. The bulb is filled with pure mercury, which must be boiled for some time to remove the film of gas or aqueous vapour which adheres obstinately to the surface of the glass.

If the thermometer is required for low temperatures only, there is usually a vacuum in the stem of the thermometer, but for high temperatures it is necessary, and for temperatures above 70° or 80° advisable, to fill the capillary

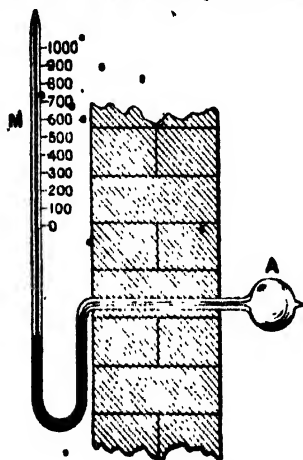


FIG. 4.

tube with nitrogen to prevent distillation of the mercury, a small bulb being blown at the upper end of the tube in order that when the mercury expands and compresses the nitrogen the pressure shall not rise too high.

An ordinary thermometer is graduated by placing it *first* in the steam from water boiling under known pressure and then in melting ice (*v. Guillaume, Traité pratique de la Thermométrie de Précision, p. 112*). The variation of the melting-point of ice with the pressure is so minute that this point may be taken as absolutely fixed, but the boiling-point of water varies considerably with the pressure, and therefore some standard pressure must be chosen. This is 760 mm. or 29.922 ins. of mercury measured at 0°C. and at the latitude of Paris for the Centigrade scale, and 29.905 ins. of mercury at 32°F. at the latitude of London for the Fahrenheit scale.

The position of the mercury in the stem is marked off at these two fixed points, and the space between these two fixed points is then usually divided into a certain number of equal parts—100 on the Centigrade scale, 180 on the Fahrenheit, and 80 on the Réaumur. On the Centigrade and Réaumur scales, the melting-point of ice is taken as the zero point, but on the Fahrenheit the zero of the scale is placed 32 divisions lower down, so that the melting-point of ice is 32°, and the boiling-point of water 212°.

A thermometer graduated in this manner does not, however, register true temperatures except at the two fixed points, for the following reasons:—1. It is impossible to obtain an absolutely cylindrical capillary tube, so that the volume corresponding to a scale division is not quite the same in all parts of the tube. Various methods have been devised for calibrating the stem (*v. Brit. Assoc. Report, 1882, 145-204, also Guillaume, l.c. 43-99*), but when this is done there remain other sources of error. 2. The position of the mercury in the stem at any

temperature depends on the expansion both of the mercury and of the glass, and in each case the rate of expansion increases with rise of temperature. Moreover, different kinds of glass have different rates of expansion, so that two thermometers made of different materials—even if the capillary tubes were perfectly cylindrical—would give different readings at the same temperature. The only really satisfactory method of correction of such a thermometer is to compare its readings either directly with an air thermometer, or with another mercurial thermometer which has previously been standardised by means of an air thermometer. Or a series of fixed points may be determined by immersing the thermometer in a number of freezing liquids (melting solids) or by heating it with the vapours of a series of pure liquids boiling under known pressures. The following table contains a list of suitable substances with their melting-points, transition-points, or boiling-points, and the variation of pressure corresponding to 1° at the boiling-points, temperatures outside the range of the mercurial thermometer being included for convenience:—

Temperature	Fixed point
-183.0°	b.p. of oxygen; $dp/dt=75.9$ mm. per degree.
-159.6	m.p. of isopentane.*
-126.3	m.p. of methylcyclohexane.*
-116.3	m.p. of ethyl ether.*
-111.6	m.p. of carbon disulphide.*
-95.1	m.p. of toluene.*
-83.6	m.p. of ethyl acetate.*
-63.5	m.p. of chloroform.*
-45.2	m.p. of chlorobenzene.*
-38.87	m.p. of mercury.
-22.9	m.p. of carbon tetrachloride.*
0	m.p. of ice.
32.38	tr.p. of sodium sulphate.
46.2	b.p. of carbon disulphide; $dp/dt=24.8$.
50.67	tr.p. of sodium bromide.
78.3	b.p. of ethyl alcohol; $dp/dt=30.5$.
100.0	b.p. of water; $dp/dt=27.1$.
132.0	b.p. of chlorobenzene; $dp/dt=20.2$.
156.2	b.p. of bromobenzene; $dp/dt=19.4$.
184.1	b.p. of aniline; $dp/dt=19.6$.
218.0	b.p. of naphthalene; $dp/dt=15.2$.
231.8	m.p. of tin.
305.9	b.p. of benzophenone; $dp/dt=15.8$.
320.9	m.p. of cadmium.
356.7	b.p. of mercury; $dp/dt=13.3$.
419.4	m.p. of zinc.
444.55	b.p. of sulphur; $dp/dt=11.1$.
630.0	m.p. of antimony.
756.0	b.p. of cadmium; $dp/dt=8.1$ (calculated).
916.0	b.p. of zinc; $dp/dt=7.0$ (calculated).
960.5	m.p. of silver.
1063	m.p. of gold.

* Timmermans, Van der Horst and Kammerlingh-Onnes, Comm. No. 157, 1922. Samples of the liquids marked with an asterisk are supplied by the Bureau des Etalons physicochimiques, (Université, Rue des Sols, Brussels). The m.p.s. are stated to be correct to 0.1° on the Leiden helium thermometer scale.

Temperature	Fixed point
1083	m.p. of copper.
1452±2	m.p. of nickel.
1549±2	m.p. of palladium.
1755±5	m.p. of platinum.
2910	m.p. (approx.) of tantalum.
3080	m.p. (approx.) of tungsten.

For additional fixed points between 0° and -160°, v. Timmermans, *Sci. Proc. Roy. Dublin Soc.* 1912, and for a few very accurately determined temperatures, v. T. W. Richards, *J. Amer. Chem. Soc.* 33, 847; 36, 485, 1825; 40, 89. Steinmetz (*ibid.* 1918, 40, 96) gives the melting-points of a number of eutectic alloys. A table of melting-points of the elements has been published by the U.S. Bureau of Standards (v. J. Soc. Chem. Ind. 1919, 38, 67R). For the accurate calibration of short-range thermometers Richards and Shipley (*ibid.* 36, 1) recommend a floating-equilibrium method, hollow floats of glass or quartz being immersed in solutions of known concentration; Richards and Thorwaldson (*ibid.* 37, 81) have employed, with very satisfactory results, a method based on the heat of dilution of hydrochloric acid; and Richards and Tamaru (*ibid.* 42, 1374) describe a calorimetric method based on electric energy.

In this way a table or curve of corrections may be constructed showing the error at any scale reading of the thermometer. 'Normal' thermometers may now be purchased; they are compared with a standard thermometer before graduation, and nearly true temperatures are registered by them; or the thermometers may be sent to the National Physical Laboratory, the Reichsanstalt (v. Warburg, *Ann. Physik.* 1916, 48, 8, 1034), or the Bureau of Standards, and the necessary table of corrections obtained. The calibration of thermometers, as carried out at the Physik-Tech. Reichsanstalt, is described by Warburg (*Ann. d. Physik.* 1916, 48, 1034).

Tables of correction of readings of mercurial thermometers to true air-thermometer temperatures have been published by various observers; but as these tables must necessarily vary for different kinds of glass—the further correction for unevenness of bore being also required—they do not seem to possess much general value. It may be useful, however, to give references.—Rudberg, *Annalen*, 36, 121; Bosscha, *Compt. rend.* 69, 875, 1185; Regnault, *ibid.* 69, 879, and *Mémoires*, 21, 239; Crafts, *ibid.* 95, 836; Recknagel, *Pogg. Ann.* 123; Guillaume, *Traité pratique de la Thermométrie de Précision*.

Even when the above corrections to true air-thermometer temperatures have been made, there remain some sources of error, the most important of which is the alteration of the capacity of the bulb, and doubtless also of the capillary tube after long-continued heating, and, indeed, after any considerable change of temperature. A vast amount of experimental work has been done on this subject, and the explanation of the observed changes has given rise to a great deal of discussion. The following references may be made to the literature of the subject:—Despretz, *Compt. rend.* 4, 926; Person, *ibid.* 19, 1314; Legrand, *ibid.* 4, 173; Crafts, *ibid.* 91, 291, 370, 413; 94, 1298; Pernet, *ibid.* 91, 471; E. J. Mills, *T. Ed. 29, Part 2*, 587,

and Nature, 41, 100, 227, 538; Young, *ibid.* 41, 152, 271, 488; Tomlinson, *ibid.* 41, 198; Pernet, *Travaux et Mém. du Bureau Int. des Poids et Mesures*, i., B. 52, and I., 17; Guillaume, *Traité pratique*; Marchis, *Zeitsch. physikal. Chem.* 1899, 29, 1; 1001, 37, 553, 605; Ezer Griffiths, *l.c.* The most important facts regarding the alteration of zero point may be shortly described as follows:—

1. If a thermometer be graduated shortly after the bulb has been blown, the zero point will rise with comparative rapidity at first, then more and more slowly, and the elevation of the zero point may go on for many years. Joule (*Scientific Papers*, i. 558) took observations with one thermometer over a course of thirty-eight years, and the change, which then amounted to almost exactly 1°F., was still proceeding.

2. If a thermometer be maintained at a high temperature for a considerable time, the rise of the zero point takes place with much greater rapidity, and so far as is known the higher the temperature the more rapid is the rise, and apparently the higher is the final point reached. A total elevation of over 20° in the case of German soda glass has in several cases been observed, while larger glass bulbs, after continuous heating to 445°, or in one case 511°, have been found by Regnault, Crafts, and Callendar and Griffiths to suffer a contraction of from 0.25 to 0.34 per cent. In all cases the rise or contraction, which is rapid at first, becomes gradually slower, and it seems doubtful whether at any given temperature actual constancy of zero point or capacity has ever been attained. If, however, a thermometer has been heated for many hours to a given high temperature and then allowed to cool very slowly, subsequent heating to lower temperatures has very little effect on the zero point, and it is advisable to subject a thermometer to this process before determining the fixed points. According to Marchis (*l.c.*), a fluctuating high temperature is more effective than a steady one in raising the zero point. Hecker (*Zeitsch. f. Instrumentenkunde*, Beib. 1901, 5, 41) describes a method of electrical heating and slow cooling. Böttcher (*ibid.* Beib. 1903, 17, 154) states that the thermometer bulb should be heated for a short time to a temperature 100° above the initial softening temperature of the glass, and that slow cooling is unnecessary. The question is discussed by Dickson (*Bureau of Standards*, 1905, 2, 180) and methods of treatment are recommended. Weibe (*Zeitsch. Instrumentenk. Beib.* 3, 21; 4, 33) states that Jena borosilicate glass 5914 thermometers should be kept at 500° for at least 10 days, and that slow cooling is of comparatively small importance.

3. Not only is the zero point liable to change, but the interval between the zero and 100° points may at the same time be increased, for the coefficient of expansion of glass suffers diminution after prolonged heating.

4. Internal or external gaseous pressure on the bulb appears to have little or no influence on the rise of zero point.

5. If a thermometer—even after its zero point has been rendered as permanent as possible—be heated and then cooled very rapidly, a fall of the zero point will be observed, but after a day or two the greater part of this

fall, will be recovered, and the remainder after a longer period. The alteration of the zero point depends greatly on the nature of the glass, and a special hard glass is used by Tonnelot of Paris, while Schott and Co. in Germany employ two kinds of glass, 'normal thermometer' glass, 16^{III}, and a boro-silicate glass, 59^{III}, for the best thermometers. The latter glass is now generally used; it has a very high melting-point and can be used up to 550°, the mercury being prevented from boiling by the introduction of carbon dioxide under pressure (*cf.* Murrie, *J. Soc. Chem. Ind.* 1885, 45, 189, 655). Glass suitable for thermometers is now being made in England, and information regarding composition and properties may be obtained from the Institute of Chemistry. It is stated by Ezer Griffiths that fused quartz is much superior to glass as regards changes of zero point.

Other possible sources of error are the following:—If the mercury in the stem of the thermometer—or a portion of it—is not heated to the same temperature as that in the bulb, a correction is required, *v.* DISTILLATION, *v.* also Dimmer, *Akad. Wiss. Wein. Ber.* 122, 2a, 1439. Wheeler (*J. Soc. Chem. Ind.* 1916, 35, 1198) gives a useful graph, based on Thorpe's formula, to facilitate this correction. In order to ascertain the mean temperature of the unheated column, Guillaume (*Compt. rend.* 1891, 112, 87) places a supplementary thermometer without a bulb at the side of the thermometer stem. Modifications of this method have been proposed by Mahlke, *Zeitsch. Instr.* 1893, 13, 55; 1894, 14, 73; and by Adon, *ibid.* 1907, 27, 101.

The bulb is slightly compressible, and considerable changes of external pressure affect the readings to some extent.

Mercury does not move very freely in a capillary tube, and in delicate thermometers, when the temperature changes, the movement of the mercury may take place in jerks instead of smoothly. This may be avoided by tapping the thermometer (Pickering, *Phil. Mag.* 1886, 21). Greater freedom of motion is attained (Ducoux and Hamelin, *J. Phys.* 1910, 9, 600) by placing dilute sulphuric acid over the mercury, and electro-capillary effects are prevented by means of a recess full of mercury at the upper end of the capillary, the mercury in recess and bulb being connected by a platinum wire. The increase in sensitiveness was found to be so great that variations in the melting-point of ice with moderate change of pressure were readily observed.

For temperatures below the freezing-point of mercury, -38.7°, various liquids have been suggested to take the place of that metal. Alcohol and toluene thermometers have been in use for many years, and, more recently, pentane has been found specially suitable for very low temperatures (Kohlrausch, *Wied. Ann.* 1897, 60, 463; Baudin, *Compt. rend.* 1901, 133, 1207; Rothe, *Zeitsch. Instr.* 1902, 22, 192; Hoffmann and Rothe, *ibid.* 1907, 27, 265). Baudin and Rothe recommend 'technical' in preference to pure pentane on account of its lower freezing-point. The h.p. is 25° to 33°, and the pentane thermometer can be used between 30° and -190°.

The molecular weight of a dissolved substance is very frequently calculated from the

depression of the freezing-point or the rise of the boiling-point of a solvent. Thermometers of small range but great sensitiveness have been devised for these determinations, by Beckmann, and a full description of various forms of the instrument is given by him (*Zeitsch. Chem.* 1905, 51, 329). The bulb is of large size and the same thermometer can be used for different temperature ranges by transferring part of the mercury from the bulb to a receptacle at the other end of the capillary. The value of a scale division is thereby slightly altered, and the necessary corrections are discussed and a table is given by Grützmacher (*Zeitsch. Instr.* 1896, 16, 171, 200).

Useful general information about mercurial thermometers is contained in the following papers: Chree (*Phil. Mag.* 1898, 45, 205, 299); Kohlrausch (*Zeitsch. Instr.* 1898, 18, 76); Scheel, (*ibid.* Beib. 1899, 9-13); Harper (Bureau of Standards, *Bull.* 8, 659); Coste (*J. Soc. Chem. Ind.* 1913, 32, 341; *v.* also Ezer Griffiths, *l.c.*)

Other methods than those dependant on the use of the mercurial thermometer are in use for the determination of temperatures, but they are of varying degrees of accuracy. The method of determining the melting-points of minerals from the heating and cooling curves necessitates the use of a considerable amount of material, whilst the microscopic method lacks accuracy. Borgström (*Jahrb. Min.* 1816, 7, ref. 9-11) has made use of a method employed for organic substances, the substance being enclosed in a capillary tube of silica-glass and immersed in a transparent bath of fused salts (mixtures of sodium and potassium nitrates, sodium, potassium, and lithium chlorides, and sodium sulphate in various proportions according to the temperature required). A connection is traced between the melting-points and the geological occurrence of mineral substances, those with higher melting-points being found at greater depths in the earth's crust (*Chem. Soc. Abstr.* 1916, n. 191).

Platinum resistance thermometers.—The measurement of temperature by the alteration of the resistance to electricity of a platinum wire was suggested by Siemens (Bakerian Lecture, *Proc. Roy. Soc.* 1871), but in consequence of an adverse report to the British Association in 1874 this method was abandoned. Subsequently, however, the subject was investigated by Callendar (*Phil. Trans.* 1887, 178 A, 161; *Phil. Mag.* 1891, 32, 104; 1899, 47, 191); Griffiths (*Phil. Trans.* 182 A, 43), and both authors (*ibid.* 182 A, 119) with very satisfactory results. In order to insure accuracy the platinum wire must be pure in the first place; it must be prevented from alloying with silicon, carbon, tin, or other impurities, and it must not be subjected to strain—such as elongation. When these conditions were fulfilled, the resistance of a wire was always found to be constant at a given temperature. The form of thermometer recommended by Callendar and Griffiths is shown in Fig. 5. Two platinum wires are inter-wound in a double-screw thread, passing through holes in a thin mica plate *AB*. Each spiral is provided with a double and single electrode, symmetrically arranged. The six electrodes are insulated, and kept in place by passing through holes in thin mica wads

(one of which is shown at c) which are cut to fit the glass tube containing the thermometer. The electrodes are best made of platinum, the ends of the wires being fused to them by the oxy-hydrogen flame.

If R_0 and R_1 be the resistance at 0° and 100° , and R that at any other temperature, the corresponding value of the platinum temperature pt is deduced by the formula

$$pt = 100(R - R_0)/(R_1 - R_0).$$

To reduce the platinum resistance temperature to that of the air thermometer the following formula is employed

$$T - pt = \delta \left[\left(\frac{T}{100} \right)^2 - T \right]$$

the value of δ , generally 1.5, depending on the wire and being determined for each thermometer from observations at 0° , 100° , and 444.5° . The formula has been found to hold up to 1000° or 1100° . To avoid errors due to variation of the room temperature, compensating leads are used, and other improvements have been adopted from time to time. For further details, v. PYROMETRY; also Mueller, Bureau of Standards, 1916, Bull. 13, 547; Sligh, J. Amer. Chem. Soc. 1921, 43, 470; Roebuck, J. Opt. Soc. Amer. 1922, 6, 865; and Ezer Griffiths, l.c.

For moderate temperatures, nickel is recommended in place of platinum by Marvin (Phys. Rev. 1910, 30, 522); Jaeger and v. Steinwehr (Ann. d. Physik, 43, 8, 1165; 45, 7, 1089) have studied mercury resistance thermometers. They are much less sensitive than platinum thermometers, but have the advantage that a preliminary determination of resistance need only be made at a single normal temperature. Metallic oxide resistance thermometers have been constructed and investigated by Brown (Phys. Rev. 5, 126; 9, 205). Boron is recommended by Heraeus (D. R. P. 316416) (l. 4. 19) on account of its high temperature coefficient.

Dewar (Proc. Roy. Soc. 1904, 73, 244) states that platinum does not give good results at very low temperatures and recommends gold or silver. Meilink also (K. Akad. Wet. Amsterdam, 1904, 13, 212, 221) obtained better results with gold than with platinum. The resistance of gold, platinum, and other metals at low temperatures has been accurately determined by Kamerlingh Onnes and Clay, Comm. 99c and 107c. Kamerlingh Onnes and Holst (Comm. 141d) found that platinum is unsuitable in the region of -200° , and that at the lowest temperatures manganin and constantan are more satisfactory than either platinum or gold; but Zernike (K. Akad. Amsterdam, Proc. 18, 6, 914) gives an interpolation formula for platinum which is claimed to be accurate to within 0.02° at all temperatures below -200° . The resistance of mercury, tin, cadmium, con-

stantan, and manganin down to the boiling-point of helium has been determined by K. Onnes and Holst (Comm. No. 142a), and of mercury with liquid helium (*ibid.* 142c); also of pure metals with liquid helium by K. Onnes and Tuya (*ibid.* 160a and b).

Comparisons of the platinum scale of temperature with the hydrogen, nitrogen, helium, or air scale have been carried out by Harker and Chappuis (Phil. Trans. 1900, 194, 374 at Sevres; Meilink (K. Akad. Wet. Amst. 1902, 10, 495); Holborn (Ann. Physik. 1901, [vi.] 2, 242); Harker (Proc. Roy. Soc. 1904, 73, 217); Travers and Gwyer (*ibid.* 1905, 74, 528); Kamerlingh Onnes and Clay (l.c.); Holborn and Henning (Ann. Physik. 1911, 35, 4, 761); Dickinson and Mueller (Washington Acad. Sci. 1912, 2, 176); Henning (Ann. Physik. 1913, 40, 4, 635); Kamerlingh Onnes and Holst (Comm. 141a); of the platinum, gold, and hydrogen thermometers by Kamerlingh Onnes and Clay (Comm. 95c, d, and e), and of platinum, gold, and helium thermometers between -218° and -246° by Cath, K. Onnes, and Burgess (Comm. 152c), completing the data from 0° to -258° ; v. also Timmermans (l.c.); Moeller, Hoffmann and Meissner (Zeitsch. Instr. 1912, 32, 217) give comparisons of mercury and platinum scales from 0° to 550° .

Thermo-electric thermometers.—The first attempt to employ a thermo-couple for the measurement of high temperatures was made by Becquerel in 1826, but he failed to obtain concordant results. In 1886, however, Le Chatelier devised an instrument which gave good results and came into practical use, and since then great improvements have been introduced.

The thermo-electric thermometer consists essentially of two fine wires of different metals or alloys, fused together at one end, and connected through a galvanometer at their other ends, the fused end being placed in the source of heat. An E.M.F. is developed, which is roughly proportional to the difference in temperature of the two ends of the couple. Le Chatelier employed wires of Pt and Pt-Rh (10 p.c. of Rh), and this couple may be used up to 1600° . The other couples which have been employed most frequently are Pt and Pt-Ir (10 p.c. Ir), and Cu and constantan (a Cu-Ni alloy with 40 p.c. Ni); the former may be used for temperatures as high as 1200° , the latter up to 500° . For full account of these thermometers v. PYROMETRY.

A great variety of couples have been tried for both high and low temperatures. For high temperatures the couples mentioned have been found to give the best results, but the Pt-Ir alloy has the disadvantage that the Ir volatilises, very slowly even at 900° , and much more rapidly at 1200° . Sosman (Amer. J. Sci. 1910, 30, 1) has investigated the Pt-Pt-Rh (10 p.c. of Rh) thermo-element between 0° and the m.p. of Pt, $1755^\circ \pm 5^\circ$, and Adams and Johnston (*ibid.* 1912, 33, 534) the Cu-constantan thermo-element between 0° and 360° , and they give a standard scale of temperature between 200° and 1100° . Hevesy and Wolff (Phys. Zeitsch. 1910, 11, 473) find that the Ag-Ni thermo-element gives good results between -80° and 920° . Kowalko (Am. Electrochem. Soc. Trans.



FIG. 5.

1916, 29, 56) considers the Co—constantan element the best; cobalt withstands the action of hot gases better than nickel, remaining malleable and ductile. For low temperatures, Holborn and Wien (Wied. Ann. 1896, 59, 213) have recommended Fe—constantan; Pellat (Compt. rend. 1901, 133, 921), Fe—Zn; Dewar (Proc. Roy. Soc. 1905, 76, 316), Pt—German silver; whilst Kamerlingh Onnes and Clay (Comm. 107a) find that Ag—Au gives the best results. At about -256° this couple is about twice as sensitive as one of constantan—steel.

Comparisons of the thermo-electric scale of temperature with the air or hydrogen scale have been made by Holborn and Wien (Wied. Ann. 1895, 55, 95; 1896, 59, 213); Harker (Proc. Roy. Soc. 1904, 73, 217); and at low temperatures (-50° to -250°) by Kamerlingh Onnes and Crommelin, Comm. 95a; and with the platinum resistance scale by Waidner and Burgess, Bureau of Standards, Bull. 1909, 6, 149. White (Phys. Rev. 1910, 31, 135) discusses the utility of thermo-elements and the relative utility of thermo-elements and resistance thermometers.

The question of the calculation of the true temperature of the hot junction when the cold one is not at 0° has been fully discussed by Offenhaus and Fischer, Electrochem. Ind., New York, 6, 1908, 362.

Vapour pressure thermometer.—This form of instrument was recommended by Lord Kelvin (Pr. E. 1880, 432), and was introduced into practice under the name of the 'Thalpotassimeter' by Schaffer and Budenberg (Dittmar, J. Soc. Chem. Ind. 1885, 44). If the vapour pressures of a given liquid have been accurately determined through a certain range of temperature, any temperature within these limits may be afterwards determined by observing the pressure exerted by the vapour of the liquid.

The method possesses the great advantage that alteration of the capacity of the vessel containing the liquid and vapour is entirely without influence on the pressure, which is solely dependent on the temperature.

Probably the most serious objection to the method is the difficulty of filling the vessel or reservoir with the pure liquid *entirely free from air*, and if this difficulty be not overcome large errors may be introduced. For high temperatures, a mercury vapour pressure thermometer is sometimes serviceable (Ramsay and Young, Chem. Soc. Trans. 47, 651). The mercury must be well boiled to remove the film of air adhering to the glass, but this may be done without much difficulty. A liquid oxygen vapour pressure thermometer is recommended for temperatures between -183° and -200° by Stock and Nielson, Ber. 1906, 13, 39, 2066, and excellent results have been obtained with such an instrument by Kamerlingh Onnes and Braak, K. Akad. Wet. Amsterdam, 1908, 11, 333. Vapour pressure thermometers and pyrometers have been devised by Fournier, and an account of these instruments is given by Marieni (Elettricità, Milan, 1908, 30, 82). H. v. Siemens (Ann. Physik. 1913, 42, 4, 871) describes a modification of Stock and Nielson's thermometer and gives the vapour pressures of CS_2 , CO , O_2 , and N_2 , which he

determined by means of a Pt resistance thermometer. Stock, Henning and Küss (Ber. 1921, 54 [B], 1119) give vapour-pressure tables for measurement of temperature between 25° and -185° , and describe the apparatus they employ.

The following papers or memoirs on the subject of thermometry may be consulted: Sur les thermomètres à gaz, D. Berthelot, Paris, 1903; Kohlrausch, Zeitsch. Instr. 1898, 18, 16; Guillaume, Thermométrie de précision; Chrec, Phil. Mag. 1898, 45, 205, 299; Scheel, Zeitsch. Instr. 1899; Callendar, Nature, 1899, 59, 494, 519; Phil. Mag. 1899, 47, 191; Barus, Int. Phys. Congress, Paris, Rep. 1, 1900, 148; Burgess, Chem. News, 1913, 107, 169 and 182; Kamerlingh Onnes, Third Int. Congress of Refrigeration, 1913, section for Physics, Chemistry and Thermometry; Ezer Griffiths, Methods of Measuring Temperature, 1918; Scheel, Zeitsch. angew. Chem. 1919, 32, 347; Kayes, J. Amer. Chem. Soc. 1920, 42, 54; Het Natuurkundig Laboratorium der Rijks-universiteit te Leiden, Articles on Thermometry and Manometry, Keesom, p. 89, Crommelin, p. 211.

For the apparatus for the determination of the heat of evaporation of liquids of high boiling-points, see Awbery and Griffiths (The Phys. Soc. of London, 1924, 36, 303).

An inter-comparison of high-temperature scales.—An inter-comparison has been made by Forsythe (Astrophys. J. 1923, 58, 294) of the high-temperature standards used in certain research laboratories in the United States of America and abroad by the method of brightness temperatures as measured by the disappearing filament optical pyrometer. The 'brightness temperature' of a non-black body, as determined by measuring the brightness for a given wave-length λ with the pyrometer, is defined as the temperature to which a black body must be raised to give the same brightness for the same wave-length. Thus if the brightness temperature of a body is 1500°K. for $\lambda=0.665\mu$, then for this wave-length the body has the same brightness as a black body for this same wave-length.

Several tungsten lamps which had been carefully aged in the Nela Research Laboratory were sent to the Bureau of Standards, the National Physical Laboratory of Great Britain, the University of Wisconsin, and the Research Laboratory of the General Electric Co., requesting that the temperatures of the lamps should be measured for specified currents. In each of the laboratories the temperatures were measured with a disappearing filament optical pyrometer, using a plate of red glass as the monochromatic screen. The results give not only a comparison of the brightness temperature of tungsten but also a valid comparison of the high-temperature scale. In each laboratory the high-temperature scale is based upon: (a) the melting-point of gold (1336°K.) or palladium (1828°K.), (b) extrapolation by means of Wien's equation using for C_1 the value 14350° . Necessary reductions due to various factors such as a difference in the standard temperature, or a different value of the constant C_2 have been considered. A table is then given of the values obtained at the various

laboratories, the agreement being very good. Part of the table is given below:

Lamp	Current	N.R.L. April, 1920	N.P.L. April, 1922	N.R.L. June, 1922	Bureau Jan., 1923	N.R.L. Jan., 1923
T-78-C.	15.4	1825	1825	1826	1824	1828
	20.4	2262	2265	2266	2265	2269
	27.4	2746	2757	2753	2755	2755

(Sci. Abstr. 1924, 27, 527).

The measurement of small sources of heat: The use of a compensated micro-calorimeter.—The instrument consists of a cell placed at the centre of a constant-temperature bath and separated from it by a thermal insulator. The evolution of the heat to be measured takes place in the cell. A thermopile, joined to a galvanometer, is connected by a series of junctions with the cell and by another series with the bath, and serves to measure the difference in temperature of the two media.

A second thermopile similarly placed is used to absorb, by the Peltier effect, the heat evolved. Compensation is effected by adjustment of the galvanometer deflection to zero. It is suggested that the method may be suitable for following the progress of chemical reactions where small changes in heat take place or for calorimetric observations in biology (A. Tian, *Compt. rend.* 1924, 178, 705; *Sci. Abstr.* 1924, 27, 527).

S. Y.

THERMONATRITE v. NATRON; TRONA.

THERMOSTATS. A thermostat may be defined to be an apparatus so arranged as to maintain the temperature of a space constant between certain definite limits. Previous to 1860, the forms of apparatus employed were comparatively few and simple, but during subsequent years refinement of physical and chemical experimental methods has led to the design of very numerous varieties of thermostats. Some few of these have been adapted to technical uses; in general these applications present little complexity and do not call for any detailed description. They have mainly been applied to the temperature regulation of steam and gas heating systems and more recently to the control of electrical heating. Among other purposes the temperature control of incubators heated by gas or electricity, of acetylene heated germinating stoves, and of pasteurising apparatus used in the sterilisation of milk are noteworthy. The automatic regulation of the temperature of fermenting worts, of dye-vats, of evaporating pans and vacuum stills, has resulted in improvements in the sugar, spirit, and dyeing industries. Similarly, thermostats are extensively adapted to secure the more exact and economical working of lacquering, brazing, tempering, annealing, and roasting ovens and kilns. Numerous systems for the central heating of public buildings and houses by steam, hot water, gas, and hot air are now automatically regulated by thermometric or electrical control apparatus. Similar thermostatic arrangements are also used in connection with steam-heating devices in railway carriages. In gas-testing stations, rooms are maintained at

a uniform temperature by thermostats controlling the gas-heating system. Automatic fire-alarm devices are usually supplied with thermometric or electrical thermostats arranged to give warning by telegraphic or mechanical signals.

The thermostats and thermo-regulators suggested may be classified as:—

I. Thermostats depending on a flow of heated liquid for the maintenance of a constant temperature.

II. Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body:

(a) Change of phase at freezing-point or cryohydric-point.

(b) Change of phase at boiling-point.

(c) Change of phase at inversion-point.

III. Other thermostats not automatically regulated through mechanical or electrical means.

IV. Self-regulating thermostats, including—

(a) Mercurial or other single-liquid thermometers:

1. Acting directly on the gas supply or other heat source;

2. Acting on the source of heat through electrical arrangements;

3. Acting on the source of heat through mechanical arrangements;

(b) Gas thermometers:

1. Acting on the gas supply by transmission of pressure through a liquid column;

2. Acting through electrical arrangements;

3. Acting through mechanical arrangements;

(c) Vapour-tension thermometers:

1. Air and vapour;

2. Vapour in contact with its own liquid only;

(d) Thermostats depending on the differential expansion of solid substances;

(e) Electrically heated thermostats with electrical control;

(f) Other mechanical regulators.

The limits of this article preclude the description of more than a few of the more typical examples of each of these classes; details of other forms and references may be obtained from: *Temperature Regulators*, J. T. Brown; *Laspeyres*, *Pogg. Ann.* 152, 132; H. Hammerl, *Carl's Rep.* 18, 1882; K. Arndt, *Zeitsch. Chem. Apparatenkunde* 1, 255-263; Fr. Grützmaier, *Zeitsch. Instrumentenkunde*, 22, 184, 193, 201; W. C. Geer, *J. Phys. Chem.* 6, 85-105, 1902, who gives a general discussion and a useful bibliography; M. Bodenstein, *Zeitsch. physikal. Chem.* 1899, 30, 113-139, who supplies a detailed account of thermostats used in gas-reaction researches, and H. W. Fischer and O. Böhmer, *Zeitsch. Elektrochem.* 1908, 14, 375. See also Cumming, *Trans. Faraday Soc.* 1912, 7, 253; Bousfield, *ibid.* 260.

1. *Thermostats depending on a flow of heated or cooled liquid for the maintenance of a constant temperature.*—The form of apparatus invented by C. Blaufuss-Weiss may be adapted for use either as a pressure or temperature regulator (D. R. P. 439,4, 1887). As used in the latter capacity, it consists essentially of a cylindrical

valve controlling the supply of hot or cold currents of either liquid or vapour to a worm arranged in the vat to be maintained at a uniform temperature. The valve is formed by an elliptical slit in a sheet cylinder, which passes half round the circumference of the cylinder, and, when the latter revolves, is brought more or less opposite to tubes opening into the sides of the drum, which serves as a valve-box. The space within the revolving cylinder is furnished with tubes passing through the head of the drum to serve as supply or exit pipes. The valve is worked by the rise and fall of a vertical piston, actuated by the expansion and contraction of a quantity of mercury, which is contained in a bell-shaped vessel of which the wider end is applied to a small chamber which forms a side continuation of the vat. The vertical movement of the piston is transformed into the circular motion of the valve in a horizontal plane by means of a pin working in a screw slot on a hollow cylinder.

A simple thermostat for use in connection with the refractometric examination of oils and fats, by T. E. Thorpe (*Chem. Soc. Trans.* 1904, 257), uses a constant current of liquid, under a defined pressure head, heated by passing through a coil in the vapour of a boiling liquid (*r. vol. v.* 662).

W. Behrens (*Zeitsch. Wiss. Mikrosk.* 1895, 12, 1) describes a neat air-worked expansion valve for controlling a hot-water current supplied to the hot stage of a microscope.

Other forms using this principle are given by J. Ph. Grünig, *D. R. P.* 75882, 1893; J. C. Schalkwijk, *Zeitsch. Inst.* 1901, 21, 338; and T. M. Lowry, *Trans. Faraday Soc.* 1907, 3, 119.

A thermostat for low temperatures has been described by Walton and Judd, *J. Phys. Chem.* 1914, 18, 717.

11. *Thermostats utilising the latent heat of the alteration of the state of aggregation or change of phase of a body.*—(a) References to types using the change of phase at the freezing-point and cryohydric point will be found in Geer's bibliography (*l.c.*). To these may be added Travers (*Zeitsch. physikal. Chem.* 1905, 52, 443), using alcohol and carbon dioxide show for low temperatures.

(b) The change of phase at the boiling-point is more generally utilised. The vapour from a liquid boiling at the required temperature is caused to surround the oven or bath to be heated. Here the temperature will vary according to the pressure under which the liquid is boiled.

The liquids used for this purpose are:—Water, ether, methyl and ethyl alcohols, benzene, toluene, acetic acid, carbon disulphide, amyl alcohol, xylene, turpentine, aniline, naphthalene, glycerol, diphenylamine, the mono hydrate of sulphuric acid, mercury, paraffin, sulphur, zinc.

The temperatures so obtained lie between 22° and 1040°. At the ordinary atmospheric pressure one definite temperature is obtained for each substance used. Intermediate temperatures may be obtained in several ways:—

(1) The pressure under which the vapour is formed is varied; (2) mixtures of liquids in various proportions are used; (3) a solid is dissolved in a liquid, the boiling-point being

thus raised, and the vessel or bath is surrounded by the boiling liquid.

L. Meyer devised an apparatus for determining the boiling-point of a liquid at any pressure below that of one atmosphere.

It may be used to control a constant-temperature bath (*Analyst*, 15, 303). The apparatus (see Fig. 1) is a pressure control valve. The mercury in AB cuts off the connection with the air-pump through H as soon as the pressure is reduced to the required point; CD is a mercury valve which admits air to the apparatus immediately the pressure falls below that fixed upon.

Brown has improved this apparatus, rendering it possible to use it for pressures higher, as well as lower, than one atmosphere. A mercury manometer is so constructed that, immediately the pressure falls below or rises above that determined upon, an electro-magnetic clutch, actuating a suitable stopcock, is placed in a battery circuit, and thus connection is made between the reservoir and the pump or outer air, as may be required for adjustment (*Phil. Mag.* 1879 [v.] 7, 411).

A. Fock has constructed a very serviceable bath, in which common petroleum is used as the mixture of liquids of different boiling-points. A double cylinder AB (Fig. 2), serving as a vapour-jacketed bath, is connected by means of the side tubes a and b with the reflux

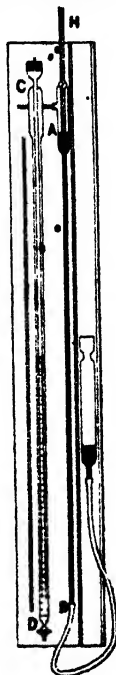


FIG. 1.

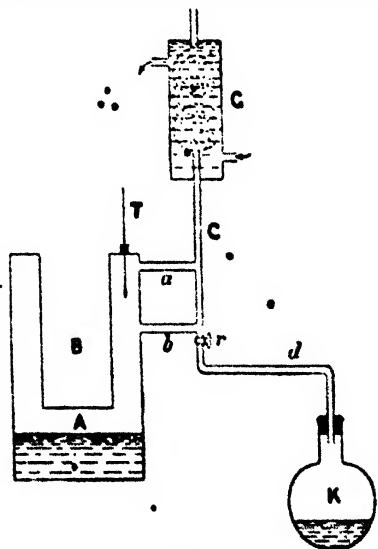


FIG. 2.

condenser c. The tube c connected with the condenser communicates, through the stopcock r and tube d, with the reservoir flask K. A mixture of liquids (e.g. common petroleum) is placed

in the bath and distilled, the distillate passing through the open stopcock *r* into the flask *x*. At the moment when the required temperature is attained, as indicated by the thermometer *t*, the stopcock *r* is closed; the distillate now returns through the tube *b* to the bath, hence the temperature of *b* will remain constant for any length of time (Ber. 1885, 18, 1124).

Ramsay has used a vapour-bath in which the temperature is controlled by regulating the pressure under which a selected pure liquid is boiled (Chem. Soc. Trans. 1885, 640).

J. Traube and L. Pincussohn (Zeitsch. Inst. Beib. 1897, 17, 49) have also devised a simple thermostat using a boiling liquid under a controlled pressure. For other forms see Geer (*loc. cit.*); F. H. Dupré and P. V. Dupré (Analyst, 1913, 38, 308); Field (J. Amer. Chem. Soc. 1914, 36, 72). Brame has described a constant temperature heating apparatus for explosives and experiments on the decomposition of nitro-celluloses (J. Soc. Chem. Ind. 1912, 31, 159).

An easily adjustable vapour thermostat has been contrived by Fletcher and Tyrer (Chem. Soc. Proc. 1911, 28, 189).

(c) Richards and Churchill (Zeitsch. physikal. Chem. 1898, 28, 313) have similarly used the change at inversion points.

III. Other thermostats not automatically regulated.—Instruments serving as indicators only have been devised by Hall (Q. J. Sci. 1818, 5, 52); Doyère (Ann. Chim. 1850, [iii.] 28,

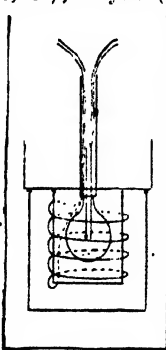


FIG. 3.

inner flask, surrounded by two concentric glass vessels, with an air space between; the three vessels are fastened above to a zinc plate. A delicate thermometer and a thermoelement are placed in the centre of the flask; the stem and wires pass through a leaden pipe attached to the zinc plate. Between the two surrounding vessels is coiled a German-silver wire, the coils hanging freely without contact with either vessel; wires pass from the coil to a battery through the leaden tube. The whole is completely immersed in melting ice, contained in a fourth vessel; the leaden tube alone projects, and serves to keep the wires from contact with the ice. By passing an electric current through the German-silver coil, the temperature of the central vessel can be maintained at any desired point above 0° (Sitz. W. 1873, 6892).

The same principle is applied by H. Crew (Phil. Mag. [v.] 33, 89). The accompanying illustration (Fig. 4) shows the points in which this instrument differs from the preceding one.

Julien storage cells are used as the source of a constant current, which is regulated by alteration of the length of a resistance wire through which the current flows, by means of a slider and controlled by means of a Thomson balance. Other non-automatic instruments are described by Mahlko (Zeitsch. Inst. 1893, 13, 197),

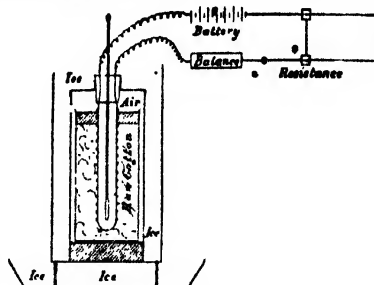


FIG. 4.

Pulfrich (Zeit. Inst. 1898, 18, 49), and Rothe (*ibid.* 143, 1899, 19).

IV. Self-regulating thermostats: (a) Single-liquid thermostats (1) acting directly on the gas supply or other heat source.—Thermostats of this and allied types have been frequently utilised in connection with technical processes and heating systems; references to a number of these are given at the end of this article.

Reichert's form of regulator is essentially that of a mercury thermometer, with a reservoir at the top of the column. The gas-supply tube is placed so that its contracted opening is vertically over and near to the surface of the top of the mercury column. The leading tube takes off gas at the side of the reservoir. A small side tube on the stem is supplied with a screw by means of which the mercury level may at any time be adjusted, and the temperature maintained thus altered at will (Fig. 5) (Zeitsch. anal. Chem. 11, 34; Pogg. Ann. 144, 467; cf. Fontaine, Ann. Chim. Anal. 1911, 16, 52; Fänder, Chem. Zeit. 1913, 37, 40).

Gerhardt's modification permits the instrument to be filled easily with mercury.

Regulators of the same type, but varying somewhat in form, have been constructed by Page (Chem. Soc. Trans. 1876, 24), Fletcher (*ibid.* 1876, 488), and Roulin (Dingl. poly. J. 227, 263);

Whitaker (Chem. News, 1913, 107, 242). The instrument devised by Roulin is made of iron and steel (r. Fig. 6). The height of the mercury column is adjusted by means of a sliding tempered-steel rod, held in position by the set screw *f*. As this rod passes down the centre of the gas-supply tube, the gas can only reach the burner tube by passing through the ring-shaped aperture *d*, near the

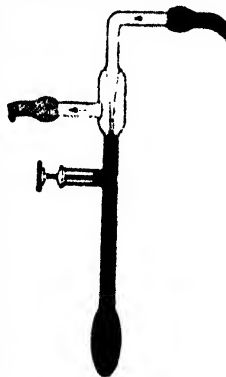


FIG. 5.

surface of the mercury. A small tap *g* maintains a sufficient supply of gas to the burner to avoid extinction of the flame by the complete interruption of the supply at *d*.

In the thermostat battery by Dibdin and Smith, in use at the metropolitan gas stations, large mercurial thermometers are employed. The tubes by which they communicate with the supply tube are provided with stopcocks, so that any one or more of them may be thrown out of action. They control the gas supply to the boiler connected with the hot-water pipes.

For more accurate work, the mercury has been replaced by 30 p.c. calcium chloride solution, alcohol, benzoline, petroleum, xylene, or toluene. The toluene regulator has gained general acceptance; a simple and easily constructed form, designed by H. Lunden and W. Tate (*Zeitsch. Chem. Appar. II.* 1, 13, 1907), is shown in the sketch (Fig. 7) with dimensions in millimetres. The column of calcium chloride solution prevents contact of the toluene with the mercury and with the stopcock *R*, thus doing away with the slow

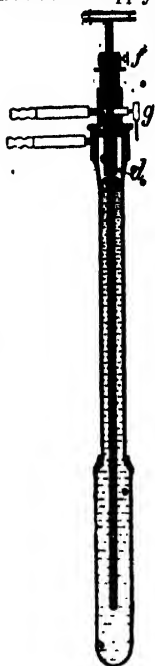


FIG. 6.

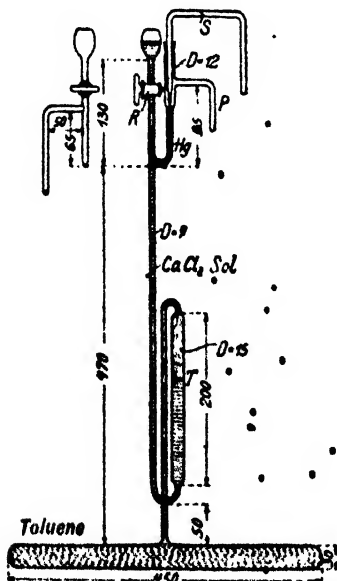


FIG. 7.

evaporation of the expanding liquid and allowing the use of ordinary lubricants with the stopcock provided to make temperature adjustments. This regulator, without the

aid of any form of pressure regulator (the gas pressure varying from 50 to 60 mm. of water), maintained the temperature of a water-bath of 150 litres capacity during 30 days constant in a room varying considerably in temperature. The greatest difference between the extreme temperatures (observed at regular and frequent intervals) was 0.02°. A small part of the heating gas only passed through the valve *D*, sufficient to heat the bath within a short interval of the required temperature was supplied direct from the main.

Another convenient form of toluene regulator is described by Lowry (*J. Soc. Chem. Ind.* 1905, 1033); there is a helical toluene reservoir tube coiled round a straight vertical stem containing mercury; it is provided with a wide bye-pass but has no provision for ready adjustment of the temperature, and the mercury and toluene are in contact near the lower end of the helix.

Slator has described (*J. Soc. Chem. Ind.* 1911, 30, 61) a modification of the ordinary toluene regulator by which it can be readily adjusted to any desired temperature.

Hannay (*Mon. Sci.* [iii.] 16, 1021) and F. W. Dufort (*Chem. Zeit.* 1886, 52, 789) have designed thermostats belonging to this class.

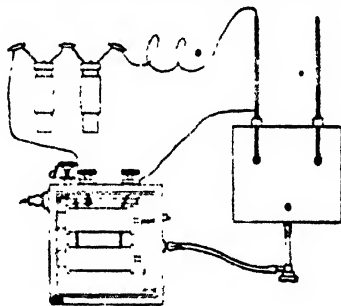


FIG. 8.

Further references are given by Geer (*J. Phys. Chem.* 1902, 6, 85); cf. Davis (*J. Amer. Chem. Soc.* 1915, 37, 1198). See also Starkey and Gordon (*J. Ind. Eng. Chem.* 1922, 14, 541).

(2) *Thermostats acting on the source of heat through electrical arrangements.*—The usual type of this class employs a mercury thermometer with one pole of a battery permanently connected with the mercury and a second adjustable pole which completes the circuit at the desired maximum temperature. An electro-magnetic arrangement in the circuit actuates a gas-cock, or works a gas valve either directly, or, by means of a plunger, indirectly controls a mercury valve of the usual type. This form of thermostat can be made very rapid in action and practically independent of variations in the gas pressure.

Scheibler has constructed an electro-thermostat, with the usual form of electric thermometer (Fig. 8). The electro-magnet is contained in the square box *A*; the upper end of the armature is provided with a leather pad, which works against the continuation of the gas-supply tube *b*, and with it forms a valve which cuts off the gas when the mercury comes into contact with the upper platinum wire. The extinction of the flame is avoided by having a small hole at *c* in the tube, more or less closed by means of the

screw *d*, through which a small stream of gas can escape into the box, and hence into the burner tube (*Zeitsch. Anal. Chem.* 1868, 88).

Kohlrusch adapted this principle to the regulation of the temperature of a hothouse (*Dingl. poly. J.* 389, 175). E. E. Reid (*Amer. Chem. J.* 1909, 41, 148-152) employs a mercury valve worked by a plunger controlled by an electro-magnet.

A high-temperature thermostat, capable of being kept constant to within 1° at 1000° , has been described by Haughton and Hanson (*J. Inst. Metals*, 1917, 18, 173).

A thermo-regulator for thermostats at temperatures close to ordinary room temperatures has been described by Powell (*J. Soc. Chem. Ind.* 1914, 33, 899).

An electrical contact vapour-pressure thermo-regulator has been contrived by Field (*J. Amer. Chem. Soc.* 1914, 36, 72). The regulator has proved sensitive to 0.1° - 0.005° .

Other forms are quoted by Geer (see iv. 1); to these we may add Clerget (*Dingl. poly. J.* 134, 23), Pfaundler (*Carl's Rep.* 18, 443), and Salet (*Bull. Soc. chim.* 1865); Morgan (*J. Amer. Chem. Soc.* 1911, 33, 344); Bunzel and Hasselring (*J. Amer. Chem. Soc.* 1914, 36, 949); Gouy (*ibid.* 1920, 42, 60).

The sensitiveness of a mercury thermo-regulator operated electrically is affected by the adherence of mercury to clean platinum. Mansfield Clark (*J. Amer. Chem. Soc.* 1913, 35, 1889) finds that by substituting a nickel or nichrome wire for platinum, the making and breaking of the circuit may be made to occur at temperatures much closer to one another.

For a description of a thermo-regulator with the characteristics of the Beckmann thermometer, see R. B. Harvey (*J. Biol. Chem.* 1920, 41, 9) in *Abstract. Chem. Soc. Trans.* 1920, ii. 161.

(3) *Thermostats acting on the source of heat through mechanical arrangements.*—Randall's apparatus (*Dingl. poly. J.* 224, 478) admits of direct technical applications, as it is adapted to the heating of large masses of water to a constant temperature by the use of steam. In Fig. 9 *b* is

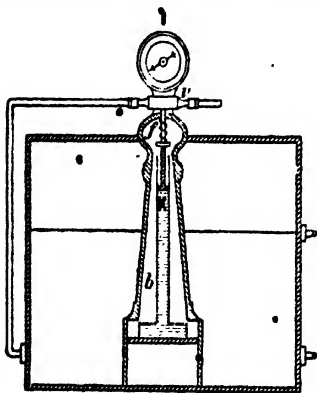


FIG. 9.

a thin-walled tubular vessel containing some expansible liquid, the movements of the surface of which are followed by the piston *x*. This piston works a valve *v*, which controls the

steam supply. The spring *f* insures the return of the piston, the movements of which are recorded by the indicator *i*, which thus acts as a thermometer.

D'Arsonval constructed a very delicate thermostat (Fig. 10) by surrounding his oven with a



FIG. 10.

screw or by a cork through which a thermometer passes. Connected with this water chamber is the side tube *o*, closed by a caoutchouc membrane. Near to the centre of the surface of the chamber completely filled with water, which is introduced through an opening *v*, closed by a membrane the gas-supply tube terminates—in a small metallic valve-box, from which the gas is led off to the burner by the tube *d*. The expansion or contraction of the large volume of water in the outer chamber causes the caoutchouc membrane to lessen or increase the distance between the supply tube and its own surface, thus forming a very sensitive valve, which controls the supply of gas to the burner. This regulator is said to keep the temperature constant to $\frac{1}{10}^{\circ}$ (*J. Pharm. Chim.* [iv.] 26, 474).

To maintain constant higher temperatures than can be employed with water, D'Arsonval substitutes a brass tube (Fig. 11), containing petroleum or glycerol, for the surrounding water chamber. The membrane is replaced by a corrugated metallic plate such as would be used in an aneroid barometer; *b* is a leaden tube prolonging the brass tube; it is hermetically closed after charging the tube. The chamber at the back of the aneroid plate communicates with the main tube by two small tubes *m* and *n*.

Several other forms of this regulator, retaining the same kind of valve, have been constructed. The valve itself has been mounted separately on a stand, and provided with a funnel and stop-cock to adjust the amount of liquid in the connected reservoir and the lower part of the valve, and with a by-pass to insure that the flame be never quite extinguished. The same type of valve has also been adapted to the

regulation of the flow of a cooling mixture, used for obtaining temperatures below that of the surrounding air.

G. Dorian (Bull. Soc. Ind. Mulhouse, 1900, 71, 249) described a combined head and moisture regulator, in which the expansion of the liquid of a thermometer with a reservoir of spirally twisted tube controls a cock regulating the current of heating fluid and a hydrometer regulator works the moisture supply. T. S. Patterson (J. Soc. Chem. Ind. 1902, 21, 456),

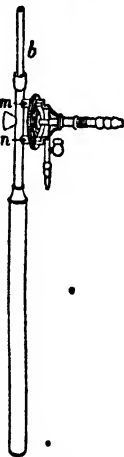


FIG. 11.

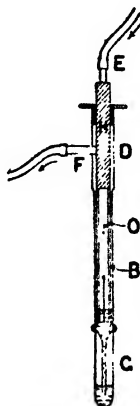


FIG. 12.

N. A. Randolph (Jour. Franklin Institute, 1883, 116, 465), V. H. Veley (Chem. Soc. Trans. 43, 370), and Nauman (Dingl. poly. J. 226, 276), give other forms, and various technical adaptations will be found in the list given at the end of this article.

(b) *Gas thermometer regulators.*

(1) *Acting on the gas supply through a liquid piston.*—A thermostat on this principle was devised by Kemp (Dingl. poly. J. 117, 352) and improved by Westly.

Bunsen's thermostat is a modification of Kemp's. The gas supply and exit tubes are arranged as shown in Fig. 12; the supply tube *x* passes through a brass cylinder *H*, which screws into the loose brass cap *D*. At its lower end is a slit, and it is provided with a minute orifice at *o*; the exit tube *F* is joined on to the side of the cylinder *H*, the latter being continued by the glass tube *B* to the same depth as the supply tube. The cap is fitted on a brass tube supplied with a slit in which the tube *F* can slide. A glass cylinder closed at the lower end continues this brass tube. In the lower part of this glass vessel is a glass air-chamber opening downwards and closed by the mercury contained in the cylinder; this air-chamber preferably takes the form shown at *o*. The expansion of air in the chamber causes the mercury to rise in the cylinder, and thus partially closes the slit; the position of the slit is regulated by the screw cap until the required temperature is attained. The minute orifice *o* insures that the gas supply should never be completely cut off (Dingl. poly. J. 143, 342).

Bunsen's low-temperature regulator has a larger air chamber, and is provided with a side tube and stopcock, by means of which the

amount of mercury present can be readily altered (Desaga's Catalogue). Pontallie divides the gas supply after passage through a Bunsen's regulator, using one part to heat the regulator only, the remainder heating the bath. As these quantities are in exact and determined proportion, the temperature of the bath is maintained constant when that of the regulator does not vary.

Schorer separates the air-thermometer reservoir from the valve to enable the instrument to be used for high temperatures (Zeitsch. anal. Chem. 9, 213).

D'Arsonval adapted his thermostat for use at temperatures between 150° and 1200° by substituting an air reservoir for the petroleum reservoir employed at lower temperatures. The reservoir was made of glass or porcelain. The aneroid valve was at the same time furnished with a lever-arm and weight *r*, by means of which the pressure on the lower surface of the aneroid plate could be more or less compensated, and the amount of gas supplied altered at will (Fig. 13) (J. Pharm. Chim. [iv.] 26, 474).

Although a number of varieties of this type have been used (see Geer's bibliography; J. Martenson, Chem. Zentr. 1872, 513; Clowes, Chem. Soc. Trans. 24, 639; L. Saarbach, J. Amer. Chem. Soc. 18, 511, 1901), and the principle has been technically applied in connection with furnaces of moderately high temperature for low temperature work the toluene thermometer forms are to be preferred for accurate long period temperature regulation; all gas and vapour thermostats suffer from the defect of needing regulation with the changes in pressure of the air.

(2) *Acting through electrical arrangements.*—These devices resemble the instruments in

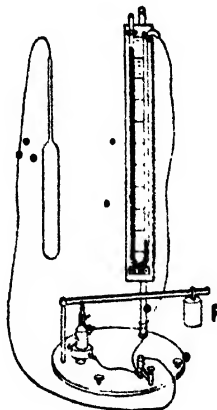


FIG. 13.

group iv. *a* (2). Pfaunder's apparatus (Carl's Rep. 18, 443) is similar to Scheibler's, the points of difference are sufficiently evident from the annexed figure (Fig. 14).

Solari (Bull. Soc. chim. 1923, [iv.] 33, 1000) has described an apparatus which consists essentially of a differential air thermometer with mercury as the moving liquid. One bulb is maintained at a constant temperature and the other is placed in a small auxiliary furnace of copper tube connected in series with the main furnace. The tube containing the mercury is

provided with three platinum contacts so arranged in connection with a resistance and a swinging commutator that automatic regulation of the current passing through the furnace is secured. If Q be the thermal capacity, R the radiating power, and C the conductivity of the tube carrying the heating coil of the main furnace, and q , r , and c the same constants for

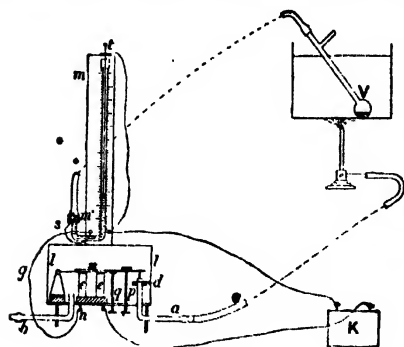


FIG. 14.

the small one, then temperature control to within $\pm 5^\circ$ may be obtained by making Qq very large, R/r very small (but r must not be too great), and C/c very small (c may be very large).

(3) *Acting through mechanical arrangements.*—Jeannel's thermostat (Fig. 15) is an air-thermometer thermostat in which the air reservoir consists of a metallic vessel of 300–400 c.c. capacity. This is connected with one limb of a

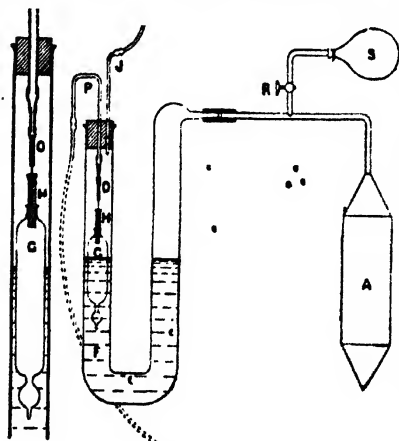


FIG. 15.

U-tube containing glycerol. In the other limb a float G carries a steel needle working loosely in a fine caoutchouc tube O . By a rise of the liquid in r , the float, guided by the steel needle, brings the flat upper surface of the sealing-wax N , in which the needle is mounted, near to the mouth of the tube O , thus forming a valve controlling the current of gas from the supply tube J to the exit tube r , of which O is a continuation. The pressure of the air in A is modified at pleasure by means of the caoutchouc pump S ,

with which connection is made through the tap R on a side tube (Ann. Chim. [iv.] 25, 380).

W. T. Richmond (Amer. Chem. J. 5, 287), Bendix and Lohse (D. R. P. 14242, 1880; Ber. 14, 2608), and Bechem (D. R. P. 18077, 1881; Ber. 15, 1226) have also devised self-acting thermo-regulators of this type.

(c) *Vapour-tension thermometers.*

(1) *Air and vapour.*—Andree's thermo-regulator is a Kemp thermostat in which the expansion of the air in the reservoir is increased by the addition of a small quantity of some readily volatile liquid. Such liquids as ether, alcohol, acetone, light petroleum and water may be employed for the purpose. Ether is particularly suitable, on account of the rapid increase of its vapour tension with increase of temperature. A thermostat of this form will maintain the temperature of a water-bath constant within 0.04 – 0.05° (Wied. Ann. 4, 614).

Lothar Meyer has also made use of the same principle (Ber. 16, 1088).

The following mixtures of liquids of constant boiling-point, for use in constant temperature heating baths, have been suggested by A. Golodetz (Chem. Zeit. 1914, 38, 1253).

B.p.	Composition of liquid.
33°	Water and ether (heterogeneous).
36.5–37.5°	Alcohol (3) and ethyl bromide (97).
38°	Carbon disulphide (87) and methyl alcohol (13).
39–40°	Carbon disulphide (71) and methyl acetate (29).
42.5°	Carbon disulphide (91) and alcohol (9).
53.5°–54.5°	Methyl alcohol (12) and chloroform (88).
55.5°	Methyl alcohol (20.6) and carbon tetrachloride (79.4).
58°	Methyl alcohol (38.4) and benzene (61.6).
59°–59.5°	Alcohol (6) and chloroform (94).
62°	Methyl alcohol (47) and ethyl acetate (53).
64.8°	Benzene (74.1), alcohol (18.5), and water (7.4).
68°	Alcohol (32.4) and benzene (67.6).
71.5°	Alcohol (31) and ethyl acetate (69).
74.8°	Carbon tetrachloride (77.16) and alcohol (22.85).
79.5°	Benzene (90.5) and isobutyl alcohol (9.5).
84.5°	Water and toluene (heterogeneous).
87.7°	Water (26.3) and propyl alcohol (71.7).
91°–91.5°	Propyl alcohol (53) and toluene (17).
92.5°	Water (41) and pyridine (59).
94°–94.5°	Water and turpentine (heterogeneous).
95°	Water (7) and chloral (93).
98.5°	Water and ethylaniline (heterogeneous).
99°	Water and diethylaniline (heterogeneous).
104°	Toluene (70) and acetic acid (30).
113°–113.5°	Acetic acid (27) and xylene (73).
121°–122°	Amyl alcohol (30) and ethylene dibromide (70).
126°–128°	Amyl alcohol (52) and <i>m</i> -xylene (48).

Benott's thermo-regulator has the thermometer reservoir separated from the valve, connection being made by means of a caoutchouc tube containing mercury.

The reservoir consists of a thin tube, drawn out at one end for convenience in filling, which contains a small quantity of air, and a few drops of some volatile liquid; the remainder of the space in the tube is occupied by mercury in connection with the mercury in the valve by means of the caoutchouc tube. The valve differs somewhat from the ordinary form. It is provided with a side tube *A* (Fig. 16), by which a small amount of gas can directly pass from the supply tube *x* to the burner tube *y*. Mercury can be added by means of the side tube *B*, or withdrawn from the cock *c* to adjust the level within the valve. The whole is mounted upon a sliding board, fixed by the clamp-screw *m*, at any convenient height (Wied. Beibl. 4, 296; Guillaume's Thermométrie, 130).

(2) *Vapour in contact with its own liquid only.*

—The instrument devised in 1886 by G. W. A.

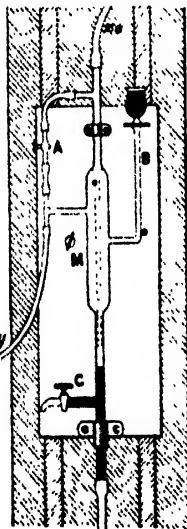


FIG. 16.

Kahlbaum belongs to this class. There is the usual mercury valve, the supply tube being bevelled off at the open end at an angle, and having a small hole opposite the exit tube to provide against total extinction of the flame. It may be adjusted according to the temperature required by the rack and pinion shown (Fig. 17). The other limb of the U-tube contains a liquid of boiling-point just below the temperature required in the bath or oven. For facility in changing the liquid, this end of the tube is closed by a tightly-fitting cork held in place by a clamp working against an india-rubber seat fixed on the collar of the glass tube.

The temperature rises just above the boiling-point of the liquid *z*, a portion of this volatilises, and mercury is forced up the limb *a*; the pressure on the liquid being now greater, its boiling-point is raised, and the temperature must increase for further volatilisation to occur. Owing to the rise of mercury in *a*, the gas supply is diminished, and hence the temperature falls.

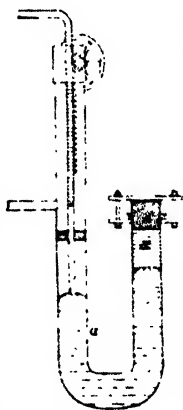


FIG. 17.

Consequent on the fall of temperature, a portion of the vapour condenses, the valve is opened to a greater extent, and the temperature again rises. These actions soon reach a point of equilibrium, and a constant temperature is then maintained (Ber. 19, 2860).

(d) *Thermostats depending upon the differential expansion of solid bodies.*—Bonnemain (Dingl. poly. J. 16, 285) and Ure (*ibid.* 42, 173) devised regulators depending upon the expansion of simple or compound metallic bars.

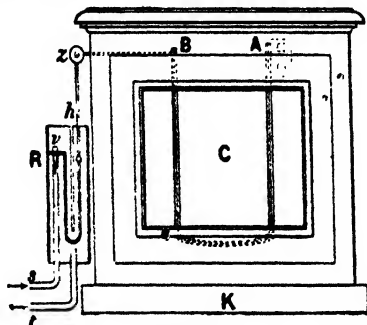


FIG. 18.

Hipp's thermostat is only available for temperatures between 30° and 40° (see Fig. 18). It consists of a copper vessel *K*, surmounted by a wooden box *C*, having glass front and back. A system of tubes on the walls of the oven communicate with the vessel *K*, and serve for the circulation of the water heated in that vessel. They are provided with openings for filling in water, and to serve as escape vents in case the

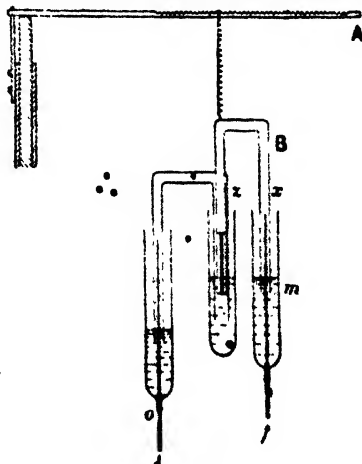


FIG. 19.

water may be accidentally boiled. The temperature is controlled by a regulator consisting of a bent compound metallic bar fixed upon the back wall of the oven at *A*; the free end *z* is connected by a copper wire with the lever *A* working a conical valve *v*; *z* is a regulating screw, by means of which any desired initial opening of the valve may be obtained; *s* is the gas-supply tube, and *t* draws off gas for the burner from the valve-box *a* (Dingl. poly. J. 191, 306).

Lothar Meyer in 1884 devised a sensitive temperature regulator on this principle (Fig. 19).

It consists of a long brass tube placed vertically in the bath, and closed at its lower extremity; in this tube a slightly longer glass rod is placed. The tube supports a rod carrying a movable lever-arm A, from which depends a floating valve B. The valve may be placed at varying distances along the lever-arm A, so that the difference between the expansions of the brass tube and glass rod may be magnified to a greater or less extent in the amount of movement imparted to the valve. The supply tube is a narrow-bore tube passing up the arm A of the valve working in the glycerol seal tube *m*. The supply tube and seal may be adjusted to any required height. A precisely similar arrangement allows of the drawing off through *o* of the gas for the burner. The valve *z* is essentially a Bunsen mercury-and-slit-tube valve. The mercury vessel is adjustable to any required height (Ber. 17, 478).

L. von. Babo arranged a gas regulator, in which the control valve depends for its action upon the unequal expansion of glass and copper. In Fig. 20, A is a copper tube, B a glass rod. The

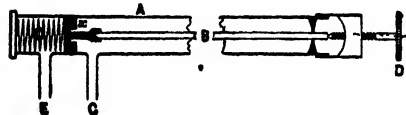


FIG. 20.

valve *z*, which regulates the flow of gas from the supply G to the burner tube E, is fixed in position by the glass rod B, against which it is pressed by a spiral spring C. The screw D serves to adjust the position of the glass rod, and renders it possible to obtain a greater or smaller supply of gas at will. As the temperature rises, the expansion of the copper tube being greater than that of the glass rod, the valve *z* is pressed by the spring C nearer to its seat, and so there is less gas supplied; the temperature then falls, and the valve partially re-opens, and so on (Ber. 13, 1221).

Kohlrausch employed a Breguet's metallic thermometer to make and break an electric current, which heated a fine platinum wire (Pogg. Ann. 125, 626).

E. Gumlich (Zeitsch. Inst. 1898, 18, 317) claims, by the use of a nickel and brass Breguet's spiral governing the gas supply through intermediary electrical arrangements, to have maintained a dry oven within 0.4° for long intervals.

Rieth's instrument consisted of a compound metallic bar working a cone valve, supplied with a regulator screw (Chem. Zentr. 1871, 615).

In Taliani's thermo-regulator (Ann. Chim. Applicata, 1914, 1, 405) two bimetallic zinc-steel vertical strips are fixed at their lower ends with the more expansive metals facing inwards. The free upper ends are connected by means of a very thin copper wire, on the middle point of which rests the valve regulating the flow of gas to the lamp of the thermostat. The valve is raised by the separation of the strips and lowered by their approach. By means of a slider operated from without the effective lengths of the strips, and consequently the constant temperature obtained, may be varied.

(e) *Electrically heated thermostats with electrical control.*—Thermostats of this type allow of more sensitive and rapid adjustment than

any other; they are particularly suitable for accurate scientific work but are not without technical applications.

Rothe (Zeitsch. Inst. 1899, 19, 143) gives a very complete account (with illustrations) of a thermostat designed for use in thermometer work at the Phys. Tech., Reichsanstalt. The same author (Zeitsch. Inst. 1902, 22, 14) adapts this principle to the construction of an instrument for use with very low temperatures. A Dewar vessel serves to prevent conduction of heat from without; the heating coil is of constantan wire wound on the ebonite ring of a stirrer, the stem of which is of glass tubing through which pass the leading wires for the current.

W. C. Geer (J. Phys. Chem. 1902, 6, 94) claims for his thermostat a variation of 0.002° only for a 9 hours' run with a 30-litre bath. A somewhat simpler form, which is essentially a modified Geer thermostat, is described by F. A. Osborn (*ibid.* 1905, 9, 297). The accompanying diagram (Fig. 21) shows its essential features. The heating of the 50-litre bath is accomplished by means of an iron wire CO carrying a current from the large storage battery B. The wire forms a layer of five turns against the sides of the bath, which latter is encased in a non-conducting layer of felt. M is a glass worm, 9.5 cm. diameter and 16 cm. long and holding 110 c.c. of mercury, serving as a reservoir of a regulating thermometer with a capillary stem. The bath is stirred by a

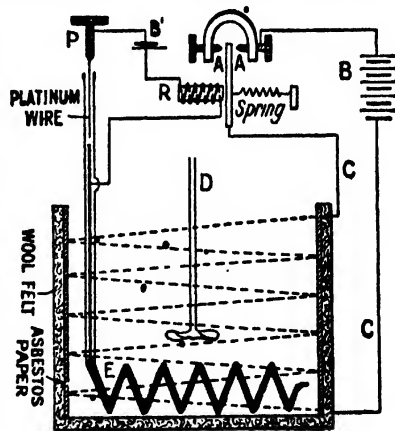


FIG. 21.

mechanically-driven stirrer represented by D. A platinum fused-in wire permanently connects an electro-magnet B with the mercury of the thermometer. B is connected through a storage cell B' with a second adjustable wire R. When the required temperature is reached, the mercury completes the circuit with P and the main current is broken at AA by the movement of the armature. The spring shown establishes the main circuit as soon as the mercury breaks contact with R.

This form can be brought to the required steady temperature in 15 minutes and shows no change of a hundredth of a degree in 8 hours.

Other forms are given by S. W. Young (J. Amer. Chem. Soc. 1901, 23, 327); C. Marie

and R. Marquis (Compt. rend. 1903, 136, 614), who use an acetone thermometer with mercury make and break and current through platinum wire; R. A. Macumber and C. G. L. Wolf (J. Path. Bact. 1904, 10, 105); H. Darwin (Phil. Mag. [vi.] 7, 408, 1904); J. P. Magnusson (J. Phys. Chem. 1907, 11, 25); Regaud and Fouilland (Ann. Chim. anal. 1909, 14, 141); L. Kolowrat (J. Phys. 1909, 8, 495), who describes the automatic regulation of an electric oven.

(f) Other mechanical regulators have been devised by J. W. Fichler and H. Hartig (D. R. P. 5492, 1878), and by Appold, whose instrument was a balance regulator (Proc. Roy. Soc. 1866, 15, 144).

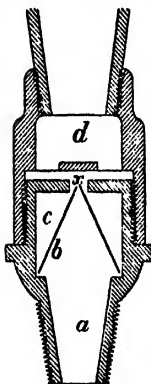


FIG. 22. A. Schwabe (D. R. P. 93152, 1896) describes a device by which an areometer works a chain controlling the source of heat.

The choice of the type of thermostat most suitable will be governed by the requirements in each special case. Technical applications of these instruments are most frequently adequately met by the use of the simple mercury thermometer valve at moderate temperatures and the air-thermometer mercury-valve at higher temperatures, some form of differential expansion instrument being used when the liability to vibration or shock has to be provided for.

For accurate work, the reliability, sensitivity, and independence of atmospheric changes are the most important considerations. Electrical thermostats with electrical control appear best able to fulfil the necessary conditions (see Geer, J. Phys. Chem. 1902, 6, 85); W. P. Bradley and A. W. Browne (*ibid.* 1902, 6, 118) claim to have constructed a thermostat sensitive to one thousandth of a degree. The toluene thermometer mercury-valve thermostat has found wide use; T. M. Lowry (J. Soc. Chem. Ind. 1905, 1030) discusses the conditions governing its sensitivity and A. W. C. Menzies (Chem. News. 1902, 85, 68), in dealing with the same subject, shows that this type is able to keep a bath at 6° above room temperature constant within one hundredth of a degree.

The principal ways in which thermostats have been applied to technical purposes have been mentioned; recent instances of such applications are to be found in the following, not otherwise readily accessible, references.

Central heating and ventilating systems.—Consolidated Car-heating Co., Wheeling, U.S.A.,

D. R. P. 67775, 72164, 1892; Senff, Ges. Ing. 1901, 24, 393; Johnson thermostat control of steam heating, Eng. Rec. 47, 277, 1903; Walker and Chambers, *ibid.* 47, 352, 1903; System Schultz, Ges. Ing. 27, 550, 1904; Narus-Gaye and Bloock, Met. Arb. 30, 99, 1904; Hainholzer Zugregulator, Tech. Zeit. 21, 485, 1904; Ohmes, Ges. Ing. 27, 545, 1904; Goebel, *ibid.* 28, 41, 1905; Webster, Eng. Rec. 53, 9; 54, 436, 1906; de Grahl, Ges. Ing. 29, 333, 1906; Mehl, Dingl. poly. J. 321, 698, 1906; Sc. Am. Supp. 64, 212, 1907; Pradel, El. Anz. 24, 1013, 1907; Gold Car Heating and Lighting Co., Railr. G. 2, 536, 1907; Fulton, Eng. Rec. 7, 56, 1907.

Incubators and germinating stoves.—Paul, Centralblatt Bakt. 1, 29, 129, 1901; El. Rev. N. Y., 1903, 43, 941; Schlössing, Gen. Civ. 1904, 44, 368; Joffin, Compt. rend. 1904, 138, 817; Rogers, Centralblatt Bakt. 2, 15, 236, 1905.

Distillation or evaporation.—Patterson, Chem. Ind. 21, 456, 1902; Bull. Sucr. 21, 619, 1903; Foth (fermenting vorts), Z. Spiritusind. 27, 257, 1904.

A number of dyes, belonging generally to the triphenylmethane class, such as methyl violet, malachite green, and erythrosin, have the property of gradually and completely disappearing without residue when heated, the time taken for disappearance depending on the temperature, other conditions being the same. Such dyes can be used as heat indicators in a number of ways for the control of industrial operations, for instance, in cases where a certain amount of heat has to be applied during a certain interval of time, the disappearance of the dye indicating the completion of heating. Another use is to determine the heat distribution in a heated body. The method may be applied in the annealing of glass, the burning of cements, or to detect overheating of electrical equipment (P. A. Kober, Ind. Eng. Chem. 1923, 15, 837-838; J. Soc. Chem. Ind. 1923, 43, 913A).

Miscellaneous.—E. Clarenbach, D. R. P. 67146, 1892; Kramer, D. R. P. 67146, 1892; G. H. Stockbridge (Fire Alarm Telegraphs), Elect. London, 1896; E. Sartorius, D. R. P. 100294, 1897; R. Janz, D. R. P. 114457, 1899; O. Bohne, D. R. P. 133429, 1899; Fedeschi, Centralblatt Bakt. 1, 30, 909, 1901; P. Breuilh, D. R. P. 150962, 1903; Regaud and Fouilland (electric stoves), Zeit. Mikr. 20, 138, 1903; Casses (pasteurising apps.), Milch. Zeit. 33, 258, 1904; Keller and Co., Tech. Rundsch. 5, 1904; Voss, Zeit. Beleucht. 10, 216, 1904; Ginsberg, Zeit. Heiz. 9, 231, 1904; Sodeau, Chem. Ind. 23, 1134, 1904; ovens, kilns, &c., Eng. News, 51, 514, 1904; Système de Rougemont, Gén. Civ. 46, 213, 1905; damper regulator for boilers, Eng. Rec. 54, suppl. 12, 47, 1906; System Kœferle, Ges. Ing. 29, 293, 1906; Zeit. Hirz. 12, 80, 1907; D. J. Beaver and J. J. Beaver, Ind. Eng. Chem. 1923, 15, 359. For a modified thermo-regulator, see Hume (J. Soc. Chem. Ind. 1924, 43, 250 T).

THESPASIA MACROPHYLLA (Blume) [T. Lampas (Dabz.).] This is a small bush common to the tropical jungles of India, Burma, and Ceylon. In Watts' Dictionary of the Economic Products of India, there is no mention of the use of this plant as a dyestuff, but, on the other hand, the capsules and flowers of the

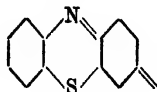
allied *T. populnea* (Soland.) are stated to give a yellow dye.

According to Perkin (Chem. Soc. Trans. 1909, 95, 1859) the flowers of the *T. macrophylla* yield quercetin and some quantity of *protocatechuic acid*.

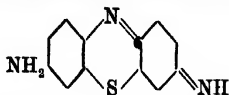
With mordanted woollen cloth* the flowers produce fairly good shades, but are in no way superior to the better-known Indian natural yellow dyestuffs. A. G. P.

THEVETIN v. DIGITALIS.

THIAZINE COLOURING MATTERS. The thiazines are colouring matters containing the group



The simplest member of this series is *thionine*

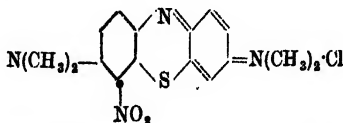


the hydrochloride of which constitutes Lauth's violet (see METHYLENE BLUE). The tetramethyl derivative is methylene blue (*q.v.*), which is by far the most important dyestuff of this class. The general method of preparation of these colouring matters has already been indicated (see METHYLENE BLUE).

Gentianine (Gy.), produced by oxidising *p*-phenylenediamine and dimethyl-*p*-phenylenediamine with ferric chloride in presence of sulphuretted hydrogen, is probably the zinc double chloride of a mixture of Lauth's violet and methylene blue; it dyes tanned cotton in bluish-violet shades.

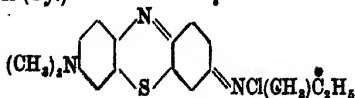
By the oxidation of methylene blue with acidified bichromate elimination of methyl groups occurs with the formation of **methylene azure**. This dye is the mixed chloride of di- and tri-methylated Lauth's violet; on cotton mordanted with tannin and tartar emetic it furnishes reddish-blue shades fast to washing.

Methylene green (S.C.I.), **Methylene green paste** (L.B.H.)



is obtained by treating methylene blue with sodium nitrite and nitric acid at 50°, the product being salted out and converted into double zinc chloride. It dyes in bluish-green shades on mordanted cotton, being the fastest green basic colouring matter used in silk dyeing and printing and in calico printing.

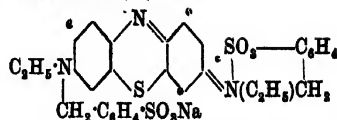
Thionine blue GO, O (M.); Thionine blue B, R (By.)



is prepared like methylene blue except that dimethyl-*p*-phenylenediaminethiosulphonic acid is oxidised together with methylethylaniline

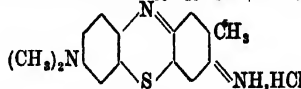
instead of dimethylaniline. It dyes tannin-mordanted cotton blue.

Thiocarmines R (C.)



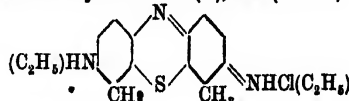
Benzylethyl-*p*-phenylenediaminethiosulphonic acid is oxidised in presence of sodium thiosulphate to sulphobenzylethyl-*p*-phenylenediaminethiosulphonic acid; the latter is oxidised together with benzylethylanilinesulphonic acid and the sulphoindaminethiosulphonate thus obtained is heated to boiling. The dyestuff is an indigo-blue powder giving a pure blue solution in water and dyeing wool and silk from an acid bath in blue shades (Cassella and Co., Eng. Pat. 4596, 1890; D. R. P. appl. C 3264; Amer. Pat. 434493; see also J. Soc. Chem. Ind. 1892, 11, 30; J. Pr. Chem. 1907, [ii.] 76, 498).

Toluidine blue O, $2C_{15}H_{13}N_2SO_2 \cdot ZnCl_2$;



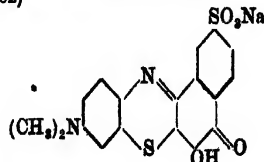
Dimethyl-*p*-phenylenediaminethiosulphonic acid (cf. METHYLENE BLUE) is oxidised together with *o*-toluidine. The insoluble green indamine formed is boiled with a solution of zinc chloride and the resulting leuco compound is oxidised. The colouring matter is a dark green powder giving a bluish-violet aqueous solution and dyeing mordanted cotton blue (Badische Anilin und Soda Fabrik; Eng. Pat. 10314, 1888; D. R. P. 47374; U.S. Pat. 416055; Meister, Lucius und Bräuning, D. R. P. 47345).

New methylene blue N (B), NSS (B.D.C)



Ethyl-*p*-tolylenediaminethiosulphonic acid, obtained by the oxidation of *p*-aminoethyl-*o*-toluidine in presence of sodium thiosulphate, is oxidised together with ethyl-*o*-toluidine and the green indamine obtained is heated. The solution of the dyestuff in water is violet-blue when cold and pure blue when hot. Tannin-mordanted cotton is dyed in redder and fuller shades than those produced by methylene blue (Cassella and Co., Eng. Pat. 8407, 1891; D. R. P. appl. C 3603; Amer. Pat. 469329). A satisfactory discharge is obtained with glucose and caustic soda.

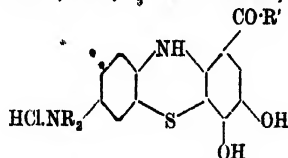
Brilliant alizarin blue (Bayer); Indochromine T (Sandoz)



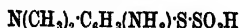
1:2-Naphthaquinone 4:6-disulphonic acid is condensed with dimethyl-*p*-phenylenediaminethiosulphonic acid. The dyestuff gives fast blue

shades on chromed wool, cotton or silk, and is suitable for calico printing (F. Bayer and Co., Eng. Pat. 825, 1893; D. R. P. 83046, 86717; Fr. Pat. 227675).

Leucogallothionine (P.H.), a generic term, covering a group of leuco compounds of the following general formula (Eng. Pats. 5692, 1893; 20397, 1906; D. R. PP. 189479, 73556)



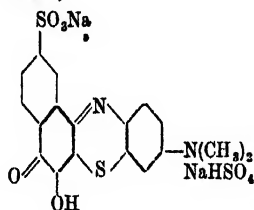
where R₂ are alkyl groups, R' is OH, NH₂, or some other substituent in the carboxylic group of gallic acid. They are produced by condensing together *as*-dialkylated diaminoarylthiosulphonic acids such as



and gallic acid or a derivative such as gallamic acid. On chrome mordanted wool these acidic leuco-compounds dye with oxidation in violet to blue shades fast to light and washing.

The Gallothionines are obtained in bulk by oxidising a mixture of gallic acid (or a derivative) and a mercaptan of an *as*-dialkylated-*p*-phenylenediamine such as $N(CH_3)_2 \cdot C_6H_4(NH_2) \cdot SH$.

Indochromogen S (Eng. Pat. 3886, 1894; D. R. P. 109273)



resulting from the action of β -naphthaquinone 4:6-disulphonic acid on *as*-diethyl-*p*-phenylenediaminethiosulphonic acid in alkaline solution. Bright greenish-blue tints are produced on chrome mordanted fabrics, the colour being discharged with alkali chlorate and ferrocyanide.

Uranla blue (W.D.C.), (Eng. Pat. 13118, 1896; D. R. P. 90275;) a bluish-violet acidic dye with bronzy lustre, obtained by oxidising with aqueous chromic acid a mixture of *as*-dimethyl-*p*-phenylenediaminethiosulphonic acid and di- β -naphthyl-*m*-phenylenediaminedisulphonic acid. It dyes wool and silk from an acid bath in pure greenish-blue shades.

G. T. M.

THIAZOL DYE STUFFS v. PRÉMULINE AND ITS DERIVATIVES.

THIET-SIE or **THITSI**. A resinous substance used as a varnish by the Burmese. It exudes from a tree in the form of a light-brown, very viscid liquid of the consistence of treacle, but on exposure to the air for a few minutes becomes quite black and hard on the surface. The same change takes place instantly in contact with potassium hydroxide. The resin spread in a thin layer on wood or other solid body quickly forms a hard deep-black coating of great brilliancy. On digesting the unaltered substance with alcohol of 80 p.c. at a gentle heat,

the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich-brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with potassium hydroxide, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves for the most part in ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This, then, is the portion of the original substance to which the property of blackening on exposure to the air is due.

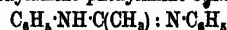
The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline acid which may be sublimed and which exhibits the characters of succinic acid. For reports of its uses and value as a lacquer, see Bull. Imp. Inst. 1917, 15, 42.

THIGAN. *Silber thiogenol.*

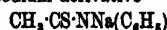
THIGENOL. Trade name for the sodium salt of ichthoform (condensation product of formaldehyde and ichthyol).

THIOACETAMIDE $CH_3 \cdot CS \cdot NH_2$ is prepared by the action of hydrogen sulphide on acetonitrile (Bernthsen, Annalen, 192, 46); or of phosphorus pentasulphide on acetamide in benzene solution (Hantzsch, *ibid.* 250, 264; cf. Hofmann, Ber. 1878, 11, 340). It crystallises in monosymmetric plates or prisms, m.p. 107.5°-108.5°, and is readily soluble in water or alcohol, less so in ether. Acids or bases decompose thioacetamide, yielding acetic acid, ammonia and hydrogen sulphide, whilst with silver nitrate solution, a precipitate of silver sulphide is obtained. It gives difficultly soluble compounds with mercuric chloride and with other metallic chlorides (Kurnakow, J. Russ. Phys. Chem. Soc. 1893, 25, 613).

THIOACETANILIDE $CH_3 \cdot C(SH) : N \cdot C_6H_5$ or $CH_3 \cdot CS \cdot NH(C_6H_5)$ is prepared by the interaction of acetanilide and phosphorus pentasulphide (Jacobson, Ber. 1886, 19, 1067; Hofmann, *ibid.* 1878, 11, 339), or of the chloride of acetanilide, $CH_3 \cdot CCl : N \cdot C_6H_5$, and hydrogen sulphide (Leo, *ibid.* 1877, 10, 2134). It crystallises from water in needles, m.p. 75°. On distillation it yields phenylamino-phenylimino-ethane



It is soluble in sodium hydroxide solution, from which it is precipitated by the addition of acids. The sodium derivative



is formed by the action of sodium ethoxide. Thioacetanilide yields two series of alkyl derivatives, viz. the normal alkyl thioacetanilides $CH_3 \cdot CS \cdot NR(C_6H_5)$ and the alkyl isothioacetanilides $CH_3 \cdot C(SR) : N \cdot C_6H_5$. The former are obtained by the action of phosphorus pentasulphide on alkylacetanilides, and the latter by the action of alkyl iodides on the sodium derivative of thioacetanilide.

THIOACETIC ACID $CH_3 \cdot COSH$ is best prepared by heating glacial acetic acid with phos-

phorus pentasulphide (Tarugi, Gazz. chim. ital. 1895, 25, i. 273; Schiff, Ber. 1895, 28, 1205; cf. Kekulé and Linnemann, Annalen, 123, 278; Kekulé, *ibid.* 90, 311). It may also be prepared by the interaction of acetyl chloride and potassium hydrosulphide (Jacquemin and Vosselmann, J. 1859, 354), or of lead acetate and anhydrous sodium thiosulphate (Frohde, Zeitsch. Chem. 1866, 543). It is an unpleasant smelling liquid, b.p. 93°, sp.gr. 1.074 at 10°, soluble in water and in alcohol: for electrical conductivity v. Ostwald, Zeitsch. physikal. Chem. 3, 182. By heating in a sealed tube with water at 180°–200° or by boiling with zinc and sodium hydroxide, the sulphur is removed (Schulze, Zeitsch. physiol. Chem. 1898, 25, 16). Strong sulphuric or nitric acid reacts explosively with thioacetic acid. Phosphorus pentachloride yields acetyl chloride, phosphorus thiochloride and hydrogen chloride, whilst zinc chloride yields ethenyl trisulphide, $C_2H_2S_3$, acetic acid and hydrogen sulphide. Thioacetic acid condenses with aldehydes, ketones and ketonic acids in the presence of hydrogen chloride (Bongartz, Ber. 1886, 19, 1934). It has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, *ibid.* 1894, 27, 3437; Tarugi and Marchionneschi, Boll. Chim. Farm. 45, 629). For salts, v. Ulrich, Annalen, 109, 275; Tarugi, Gazz. chim. ital. 1895, 25, i. 341; 1897, 27, i. 316; ii. 153.

Ethyl ester.—Prepared by the interaction of acetyl chloride and ethyl hydrosulphide, but not from ethyl acetate and phosphorus pentasulphide (Michler, Annalen, 176, 182). Unpleasant-smelling liquid, b.p. 116.0°–116.2° at 749.3 mm. (Beckmann, J. pr. Chem. [iii.] 17, 461).

Dithioacetic acid, methylcarbithionic acid $CH_3CS\cdot SH$ is prepared by the action of carbon disulphide on magnesium methyl iodide in well-cooled ethereal solution. The product is decomposed with ice and hydrochloric acid. It is a reddish-yellow oil, b.p. 37°/15 mm., sp.gr. 1.24 at 20°, readily soluble in organic solvents. It displaces acetic and formic acids from their salts. It is readily oxidised to thioacetyl disulphide by water and produces black spots on the skin. The alkali, alkaline earth, silver and magnesium salts are soluble in water, giving coloured precipitates with the salts of the heavy metals (Houben and Pohl, Ber. 1907, 40, 1303).

Methyl ester.—Prepared as the acid, substituting ammonium chloride for hydrochloric acid. The product is shaken with methyl sulphate, and the red oil so formed distilled; b.p. 140°/760 mm., 80°–81°/95 mm., 71°/70 mm.; sp.gr. 1.096 at 21°/4° (Houben and Schultze, Ber. 1910, 43, 2481).

THIOANTIPYRINE or **THIOPYRINE**, $C_{11}H_{11}N_2S$. Prepared by treating the methochloride or methiodide of 1-phenyl-3-methyl-5-chloropyrazole with potassium hydrogen sulphide. Large soluble crystals, m.p. 166° (Michaelis and Bindewald, Ber. 1900, 2873).

THIOBENZENYL DYE STUFFS v. PRIMULINE AND ITS DERIVATIVES.

THIOBENZOPHENONE v. KETONES.

THIOCHROMOGEN v. PRIMULINE AND ITS DERIVATIVES.

THIOCELL v. SYNTHETIC DRUGS.

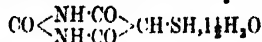
THIOCYANATES v. CYANIDES.

For the chlorides of thiocyanogen, see Kaufmann and Liepe (Ber. 1924, 57, [B] 923; Chem. Soc. Abstr. 1924, 126, 1, 839).

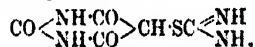
Addition of excess of a ferric salt to the solution of a commercial ferrocyanide, followed by filtration, results in a blood-red coloration in the filtrate if the ferrocyanide is contaminated with thiocyanate. The quantity of thiocyanate may be determined as follows: 10 grms. of ferrocyanide are dissolved in water to 100 c.c., the solution is filtered, and 10 c.c. of the filtrate are introduced into a 300 c.c. beaker, diluted with 50 c.c. of water, mixed with 25 c.c. of 5 p.c. ferric chloride solution, and filtered through a pleated paper into a 500 c.c. cylinder; the filter is washed with 0.5 p.c. potassium chloride solution until the latter passes through colourless, the total filtrate being then made up to 500 c.c. Into a similar 500 c.c. cylinder containing 10 c.c. of 5 p.c. ferric chloride solution, 1 p.c. ammonium thiocyanate is run from a burette until the two cylinders exhibit equal depths of colour. The method gives satisfactory results (F. Perciabosco, Annali Chim. Appl. 1923, 13, 346; J. Soc. Chem. Ind. 1924, 43, B, 252).

For the production of thiocyanogen by electrolysis of alkali thiocyanates, see Korstein and R. Hoffmann (Ber. 1924, 57, [B] 491; Chem. Soc. Abstr. 1924, 126, i. 717).

THIODIALURIC ACID



obtained by hydrolysing with dilute potassium hydroxide thiopseudouric acid



(Nencki, Ber. 1871, 4, 772), or potassium thio-

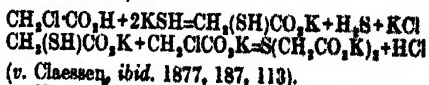
cyanobarbiturate $CO \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} \text{CH}\cdot\text{SCN}$ (Trz-

cinski, *ibid.* 1883, 16, 1057); forms bright microscopic plates. The potassium salt is a yellow crystalline compound, sparingly soluble in water. Thiodialuric acid dissolves in nitric acid to form a pale red solution, and on warming a violent reaction takes place and dilituric acid is formed.

THIOFLAVINE T S v. PRIMULINE AND ITS DERIVATIVES.

THIOFORM and **THIOGENOL**, v. SYNTHETIC DRUGS.

THIOGLYCOLLIC ACID, α -thioacetic acid, $SH\cdot CH_2\cdot CO_2H$, was first prepared by Carius (Annalen, 1862, 124, 43) by heating 3 parts of monochloroacetic acid in concentrated aqueous solution with 5 parts of potassium hydrogen sulphide. Thiodiglycollic acid is formed at the same time, thus:



(v. Claessen, *ibid.* 1877, 187, 113).

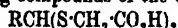
Thioglycollic acid is also formed by treating sulphochloroacetyl chloride, $SO_2Cl\cdot CHCl\cdot COCl$ with tin and hydrochloric acid (Siemens, Ber. 1873, 6, 659); by treating glyoxylic acid with sulphurated hydrogen in presence of silver oxide, thiodiglycollic acid also being formed in this case (Böttinger, Annalen, 1879, 198, 215); by boiling

thiohydantoin or rhodanic acid with baryta (Andreasch, Ber. 1879, 12, 1385; Ginsburg and Bondzynski, *ibid.* 1886, 19, 117); or by treating salts of chloroacetic acid with alkali or alkaline earth polysulphides and subjecting the products, thus formed to the action of reducing agents (Kalle and Co., D. R. P. 180875).

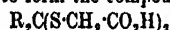
Thioglycollic acid is an uncrystallisable oil, soluble in water, alcohol, and ether. It has a faint smell, acts as a strong acid and forms a number of metallic salts (Claessen, *l.c.*; Ber. 1877, 10, 1354).

These are generally crystalline substances, readily soluble in water, but decomposing in aqueous solution especially in light, with production of a metallic sulphide (Myers, J. Lab. Clin. Med. 1921, 6, 359).

If a drop of ferric chloride is added to a slightly acidified thioglycolate, a transient indigo-blue colour appears, which changes to a deep violet-red on adding excess of ammonia and shaking in air. On standing the colour disappears, but it is reproduced by shaking the solution with air (Andreasch, Ber. 1879, 12, 1390). Thiodiglycollic acid does not give this reaction. Thioglycollic acid reacts with aldehydes yielding compounds of the type



with ketones to form the compounds



and also with ketonic acids (Bongartz, Ber. 1886, 19, 1931; *ibid.* 1888, 21, 478). It also unites with cyanamides forming hydantoin (Andreasch, Monatsh. 1881, 2, 745; Ber. 1880, 13, 1421).

Thioglycollamide $CH_2(SH)CONH_2$, forms thin white leaflets, m.p. 149° (Holmberg, J. pr. Chem. 1905, [ii.] 71, 264).

Ethyl thioglycolate $CH_2(SH)CO_2C_2H_5$ is formed by boiling the acid with absolute alcohol in the presence of a few drops of sulphuric acid (Claessen). It is an offensive smelling heavy oil, b.p. above 155° (decomp.), insoluble in water and in alcohol. For some of its derivatives, see Wislicenus, Annalen, 1868, 146, 145; Heintz, *ibid.* 1865, 136, 223; Letts and Collie, J. 1878, 685.

Ethylthioglycollic acid $CH_2(C_2H_5S)CO_2H$ is formed by the interaction of ethyl chloracetate and sodium mercaptide, the ethyl ester thus formed being hydrolysed with baryta water (Claessen, Bull. Soc. chim. [ii.] 23, 444). It is an oil soluble in water, alcohol, and ether, and yields metallic salts and esters. Its amide



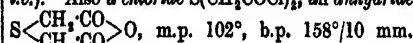
has m.p. 440° .

Nitrosothioglycollic acid $(SH)CH(NO)CO_2H$ is obtained, together with cyanamide and dicyanamide, by boiling nitrosothiohydantoin with baryta water. A number of its metallic salts have been prepared (Andreasch, Ber. 1880, 13, 601).

Dithioglycollic acid $(SCH_2\cdot CO_2H)_2$, forms leaflets or prisms, m.p. 100° , gives metallic salts, an ethyl ester, b.p. 290° (decomp.), and is reduced by zinc and hydrochloric acid to thioglycollic acid (Claessen, Ber. 1881, 14, 410; Ginsburg and Bondzynski, *l.c.*).

Thiodiglycollic acid $S(CH_2\cdot CO_2H)_2$, may be prepared by treating calcium chloracetate with calcium hydrogen sulphide in presence of hydrogen sulphide (Schräber, J. pr. Chem. [ii.] 13,

472); or by mixing a concentrated aqueous solution of sodium chloracetate with an equivalent amount of sodium sulphide dissolved in the smallest quantity of water. The mixture is acidified with sulphuric acid and the thiodiglycollic acid is shaken out with ether (Lovén, Ber. 1884, 17, 2818; *ibid.* 1894, 27, 3059). It forms rhombic tablets, m.p. 192° ; gives metallic salts; a dimethyl ester, b.p. $135^\circ/11$ mm. (Anschütz and Biernaux, Annalen, 1893, 273, 69), and a diethyl ester, b.p. 267° – 268° (corr.) (Wislicenus, *l.c.*). Also a chloride $S(CH_2\cdot COCl)_2$, an anhydride



(Anschütz and Biernaux, *l.c.*), and amides.

THIOINDIGO DYESTUFFS v. INDIGO, ARTIFICIAL, AND INDIGOID DYESTUFFS; VAT DYES.

THIOINDOXYL. *Thioindoxyl carboxylic acid* v. 2-HYDROXYTHIONAPHTHEN-1-CARBOXYLIC ACID.

THIOKETONES v. KETONES.

THIOL v. SYNTHETIC DRUGS.

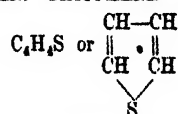
o-THIOBENZOIC ACID. *Thiosalicylic acid*.

THIOLINE v. ARISTENE.

THIOMINE v. METHYLENE BLUE and THIAZINE COLOURING MATTERS.

THIONURIC ACID v. PYRIMIDINES.

THIOPHEN. **THIOPHENE**. *Thiofurfuran*

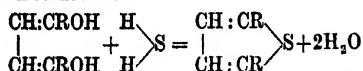


Discovered by Victor Meyer in coal-tar benzene, which contains about 0.5 p.c. of thiophen (Ber. 1883, 16, 1465; see also Bull. Soc. chim. 1900, 23, 384; *ibid.* 24, 357; Heusler, Ber. 1895, 28, 488; Witzack, Chem. Zentr. 1903, i. 1053). In order to extract the thiophen, a large quantity of the best commercial benzene was shaken for some hours with one-tenth of its volume of concentrated sulphuric acid, the black acid layer separated, diluted with water, and converted into the lead salt of the sulphonic acid thus obtained. This lead thiophen-sulphonate, which was contaminated with lead benzene-sulphonate, was dried, mixed with one-fourth of its weight of ammonium chloride, and distilled. The sulphonic acid was thus hydrolysed, and an oil passed over which was purified by shaking with caustic alkali to remove mercaptans, dried over calcium chloride and rectified.

K. E. Schulze (Ber. 1885, 18, 497) recommends that the thiophen sulphonic acid, after diluting the crude acid with water, should be hydrolysed by steam-distillation. Thiophen may also be completely removed from commercial benzene by treating the latter with form- or acet-aldehyde or with phthalic anhydride (D. R. P. 211239; Frdl. 1908–1910, 9, 96).

According to Steinkopf (Chem. Zeit. 1911, 35, 1098), thiophen may be very readily prepared by passing acetylene over pyrites or marcasite heated to 300° , the thiophen being separated from the other products by fractional distillation. Among the products occurs a substance $C_4H_4S_2$, b.p. 36° – 38° of garlic-like smell which, when treated with alkalis, gives some sulphur and also its unpleasant smell. Thiophen has been artificially prepared by numerous methods: amongst others by passing

ethylene or acetylene into boiling sulphur (Victor Meyer and Sandmeyer, Ber. 1883, 16, 2176); by heating succinic anhydride with phosphorus pentasulphide, or better, sodium succinate with phosphorus trisulphide (Volhard and Erdmann, Ber. 1885, 18, 454; Friedburg, J. Soc. Chem. Ind. 1890, 1062); and in a similar way from erythrol and phosphorus pentasulphide (Paal and Tafel, Ber. 1885, 18, 688); also by the action of sulphuretted hydrogen on diketones thus:



(Paal, *ibid.* 367, 2251); or by passing a mixture of acetylene and sulphuretted hydrogen over bauxite at a temperature of 320° (Eng. Pat. 109983 of 1916).

Liquid, with a faint smell. Boils at 84.3° (corr.), and sp.gr. 1.0884 0°/0° (Thorpe and Rodger). Gives with isatin and sulphuric acid a blue colouring matter, *thiophenin*, $\text{C}_{12}\text{H}_7\text{NOS}$ in presence of oxygen or oxidising agents (test for thiophen in benzene) (Bauer, Ber. 1904, 37, 1244; *ibid.* 3128; Schwalbe, Chem. Zeit. 1905, 29, 895; cf. Wray, J. Soc. Chem. Ind. 1919, 83 T). Thiophen gives similar coloured condensation products with all compounds containing the group $\text{CO}\cdot\text{CO}$ (see Denigès, Bull. Soc. chim. [iii.] 13, 538; *ibid.* 1915, 17, [4] 353; Meyer, Ber. 1883, 16, 1473; Liebermann, *ibid.* 1887, 20, 3231; Claisen, *ibid.* 2197; Oster, *ibid.* 1904, 37, 3348). It gives an intensely red coloration with lactic acid in the presence of sulphuric acid and copper sulphate (Fletcher and Hopkins, Chem. Zentr. 1907, i. 1442), and various colours with different aldehydes (Steensma, *ibid.* 1908, i. 1492).

Thiophen may be determined by shaking 1 gm. of it with 15.15 grms. of mercuric acetate in 60 grms. of water when a white insoluble crystalline powder separates, having the composition $\text{C}_4\text{H}_4\text{S}(\text{HgO}\cdot\text{CO}\cdot\text{CH}_3)_2$, and which may be weighed as such. When heated with aqueous sodium chloride this yields the corresponding chloride, $\text{C}_4\text{H}_4\text{S}(\text{HgCl})_2$, as a white insoluble microcrystalline powder. When heated with alkalis, the chloro compound yields the hydroxy derivative $\text{C}_4\text{H}_4\text{S}(\text{HgOH})_2$, which explodes on heating, metallic mercury separating in the form of a mirror (Paolini, Gazz. chim. ital. 1907, 37, i. 58).

Denigès finds that basic mercuric sulphate may be substituted for the acetate with advantage. The reagent is made by dissolving 5 grms. of mercuric oxide in 20 c.c. of concentrated sulphuric acid and 100 c.c. of water, mixed with 60 c.c. of absolute alcohol. In presence of thiophen this forms $\text{SO}_4(\text{HgO})\text{Hg}\cdot\text{C}_4\text{H}_4\text{S}$. The weight of the precipitate multiplied by 0.1032 gives the weight of thiophen in the quantity of the sample taken (cf. Spielmann and Jones, J. Chem. Soc. Ind. 1919, 38, 185 T; Spielmann and Schotz, *ibid.* 1919, 33, 188 T). Meyer (Compt. rend. 1919, 169, 1402) employs methyl alcohol in place of ethyl alcohol. 20 c.c. of Denigès' solution (without the ethyl alcohol) are mixed with 75 c.c. of methyl alcohol and 5 c.c. of the benzene under examination in a stoppered bottle. The mixture is shaken from time to time and after 30 minutes is filtered. 10 c.c.

of the filtrate is diluted with 20 c.c. of water and a few drops of nitric acid and 1 c.c. of a 20 p.c. solution of ferrous ammonium alum are added and the whole is titrated with N/10 ammonium thiocyanate solution. To allow for the possibility of acetone in the methyl alcohol a blank estimation is made on 5 c.c. of pure benzene. The two titration readings being n_1 and n respectively, the amount of thiophen in 1 litre of the benzene is given by

$$0.01 \times 2000 \times (n - n_1) \times 0.14$$

Thiophen may be estimated colorimetrically in benzene by charging 2 measures with 25 c.c. of isatin solution (containing 0.5 gm. isatin in 1000 grms. of pure conc. sulphuric acid) and 25 c.c. pure conc. sulphuric acid. To one of these 1 c.c. of the benzene to be tested is added, to the other 1 c.c. of a test solution containing a definite quantity (from 0.01–0.5 p.c.) of thiophen in benzene and the colours after shaking for 5 minutes are compared on a white base (Schwalbe, Chem. Zeit. 1905, 29, 895).

When boiled with aluminium chloride, thiophen forms an insoluble resin (Heusler, Zeitsch. angew. Chem. 1896, 11, 750; Böttker, Compt. rend. 1896, 123, 310; Haller and Mielbel, Bull. Soc. chim. 1896, 15, 1065).

Thiophen combines with mercuric chloride and sulphate (Dimroth, Chem. Zentr. 1901, i. 450; Schwalbe, Ber. 1905, 38, 2208), and also with the acetate as above.

A small quantity of thiophen, mixed with vanillin and concentrated sulphuric acid gives a green or bluish-green colour. A green colour is also formed gradually when wood is moistened with 1–2 drops of thiophen and 10 times the amount of alcohol mixed with an equal volume of sulphuric acid is added (Ihl, Chem. Zeit. 14, 1707). According to Thomas (Bull. Soc. chim. 1909, [iv.] 5, 182, 730), pure thiophen is not reduced by Sabatier and Senderens' method.

When treated with hydrogen peroxide (1–3 p.c. solution), thiophen yields *oxythiophen* $\text{C}_4\text{H}_4\text{O}_2\text{S}$, b.p. 130°, and *tetraoxythiophen*, b.p. 158°–160°. Both have a pleasant smell, a burning taste, and give a green coloration with isatin and sulphuric acid. If 25 p.c. hydrogen peroxide is used the oxythiophenes are decomposed forming sulphuric acid and yellow resinous products (Lanfry, Compt. rend. 1911, 153, 73).

Both in its physical properties and in its chemical reactions, thiophen closely resembles benzene. Benzene boils at 80°, thiophen at 84°. Like benzene it combines with certain substances as thiophen of crystallisation (Liebermann, Ber. 1893, 26, 853; Prokofjeff, J. Russ. Phys. Chem. Soc. 1897, 29, 87). The halogens, nitric acid, and sulphuric acid react with thiophen, yielding substitution products corresponding with and very similar in properties to those of benzene, excepting that thiophen, owing to its unsymmetrical constitution, forms two series of mono-substitution compounds— α -compounds, in which a hydrogen atom adjacent to sulphur is replaced, and β -compounds, in which the substitution takes place with a hydrogen atom in the meta-position to sulphur (Bamberger, Ber. 1897, 30, 369; Willgerodt, J. pr. Chem. 1886, 33, 150; Rosenberg, Ber. 1886, 19, 650; Schleicher, *ibid.* 1885, 18, 3015; Ciamician and Angeli, *ibid.* 1891, 24,

74, 1347, *Mårnsson*, *ibid.* 1893, 26, 2457; *Töhl* and *Schultz*, *ibid.* 1894, 27, 2834; *ibid.* 1895, 28, 2217; *Eberhard*, *ibid.* 2385).

Thiophen diiodide $C_4H_2I_2S$ forms crystalline plates, m.p. 40.5° , and is sometimes used as a substitute for iodoform in surgical cases.

In the presence of anhydrous ether, magnesium dissolves in 2-iodothiophen giving magnesium thiophen iodide which reacts with ketones forming tertiary alcohols, some of which products are described by Thomas (*Compt. rend.* 1908, 146, 642; see also Tschelintzeff, *Chem. Zentr.* 1905, i, 146).

Tetra-iodothiophen C_4I_4S is an odourless, tasteless, pale yellow, crystalline powder, m.p. 198° (*Paolini* and *Silbermann*, *Atti R. Accad. Lincei*, 1915, [v.] 24, ii, 206).

Sodium thiophen sulphonate $C_4H_2S \cdot NaSO_3$ is a white crystalline powder which has been employed in prurigo, being non-toxic and non-irritant: it has proved more effective than β -naphthol. Nitrothiophen (*Stadler*, *Ber.* 1885, 18, 530), like nitrobenzene, yields, with reducing agents, the corresponding amino compound (*Stadler*, *ibid.* 1490; 2316; *Goldschmidt* and *Schulthess*, *ibid.* 1887, 20, 1701).

Homologues of thiophen are present in coal-tar benzene and may be separated by methods similar to those used for separating thiophen (*Messinger*, *Ber.* 1885, 18, 563, 1636; *Keiser*, *ibid.* 1896, 29, 2560). Many of these α - and β -homologues are known and may be obtained by a variety of synthetic methods. By treating a mixture of 2-iodo-thiophen and methyl iodide with sodium, 2-methylthiophen (thiotolene) can be obtained (*Kues* and *Paal*, *Ber.* 1886, 19, 555; *Meyer* and *Kreis*, *ibid.* 1884, 17, 1558). 2-Ethylthiophen may be obtained similarly. For various homologues and their halogen and other derivatives, see *Grünwald* (*Ber.* 1887, 20, 2585); *Zelinsky* (*ibid.* 2017; *ibid.* 1888, 21, 1835); *Thiele* (*Annalen*, 1892, 267, 133); *Opolski* (*Chem. Zentr.* 1905, i, 1255; *ibid.* ii, 1796) amongst others.

2-Phenylthiophen is obtained by distilling β -benzoylpropionic acid or benzoylsuccinic acid with phosphorus tri- or penta-sulphide (*Kues* and *Paal*, *ibid.* 1886, 19, 3142). It crystallises in small plates, m.p. $40-44^\circ$.

3-Phenylthiophen is obtained by the interaction of thiophen and nitroacetanilide. The compound obtained by *Möhlau* and *Berger* (*ibid.* 1893, 26, 2001) from diazobenzene chloride and thiophen in the presence of aluminium chloride is a mixture of 2- and 3-phenylthiophens (*Bamberger*, *ibid.* 1897, 30, 36). 3-Phenylthiophen crystallises in plates, m.p. $90-90.5^\circ$, b.p. $254-260^\circ$. *Renard* (*Compt. rend.* 1889, 109, 699) describes another phenylthiophen, m.p. 330° , which was obtained by passing a mixture of the vapours of toluene and sulphur through an iron tube heated to redness.

Diphenyl-, ditolyl-, and other diarylthiophens may be obtained by heating mixed aliphatic aromatic ketones in the presence of water and ammonium sulphide at 215° under pressure (*Willgerodt* and *Scholtz*, *Chem. Zentr.* 1910, 1909). For another method of obtaining the phenylthiophens, v. *Baumann* and *Fromm* (*Ber.* 1895, 28, 2001).

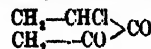
Dianaphthalenethiophen $C_{12}H_8S$, and benzodithiophen $C_{12}H_6S_2$, have been isolated from the pro-

duct obtained from the interaction of the vapours of sulphur and naphthalene at a red heat. The former crystallises in pearly yellow scales, melts at 250.5° (corr.), and boils above 440° . It yields a hexabromo derivative $C_{12}H_4Br_6S$, m.p. 260° , and a tetranitro derivative $C_{12}H_2(NO_2)_4S$, m.p. 210° (cigo). Oxidation with chromic acid gives phthalic acid. The latter crystallises in ruby red leaflets, melts at 118.5° (corr.), and boils at 345° . It gives the thiophen reaction with sulphuric acid and isatin. From it a tetrabromo derivative $C_{12}H_2Br_4S$, m.p. $247-248^\circ$, and a tetranitro derivative $C_{12}H_2(NO_2)_4S$, decomposing at 300° , have been obtained (*Lanfry*, *Compt. rend.* 1911, 152, 92, 1254). Other naphthalene thiophens have been described by *Dziewonski* (*Bull. Soc. chim.* 1904, [iii.] 31, 925).

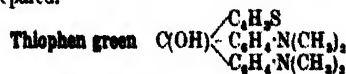
Dithienyl ($C_8H_4S_2$), m.p. 83° , is formed when the vapour of thiophen is passed through a red-hot tube, just as diphenyl (C_6H_4) is formed under these conditions from benzene (*Nahnsen*, *Ber.* 1884, 17, 789). *Töhl* (*ibid.* 1894, 27, 665) obtained another dithienyl, m.p. 33° , by the action of anhydrous ferrous fuming sulphuric acid on ice cold thiophen. A third dithienyl, m.p. 132° , was obtained by *Auwers* and *Precht* (*ibid.* 1741) by heating butane tetracarboxylic acid with phosphorus sulphide.

Thiophen carboxylic acids may be obtained by oxidising the corresponding alkyl thiophens and also by various other methods (*Nahnsen*, *Ber.* 1884, 17, 2197; *Peter*, *Ber.* 1885, 18, 542; *Messinger*, *ibid.* 563; *Nahnsen*, *ibid.* 2304; *Schleicher*, *ibid.* 3015; *Damsky*, *ibid.* 1886, 19, 3282; *Levi*, *ibid.* 656; *Curtius*, *Chem. Zentr.* 1902, i, 457; *Holleman* and *Voerman*, *Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 514; *Rec. trav. chim.* 1907, 26, 293; *Schorigin*, *Ber.* 1910, 43, 1938). Thiophen 2-carboxylic acid, m.p. $126-127^\circ$; thiophen 3-carboxylic acid, m.p. 136° ; and three dicarboxylic acids are known.

Thiophen aldehyde $C_4H_2S \cdot CHO$, a pale yellow oil, b.p. 198° , having a pleasant smell, is obtained by the distillation of α -thienylglyoxylic acid $C_4H_2S \cdot CO \cdot CO_2H$ (*Biedermann*, *Ber.* 1886, 19, 1853) or by the action of sulphuretted hydrogen on chlorodiketopentamethylene



(*Hantzsch*, *ibid.* 1880, 22, 2838; *Hantzsch* and *Witz*, *ibid.* 1901, 34, 841). On oxidation it yields the α -acid. Many of its derivatives are known. Thiophen ketones and a large number of other derivatives of thiophen have been prepared.



This compound, which was discovered by *L. E. Levi* (*Ber.* 1887, 20, 513), is an analogue of malachite green. The leuco base



is first prepared by heating a mixture of one part of thiophen aldehyde, 2 parts of dimethylaniline with a little alcohol, and 3 to 4 parts of zinc chloride for 6 hours, adding the zinc chloride gradually, and, if the mass becomes thick, diluting slightly with water. The product

is made alkaline with caustic soda, steam-distilled, extracted with ether, and the crystalline residue which is left on evaporating the ether recrystallised from alcohol. This crystalline leuco base is then oxidised with manganese dioxide and dilute sulphuric acid, when it yields thiophen green. The colouring matter is extracted with hot water, filtered from manganese dioxide, precipitated with ammonium chloride and ammonia, and extracted with ether. It is, as represented by the formula, the carbinol corresponding with the leuco base. Like malachite green, it forms a double salt with zinc chloride. It dyes silk and wool a shade very much like that of malachite green, but somewhat yellower.

W. Krause (Internat. Monatschr. Anat. u. Physiol. 4, 2; J. Soc. Chem. Ind. 1887, 507) recommends the use of the zinc double salt of thiophen green for staining sections, especially as a complementary colour to carmine. It dissolves readily in water, alcohol, and chloroform, but is insoluble in benzene.

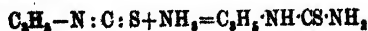
THIOSACCHARIN $C_6H_4 \begin{smallmatrix} CS \\ SO_2 \end{smallmatrix} NH$, obtained by heating an intimate mixture in equimolecular proportions of saccharin and phosphorus pentasulphide to 220° and extracting with boiling benzene. Crystallises in yellow needles, m.p. 180°. Has a bitter taste. Hydrolysed by water, alkali hydroxides and carbonates with production of saccharin and hydrogen sulphide. Soluble in ammonia solution from which it is precipitated unchanged by acids. Heated with dilute hydrochloric acid forms ammonium o-sulphobenzoate (Mannessier, Gazz. chim. ital. 1915, 45, i. 540).

THIOSALICYLIC ACID (*o*-Thiolbenzoic acid) SO_2H
 $CO_2H \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ (1) Formed by heating sodium *o*-chlorobenzozate with sodium hydrogen sulphide and copper powder to 150°–250°, dissolving the product in water and precipitating by acid (Cassella & Co., D. R. P. 189200). (2) A mixture of anthranilic acid and strong hydrochloric acid is diazotised, and the solution is mixed with a cooled aqueous alkaline solution of sodium sulphide containing sulphur in suspension. After nitrogen ceases to be evolved, the solution is acidified with hydrochloric acid, filtered, the residue dissolved in sodium carbonate solution, filtered from sulphur, and heated with finely divided iron or zinc dust until no hydrogen sulphide is evolved after acidification. The product is then treated with hot sodium hydroxide solution, filtered, and the thiosalicylic acid precipitated by hydrochloric acid (Kalle & Co., D. R. P. 205450). Colourless or pale yellow crystals, m.p. 164°–165°.

THIOSEMICARBAZIDE v. HYDRAZINES.
THIOSINAMINE, allyl-thiourea



Formed by the action of ammonia on allyl-mustard oil



A white crystalline substance, sparingly soluble in water. Used in the treatment of lupus, and in relaxing scar-tissue. With ethyl iodide forms *iodina*, which is readily soluble in water.

THIOSTANNIC ACID v. **TIN SALTS AND OXIDES.**

THOLAFORM. Trade name for a mixture of menthol and trioxymethylene.

THOMAS SLAG v. **FERTILISERS.**

THOMSONITE. A zeolitic mineral with the composition $(Na, Ca)O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 24H_2O$ crystallised in the orthorhombic system. Sp.gr. 2.3–2.4; H. 5–5½. A massive variety known as *lintonite*, with a radially fibrous structure and concentric bands of green, red, and white, is occasionally used as a gem-stone. This occurs in amygdaloidal basalt at Grand Marais in Minnesota, and is collected as water-worn pebbles on the shores of Lake Superior.

L. J. S.

THORIANITE. A heavy, black mineral consisting of thorium (51–80 p.c.) with uranium oxides (11–32.7 p.c.), &c. It is isomorphous with pitchblende (*q.v.*) and very similar to the crystallised varieties of this in most of its characters. The principal difference between the two minerals is in the relative amounts of the thorium and uranium oxides, thorianite being essentially $(Th, U)O_2$ and pitchblende $(U, Th)O_2$. Thorianite is derived principally from Ceylon, where it is found in the stream-beds and in the gem-bearing alluvial gravels at several spots in the Central, Sabaragamuwa, and Southern provinces. The heavy minerals occurring with it, and separated by the gemmers from the alluvia by a simple process of washing, are zircon, ilmenite, thorite, gold, &c. The largest amounts have been obtained from the Kuda Pandi-oya, a small stream in the Bambarabotuwa district, about 20 miles from Balangoda in the Sabaragamuwa province; but the deposits are of limited extent, and soon become exhausted. The occurrence of the mineral *in situ* has also been noted at one or two places (Gampola and Maddegama) in Central province, a few crystals having been found in pegmatite-veins. Prospecting for the original sources is, however, difficult, owing to the thick growths of jungle.

Two isolated crystals from an unknown locality in province Betroka in the south of Madagascar have been described by A. Lacroix (1914). This material is richer in thorium than the Ceylon thorianite; analysis gave: ThO_2 , 93.02; UO_2 , 4.73; Fe_2O_3 , 0.29; PbO , 1.80 = 99.84; sp.gr. 9.33. The mineral has also been found as water-worn grains in the gold-sands of the Boshogocha river, Transbaikai, Siberia. Analysis of this material gave: ThO_2 , 74.2; UO_2 , 14.1; Ce_2O_3 , etc., 6.3; Fe_2O_3 , 3.1; SiO_2 , 0.8 = 98.5 (S. D. Kuznetsov, Bull. Acad. St. Pétersbourg, 1912, 6, 361). It is recorded from Travancore, a preliminary analysis showing ThO_2 , 32.27; U_2O_5 , 39.86 p.c. (Rec. Geol. Survey, India, 1917, 48, 9).

Thorianite is found as small, simple cubes, usually only a few mm. across, and only exceptionally reaching 2 or 3 cm. Interpenetration twins, like those of fluor-spar, are occasionally met with. The colour is jet-black, and, when the surface is not water-worn and dulled, the lustre is bright and pitchy. The streak is brown with a tinge of green; thin sections are translucent and optically isotropic. The high sp.gr. of about 9.5 is a striking feature; hardness nearly 7. The mineral is soluble in nitric acid.

and in sulphuric acid, but is scarcely attacked by hydrochloric acid. It is the richest known source of helium, 8.2-8.5 c.c. per gram being given off when the mineral is heated or dissolved in acid. Its radioactivity is less than that of pitchblende, there being less radium but more radiothorium. Nipponium and some other possibly new elements, have been extracted from thorianite (M. Ogawa, 1908; C. de B. Evans, 1908).

Analysis I of thorianite from near Balan-goda (W. R. Dunstan and B. M. Jones, Proc. Roy. Soc. 1906, A, 77, 546). II, same locality (Dunstan and G. S. Blake, *ibid.* 1905, A, 76, 253). III, ditto (Dunstan, Nature, 1904, 69, 510). IV, ditto (E. H. Buchner, Proc. Roy. Soc. 1906, A, 76, 385). V, and VI, from Galle, Southern province (Dunstan and Jones, *l.c.*).

	I	II ¹	III ²	IV ³	V	VI
ThO ₂	78.98	78.86	72.24	70.96	62.16	58.84
UO ₂		6.03			10.32	
UO ₃	13.40	9.07	11.19	13.12	18.88	32.74
Ce ₂ O ₃		1.02	6.39			
(La,Di) ₂ O ₃	1.47	—	0.51	1.96	1.84	0.85
PbO	2.54	2.59	2.25	2.42	2.29	2.56
Fe ₂ O ₃	0.87	0.46	1.92	2.05	1.11	1.31
CaO	0.91	1.13	—	0.13	0.59	0.19
H ₂ O	1.28	—	—	3.20	1.05	1.26
Insol.	0.47	0.20	0.41	—	0.77	0.45

¹ Also He, 0.39.
² Also ZrO₂, 3.68 (due to enclosed zircon); SiO₂, 1.84; sp.gr. 8.98.
³ Also ZrO₂, 0.23; SnO₂, 0.65; Sb₂O₃, 0.11; Al₂O₃, 0.15; etc.

Thorianite contains a higher percentage of thorium than any other known mineral, and it has been employed as a source of thorium for use in incandescent gas mantles. The amount exported from Ceylon in 1905 was about 9 tons, which sold for £1600 to £1700 per ton; since then, however, the price of thorium has fallen considerably.

For local details of occurrence, &c., see Administration Reports, Ceylon, Colombo, 1903-6, &c.; Colonial Reports, Miscell. Ser., Ceylon Mineral Survey, London, 1904-14, &c.; Bull. Imp. Inst. London, 1916, 14, 321.

L. J. S.

THORITE. A mineral consisting essentially of thorium silicate, ThSiO₄, crystallising in the tetragonal system and isomorphous with zircon. Analyses show: SiO₂, 12-19; ThO₂, 48-74 (the formula requires 81.5); U₂O₃, 1-10; Ce₂O₃, 0-3; H₂O, 6-10 p.c. The presence of water appears to be due to secondary alteration; and the fact that the mineral is frequently optically isotropic and amorphous indicates that it is not fresh. The colour is yellow to dark brown, and in the orangite variety (q.v.) a bright orange-yellow; the lustre is resinous; sp.gr. 4.4-5.4. The mineral occurs as small masses and indistinct crystals in the augite-syenite on the Langesund-fjord and near Arendal, and a few other places in the south of Norway. It is also found, together with thorianite, in the gem-gravels of Ceylon. Small amounts are collected for the preparation of thorium compounds and used principally for the mantles of incandescent gas-lights.

L. J. S.

THORIUM. Sym. Th. At.wt. 232.2 This element, which has the highest atomic weight of

the metals of the rare earth series, was identified by Berzelius in 1829 as occurring in the form of silicate in the mineral thorite, obtained from the island of Løv-ön (near Brevig, Norway).

• For position in the Periodic system, see Vogel (Zeitsch. anorg. Chem. 1918, 102, 177-200).

Occurrence.—Thorium occurs as a constituent of most rocks of volcanic origin to the extent of 2.3×10^{-3} in acid, and 0.22×10^{-3} in basic deposits. It is present as the main constituent in thorite, orangite, and their alteration products, mackintoshite, auelite, calclithorite, and freyalite, and in thorianite (Dunstan and Jones, Proc. Roy. Soc. 1905, 76 A, 253; 1906, 77 A, 546; Szilard, Compt. rend. 1907, 135, 463). It occurs also in yttracrasite (Amer. J. Sci. 1906, [iv.] 22, 515). The only source of commercial importance, however, is monazite sand, which contains from 2 to 10 p.c. ThO₂.

Extraction and Purification.

1. **Separation from thorite, orangite, and thorianite.**—These minerals are easily decomposed by the strong mineral acids when silicic acid separates, and the solution containing the metallic constituents is freed from lead, bismuth, &c., by hydrogen sulphide. Thorium is then separated in the form of its octahydrated sulphate Th(SO₄)₂.8H₂O, which separates from aqueous solutions below 47°, by stirring into the cold chloride or nitrate solution (about 20 p.c.) a moderate excess of cold 50 p.c. sulphuric acid. This salt is re-dissolved in water, and oxalic acid added to precipitate thorium oxalate, which is then ignited to thorium and the cycle of operations repeated. For this purpose the thorium must be attacked by concentrated sulphuric acid; the product is dissolved in ice and water, and the solution warmed to 20° or 30° to separate the hydrated thorium sulphate (Krüss and Nilson, Ber. 1887, 20, 1665).

Thorium salts may be separated from those of the cerite metals by solution in excess of alkali carbonate or oxalate. But this process brings into solution also small amounts of the cerium and yttrium earths, which, however, do not occur in thorium minerals except monazite to any large extent; moreover, the extraction of the thorium is never complete. Solutions of thorium salts readily undergo hydrolytic change when boiled with sodium thiosulphate, a basic thorium thiosulphate being precipitated mixed with sulphur; this operation separates thorium from all rare earth metals excepting scandium and zirconium, but the separation is not perfect if more than 2 to 3 p.c. of other earths are present (Bunsen, Pogg. Ann. 1875, 155, 379; Moissan and Étard, Compt. rend. 1896, 122, 573; Urbain, Bull. Soc. chim. 1896, [iii.] 15, 338; Brauner, Chem. Soc. Trans. 1898, 73, 951).

2. **Separation from monazite sand.**—Monazite, an orthophosphate of the cerite metals which contains varying proportions of thorium, is very widely diffused in the earth's crust, occurring primarily as an accessory constituent of certain plutonic rocks (granites, diorites, gneisses, &c.). It is, however, chiefly in its secondary form of monazite sand that the mineral is exploited for the gas-mantle industry. The erosive action of rivers and tides on the original monazite

containing rocks gives rise to enormous accumulations of monazite sands found in littoral and fluviatile deposits.

Up to 1909 the deposits on the coast of Brazil (6 to 7 p.c. ThO_2), and since then the richer sand discovered on the coast of Travancore (9 to 10 p.c. ThO_2) have been exploited to the extent of 1600 to 2000 tons annually. Attempts have also been made to work commercially the sand of Ceylon (Bull. Imp. Inst. 1916, 14, 321-369). Monazite is also found in Australia, North and South Carolina, and the Malay Archipelago.

For an account of the Travancore workings, see E. White (Pharm. J. 1922, 440).

In addition to the yellow grains of monazite, the sand contains fragments of magnetite, chromite, titanite, quartz, felspar, hornblende, rutile, brookite, zircon, and small quantities of rare-earth minerals (e.g. samarskite, aschynite). The sand is concentrated by washing, followed by electromagnetic concentrations, until it contains 90 to 96 p.c. of actual monazite.

The monazite sand is decomposed by heating with a minimum of concentrated sulphuric acid, and the product dissolved in cold water, the residue containing the unattacked constituents of the sand, quartz, zircon, titanite, &c. Another way of effecting the initial breakdown of the monazite by fusing in an electric furnace with carbon, lime, and calcium fluoride, slaking the product with water and washing off the lime from the residual heavy rare earth carbides, is recommended by Baskerville (U.S. Pat. 1087099, 1914), but does not appear to be used. The acid solution is partially neutralised with magnesia, sodium hydroxide or ammonia, or suitably diluted with water, until precipitation of the phosphates of the rare-earth metals occurs, when thorium phosphate, being the least soluble of this series, is concentrated in the first fractions. The use under varying conditions of acidity and dilution of pyrophosphoric acid (J. Amer. Chem. Soc. 1914, 36, 1134-11439; D. R. P. 286087, 1914; U.S. Pat. 1182880, 1916; Eng. Pat. 112380, 1917) and of sodium hypophosphate (Koss, Chem. Zeit. 1912, 36, 686; Fr. Pat. 444798, 1912; Wirth, Chem. Zeit. 1913, 37, 773-774) have been proposed for the separation of thorium at this stage. The phosphate is dissolved in hydrochloric or sulphuric acid and the thorium precipitated by oxalic acid. The greater part of the phosphoric acid is thus removed. The sparing solubility of thorium oxalate in solutions containing excess of mineral acid serves also to separate thorium from the commoner metals (iron, manganese, calcium, &c.). Sometimes the separation with oxalic acid is replaced by precipitation with hydrofluoric acid.

The crude, well-washed thorium oxalate when warmed with excess of aqueous sodium carbonate yields a solution containing the greater part of the thorium, together with small quantities of the cerium and yttrium earths.

The thorium in the filtered carbonate solution is precipitated either as oxalate by adding acid or as hydroxide by adding caustic soda. Alternatively, the oxalate may be converted into sulphate previous to solution in sodium carbonate. Final purification is effected by converting the nearly pure oxalate or hydroxide into sulphate and crystallising repeatedly the

octahydrated salt until it is free from didymium and phosphate (Koppel and Holtkamp, Zeitsch. anorg. Chem. 1910, 67, 266).

Pure thorium sulphate obtained by the foregoing or by a slightly modified process is converted almost exclusively, via the hydroxide, into thorium nitrate. For this purpose it may be dissolved in slight excess of ammonium carbonate, the diluted solution freed from iron and heavy metals with hydrogen sulphide and boiled until ammonia ceases to be evolved. The precipitated thorium is washed and dissolved in nitric acid.

It is customary to adjust the solution so that the finished nitrate will contain sulphate equivalent to 1 or 2 p.c. H_2SO_4 , since in this form it is most generally suitable for use in the gas mantle industry. It is then concentrated until it contains 48 p.c. ThO_2 , and vigorously stirred as it cools, when the granular thorium nitrate of commerce is obtained.

Few commercial chemicals attain such a high degree of purity as thorium nitrate, since an extremely pure product is essential for the manufacture of gas mantles. Didymium and other rare earths must be entirely absent, phosphoric acid must not exceed 0.004 p.c. P_2O_5 , and lead, iron, lime, silica and soda are not permissible except in the merest traces.

Many processes for the separation of thorium from the other rare earths have been described, most of which have no commercial value. Hydrated thorium peroxide is precipitated by hydrogen peroxide from very slightly acid (preferably nitric) solutions of thorium salts, but in presence of cerite metals a certain amount of cerium is co-precipitated. The operation must be repeated several times to effect a complete separation (Wyrouboff and Verneuil, Bull. Soc. chim. 1898, [iii.] 19, 219; Compt. rend. 1898, 127, 412).

A separation of thorium and zirconium from the cerium and yttrium elements is brought about by stirring thoroughly into a dilute solution of the nitrates (containing trivalent cerium) an excess of freshly-prepared lead carbonate. After 12 hours the hydrates of thorium, zirconia, and ferric oxide are completely precipitated, the hydroxides of aluminium, chromium, and uranium are partially deposited, whilst cerium, yttrium, and other rare earth metals remain in solution. The precipitate is redissolved and the thorium present is further purified (Giles, Chem. News, 1905, 92, 130). The sparingly soluble basic acetate (Böhm, Die Darstellung der seltenen Erden, vol. i. 40, 1290) and the chromate (Ber. 1900, 33, 2028) have been recommended for separating thorium from the cerite metals, and the acetate method has been used commercially. The acetylacetone may be employed in purifying small quantities of thorium; the well-dried salt is extracted with chloroform, in which thorium acetylacetone alone dissolves (Urban, Bull. Soc. chim. 1896, [iii.] 15, 338, 347; Ann. Chim. 1900, [vii.] 19, 184). Repeated precipitation of thorium by potassium azide is recommended as a mode of separation and purification (Dennis and Kortright, Amer. Chem. J. 1894, 16, 79; J. Amer. Chem. Soc. 1896, 18, 947).

Thorium is precipitated quantitatively as iodate from even very dilute solutions by iodine

acid or potassium iodate in the presence of excess of nitric acid; hydrochloric acid should be absent (Meyer, *Zeit. anorg. Chem.* 1911, 71, 65-69).

Thorium in neutral solution is precipitated quantitatively by sebacio acid at the boiling-point (D. R. P. 266459, 1912), by phenoxacetic and pyrotartaric acids (Smith and James, *Chem. News*, 1912, 105-109), and by the ammonium salt of nitrosophenylhydroxylamine (Thornton, *Chem. News*, 1916, 114, 13-14). Thorium can be determined volumetrically as molybdate (J. Ind. Eng. Chem. 1912, 4, 493-495).

m-Nitrobenzoic acid precipitates thorium quantitatively as thorium *m*-nitrobenzoate from neutral solutions of the rare-earth nitrates derived from monazite, and a repetition of the process affords a complete separation from cerium, lanthanum, neodymium, and praseodymium, but the first of these elements must be in the tervalent condition, otherwise the sparingly soluble yellow ceric *m*-nitrobenzoate is deposited (J. Amer. Chem. Soc. 1904, 26, 780; *Zeitsch. angew. Chem.* 1905, 18, 92). This method avoids the use of alcohol, which is required in the separation of these metals with fumaric acid.

Certain organic bases have a selective action in the precipitation of the hydroxides of the rare earths; *p*-toluidine separates thorium and zirconium from lanthanum, neodymium, and praseodymium, whilst hexamethylenetetramine and the chloranilines serve to separate thorium from zirconium (Hartwell, J. Amer. Chem. Soc. 1903, 25, 1128).

The separation of thorium from rare earth mixtures by the electrolysis of solutions with a mercury cathode (Dennis and Ray, J. Amer. Chem. Soc. 1918, 40, 174-181; U.S. Pat. 1115513, 1914), and from tungsten by fusion with sodium carbonate are described (Ann. Chem. Analyst, 1913, 18, 257-260).

For the estimation of thorium in monazite sand by an emanation method, see Helmick, J. Amer. Chem. Soc. 1921, 43, 2003; J. Soc. Chem. Ind. 1922, 96 A.

Metallie thorium. The isolation of the metal in a pure state is a matter of considerable difficulty owing to its infusibility, and to its power of combining with nitrogen, hydrogen, carbon, silicon, and the metals. The reduction of thoria with magnesium is not complete (Ber. 1891, 24, 873); the action of silicon and aluminium on thoria or on potassium thorium fluoride leads respectively to the formation of a silicide ThSi_2 , and an alloy ThAl , (Compt. rend. 1906, 142, 157, 280). Thorium can also be obtained by passing the vapour of the iodide over a heated tungsten filament (van Arkel and de Boer, *Zeitsch. anorg. Chem.* 1925, 148, 345; *Chem. Soc. Abstr.* 1925, ii, 1193). The pure metal is said to be obtained by the action of metallic calcium on the oxide (Fr. Pat. 419043, 1909; U.S. Pat. 1065098, 1914), and by the treatment at 500°C. of the anhydrous chloride with sodium in a steel bomb exhausted of air (*Zeit. anorg. Chem.* 1914, 87, 209-228). So prepared the metal is leaden grey in colour, ductile and in the coarse form unattacked by water. A rolled specimen of the metal obtained by reduction melted at 1450° and had sp.gr. 12.14 (Ber. 1883, 16, 153; Compt.

rend. 1883, 96, 346; *Ann. Chim.* 1906, [viii.] 8, 182; *Zeitsch. Elektrochem.* 1908, 14, 768). Electrolysis of thorium chloride dissolved in a fused mixture of sodium and potassium chlorides contained in a graphite crucible affords a product melting at 1700° (*ibid.* 1909, 15, 866). Alloys of thorium are obtained by reducing, with sodium or with carbon and sodium hydroxide, mixtures of thorium salts with those of more fusible metals (Sn, Pb, Sb, Al, or Cu), and thorium fluoride heated with tin or lead gives thorium alloys of these metals (D. R. P. 146503). The alloys of thorium with tungsten are of commercial importance (Grotthus *Metall. u. Erz.* 1913, 10, 844; D. R. P. 2939532, 1913).

Reduction of thoria by amorphous boron leads to the formation of two thorium borides, ThB_4 , prismatic crystals, sp.gr. 7.5 at 15°, and ThB_3 , reddish-violet mass, sp.gr. 6.4 at 15°; the former is soluble and the latter insoluble in concentrated hydrochloric acid (Compt. rend. 1905, 141, 191).

Thoria is reduced to thorium by heating with tungsten, the tungsten oxide combining with unchanged thoria to form a thorium-tungsten bronze.

Colloidal thorium is prepared by rubbing 95-96 p.c. thorium with cold dilute hydrochloric acid and washing the mass on a filter until a grey opalescent solution passes through; this liquid is stable to acids, but not to alkalis. On electrification the thorium particles are found to carry a positive charge (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 191).

Thorium hydride ThH_2 . is stated to be produced by direct combination of the metal and hydrogen at red heat, or by absorption of the gas by a heated mixture of thoria and magnesium. It is not decomposed by water, but evolves hydrogen on treatment with hydrochloric acid (Ber. 1891, 24, 873; Compt. rend. 1900, 131, 891; 1901, 132, 36; *Ann. Chim.* 1907, [viii.] 10, 130). Its existence has also been observed by Klauber and von Mellenheim (*Zeitsch. anorg. Chem.* 1920, 113, 306), who formed it by the action of water or dilute acids upon an alloy of thorium and magnesium. It was said to be decomposed by heat yielding metallic thorium. Its existence is denied by Schwarz and Konrad (Ber. 1921, 54, [B] 2122).

Thorium carbide ThC_2 . yellow microscopic crystals, sp.gr. 8.96 at 18°, prepared by heating an intimate mixture of thoria and carbon in the electric furnace (900 amperes, 50 volts), is decomposed by cold water evolving acetylene, methane, ethylene, and hydrogen (Compt. rend. 1893, 116, 1227; 1896, 122, 573; *Ann. Chim.* 1897, [vii.] 12, 427; *Bull. Soc. chim.* 1914, 15, 367-370).

Thorium silicide ThSi_2 . quadratic plates, sp.gr. 7.96/16°, produced by heating to 1200° a mixture of potassium silico- and thorofluorides and aluminium (*Chem. Zeit.* 1906, 29, 1031; Compt. rend. 1906, 142, 157).

Thorium nitride Th_3N_4 . brown powder, obtained by direct union of its components at high temperatures, rapid cooling of the product is said to cause decomposition; by heating a mixture of thorium and ammonium chlorides in hydrogen chloride, or by passing ammonia over heated thorium carbide; it is decomposed by water with evolution of ammonia (Compt. rend. 1896, 122,

573; 1900, 131, 837; 1901, 132, 36; Ann. Chim. 1897, [vii.] 12, 427; 1907, [viii.] 10, 130).

Thorium sulphide ThS_2 , dark-brown lamellae, sp. gr. 6.7 at 0°, and **thorium oxysulphide** ThOS , yellow crystalline powder, sp. gr. 8.42 at 0°, are produced by passing hydrogen sulphide over a mixture of thorium chloride and excess of sodium or potassium chloride at red heat (Compt. rend. 1908, 146, 815; cf. Zeitsch. anorg. Chem. 1907, 53, 74), or at a temperature below that at which the chloride sublimes (U.S. Pat. 941071, 1909).

Thorium fluoride ThF_4 , white amorphous powder, resulting from the interaction of hydrogen fluoride and thorium chloride or bromide at 354°–400° (Compt. rend. 1908, 146, 973). The *hydrate* $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$, a gelatinous precipitate, obtained on adding hydrofluoric acid to solutions of thorium salts, changes to a heavy white powder, the insolubility of which in excess of the precipitant serves as a separation of thorium from zirconium (Bull. Soc. chim. 1897, [iii.] 20, 69); *double fluorides* have been prepared approximating to the composition $\text{KTh}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$ and $\text{KThF}_5 \cdot \text{H}_2\text{O}$, and not to the typical fourth-group formula $\text{K}_2\text{R}^{\text{IV}}\text{F}_6$ (Zeitsch. anorg. Chem. 1903, 35, 424).

Thorium chloride ThCl_4 can be prepared by the following methods, but unless oxygen and moisture are carefully excluded, the product is always contaminated with oxychloride: (i.) heating metallic thorium in hydrogen chloride (Ber. 1887, 20, 1665; Zeitsch. physikal. Chem. 1887, 1, 301); (ii.) heating thorium in carbon tetrachloride vapour or in a mixture of carbon monoxide and chlorine (Compt. rend. 1901, 132, 36, 1908; 147, 1046; Ann. Chim. 1907, [viii.] 10, 130); (iii.) heating thorium in the vapour of sulphur chloride (Bourion, Ann. Chim. 1910, [viii.] 20, 547; 21, 49; cf. Compt. rend. 1904, 138, 631; Ber. 1905, 38, 817; Zeitsch. anorg. Chem. 1914, 87, 209–228); (iv.) decomposing the heated carbide with chlorine (Compt. rend. 1905, 140, 1510). When purified by sublimation *in vacuo* (720°–750°) the chloride is obtained in colourless needles or prisms, sp. gr. 4.59, m.p. 820°.

Thorium oxychloride ThOCl_2 is an intermediate product obtained in the foregoing operation (No. ii.); it crystallises from alcohol and absorbs $6\text{H}_2\text{O}$ from moist air. The *hydrate* $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ is readily soluble in water or alcohol, and the soluble *hydroxy-chlorides* $\text{Th}(\text{OH})\text{Cl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{Th}(\text{OH})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ have been isolated.

Thorium chloride combines with ammonia to form several additive compounds, of which $\text{ThCl}_4 \cdot 4\text{NH}_3$ alone is stable above 120° (Compt. rend. 1910, 151, 387). Additive compounds are also formed with organic bases and with alcohols, aldehydes, and ketones (Zeitsch. anorg. Chem. 1903, 35, 424; Ber. 1904, 37, 3662; Jantech and Urbach, Helv. Chim. Acta, 1919, 2, 490).

Thorium bromide ThBr_4 , transparent colourless needles, sp. gr. 5.62, unstable in the light, evolving bromine, boils at 725° and sublimes *in vacuo* at 600°–620° (Compt. rend. 1905, 140, 1510; 1907, 145, 243).

Thorium platinoeyanide $\text{Th}[\text{Pt}(\text{CN})_4]_2 \cdot 16\text{H}_2\text{O}$, yellow rhombic prisms from thorium sulphate and barium platinoeyanide.

Thorium hydroxide $\text{Th}(\text{OH})_4$, heavy white

powder, readily soluble in mineral acids or in aqueous alkali carbonates. It dissolves readily in less than its equivalent of hydrochloric or nitric acid, forming solutions which are colloidal, but which readily revert to the normal salts on boiling with a slight excess of acid. The hydrosol form of this hydroxide is produced by dialysing solutions of thorium nitrate or by adding thorium nitrate solution gradually to the well-washed hydrosol and boiling the mixture until an opalescent solution is obtained. Thorium hydroxide hydrogel is also converted into the hydrosol form by diluted (N/20) hydrochloric acid, or by solutions of aluminium or ferric chloride (Biltz, Ber. 1902, 35, 4436; 1904, 37, 1100; Müller, *ibid.* 39, 2857; Zeitsch. anorg. Chem. 1908, 57, 314; J. Chim. Phys. 1907, 5, 488, 495; Zeitsch. Electrochem. 1916, 22, 145–161; J. Soc. Chem. Ind. 1916, 688; Lemoine, Compt. rend. 1916, 162, 702–706).

The electrometric precipitation of thorium hydroxide has been studied by Britton (Chem. Soc. Trans. 1925, 127, 2110).

The so-called *thorium meta-oxide* is a soluble modification of thorium, produced by igniting the oxalate or hydroxide at comparatively low temperatures and evaporating the residue with hydrochloric or nitric acid until a syrup is left, which dissolves in water to a milky solution, appearing yellow by transmitted light (Cleve, Jahrb. Min. 1874, 161; Stevens, Zeitsch. anorg. Chem. 1901, 27, 41; Wyruboff and Verneuil, *ibid.* 28, 90; Compt. rend. 1898, 127, 863). It corresponds with the colloidal hydroxide described by D. R. P. 228203, 1909.

Thorium dioxide (*thoria*) ThO_2 , white powder, sp. gr. 10.220 at 17°, is obtained by heating the hydroxide or the thorium salts of volatile acids.

It is ordinarily very resistant to the action of even concentrated hydrochloric and nitric acids, but particles reduced to sizes less than 1μ are soluble in hydrochloric acid (J. Chem. Soc. 1917, 112, [ii.] 300). It melts and volatilises at 2000°C. in the cathode ray furnace (Zeitsch. anorg. Chem. 1914, 87, 129–168). Advantage is taken of the refractory nature of the oxide for the making of cupels, &c. (U.S. Pats. 1121988; 1121890, 1914).

The resolution of thorium into three chlorides differing in volatility and containing respectively three elements with different atomic weights has not been confirmed (Baskerville, *ibid.* 1904, 26, 922; Ber. 1905, 38, 1444; cf. R. J. Meyer and Gumpertz, *ibid.* 1905, 38, 817; Eberhard, *ibid.* 38, 826).

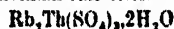
Thorium peroxide is a gelatinous white precipitate, retaining acid and of somewhat uncertain composition, formed by adding hydrogen peroxide to solutions of thorium salts; its peroxide character is manifested by the liberation of iodine from potassium iodide (Compt. rend. 1898, 126, 340; Bull. Soc. chim. 1898, [iii.] 19, 219; Ann. Chim. 1906, [viii.] 6, 441; Zeitsch. anorg. Chem. 1900, 25, 378; 1902, 31, 359; R. Accad. Sci. Torino, 1911, 46, 195; Gazz. chim. ital. 1912, 42, ii. 21–28).

Thorium sulphate $\text{Th}(\text{SO}_4)_2$, obtained in the anhydrous condition by treating thorium with concentrated sulphuric acid, dissolves in ice-cold water to a 25 p.c. solution, which is super-saturated at all temperatures from 0° to 100° and yields between 0° and 43° either upon

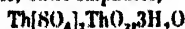
taneously or after seeding, monoclinic prisms of the nonhydrate $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$, and above the latter temperature needles of the tetrahydrate $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$; these hydrates are isomorphous with the corresponding uranous compounds $\text{U}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ and $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Zeitsch. Krist. 1900, 32, 250; 1901, 34, 307).

The octohydrate $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, prismatic crystals, separates under conditions similar to those which favour the formation of the more stable nonhydrate, and is the hydrate usually obtained in practice. It owes its production to the existence of a metastable phase having a very low velocity of transformation (Bull. Soc. chim. 1901, [iii.] 25, 105; Bull. Soc. Min. 1901, 24, 105; Ber. 1887, 20, 1665; 1905, 38, 817). The octo- and nonhydrates are very sparingly soluble in cold water and (in presence of excess of sulphuric acid) in mineral acids. For the solubility of the sulphate, see Wirth (Zeitsch. anorg. Chem. 1912, 76, 174-200; Bull. Soc. chim. 1912, 11, 645-648).

The acid sulphate $\text{ThSO}_4(\text{HSO}_4)_2$, needles, is obtained by drying *in vacuo* at 130° , the product of the action of concentrated sulphuric acid on a saturated solution of the anhydrous normal sulphate (Zeitsch. anorg. Chem. 1904, 38, 322); a hydrated acid sulphate $2\text{Th}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Gazz. chim. ital. 1903, 32, ii. 523); and a basic sulphate $\text{ThOSO}_4 \cdot 2\text{H}_2\text{O}$ (Compt. rend. 1883, 96, 1860; 1910, 151, 70; Ber. 1910, 43, 2776) have been described. The following double sulphates have been isolated: $\text{K}_2\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, sparingly soluble; $\text{K}_2\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$; the corresponding ammonium salt series:



$\text{Cs}_2\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$; $\text{Na}_2\text{Th}(\text{SO}_4)_4 \cdot 4$ and $12\text{H}_2\text{O}$ (Bull. Soc. Min. 1901, 24, 105; Zeitsch. anorg. Chem. 1903, 35, 424; Gazz. chim. ital. 1903, 32, ii. 523). On heating the sulphate to 55°C . with excess of water, basic sulphates,



and $6\text{H}_2\text{O}$ are formed (Barré, Compt. rend. 1910, 151, 70-72).

Thorium ethylsulphate has been described as intermediate in the production of pure thorium nitrate (Fr. Pat. 414463, 1910).

Thorium nitrate $\text{Th}(\text{NO}_3)_4$, with 5, 6, and $12\text{H}_2\text{O}$, the dodecahydrate separating in hygroscopic plates (Cleve, l.c.; cf. Zeitsch. angew. Chem. 1897, 115; Chem. Soc. Trans. 1898, 73, 951). The commercial product, which is not a definite hydrate, but approximates to $\text{Th}(\text{NO}_3)_4$ with $4\text{H}_2\text{O}$, contains sulphate equivalent to 1 to 3 p.c. H_2SO_4 , and swells considerably on heating, leaving a finely divided residue of snow-white thorium. Commercial thorium nitrate should contain a minimum of 48 p.c. of ThO_2 .

Thorium nitrate unites with the nitrates of univalent and divalent metals, forming complex nitrates, having respectively the general formulae $\text{R}_2\text{Th}(\text{NO}_3)_6$ and $\text{R}'\text{Th}(\text{NO}_3)_8 \cdot 8\text{H}_2\text{O}$, which correspond with the double nitrates containing quadrivalent cerium. Similar double nitrates (and sulphates) are formed with organic bases (Zeitsch. anorg. Chem. 1901, 27, 350; 1908, 60, 123).

Complex thorium carbonates. Normal thorium carbonate is not known, but complex carbonates are prepared by adding soluble carbonates to thorium solutions until the pre-

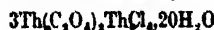
cipitate first formed redissolves or by dissolving thorium hydroxide in aqueous alkali bicarbonate, saturated with carbon dioxide, and precipitating with alcohol or by the interaction of thorium and carbon dioxide under pressure (Compt. rend. 1911, 153, 66-68). Sodium thorium carbonate $\text{Na}_2\text{Th}(\text{CO}_3)_2 \cdot 12\text{H}_2\text{O}$ separates in prismatic crystals; the thallous salt $\text{Tl}_2\text{Th}(\text{CO}_3)_2$ is precipitated as a crystalline powder on adding a soluble thallous salt to a solution of ammonium thorium carbonate (Cleve, l.c.; cf. Zeitsch. anorg. Chem. 1903, 35, 424). For the thorium chromates, see H. T. S. Britton, Chem. Soc. Trans. 1923, 123, 1429.

Thorium molybdate $\text{Th}(\text{MoO}_4)_2$, obtained by fusing partly dehydrated thorium chloride with excess of anhydrous sodium molybdate, forms tetragonal crystals, $a:c=1:0.73565$, $d^{100} 4.92$, which exhibit mutual miscibility in the solid state with cerous molybdate (Ferruccio Zambonini, Atti R. Accad. Lincei, 1923, [v.] 32, i. 518-524; cf. A. 1916, ii. 249).

Thorium formate $\text{Th}(\text{HCO}_2)_4 \cdot 3\text{H}_2\text{O}$ and thorium acetate $\text{Th}(\text{CH}_3\text{CO}_2)_4$, crystallising respectively in leaflets and needles, are produced by dissolving thorium in the corresponding acids; interaction between thorium salts and soluble formates and acetates leads to basic salts $\text{Th}(\text{OH})_2(\text{HCO}_2)_2$ and $\text{Th}(\text{OH})_2(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ (Haber, Monatsch. 1897, 18, 687).

Thorium oxalate $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ is precipitated completely by adding oxalic acid to thorium solutions even in the presence of considerable proportions of mineral acid (Brauner, Chem. Soc. Trans. 1898, 73, 951). Complex oxalates such as $\text{K}_2\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{Th}(\text{C}_2\text{O}_4)_4 \cdot 6\text{H}_2\text{O}$ are produced by dissolving thorium oxalate in concentrated solutions of alkali oxalates (Cleve, l.c.; and Brauner, l.c.). The existence of double oxalates with ammonium oxalate $2\text{Th}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$ is established by solubility curves (James, J. Amer. Chem. Soc. 1914, 36, 1853-1856).

Complex chloro-oxalates, e.g.



have been described (Compt. rend. 1913, 156, 1075-1076; *ibid.* 1913, 156, 1907-1909).

Thorium acetylacetonate $\text{Th}(\text{CH}(\text{CO}-\text{CH}_3)_2)_4$, m.p. 171° , soluble in alcohol or chloroform, is prepared by adding acetylacetone dissolved in aqueous ammonia to 13 p.c. thorium nitrate solution. This salt can be distilled *in vacuo* (Urbain, Bull. Soc. chim. 1896, [iii.] 15, 1338; Biltz, Annalen, 1904, 331, 334; Zeitsch. anorg. Chem. 1904, 40, 218).

Thorium tartrates and complex tartrates, v. Cleve, l.c.; Haber, l.c.; Rosenheim, Zeitsch. anorg. Chem. 1903, 35, 424.

Thorium salts of other organic acids, v. Morgan, Pharm. J. 1904, [iv.] 10, 472; and Karl, Ber. 1910, 43, 2068.

Thorium oleate has been employed therapeutically in ointment form for carbuncles and other skin troubles (Martindale, Extra Pharmacopoeia).

Pharmacological action of thorium, v. Sollmann and Brown, Amer. J. Physiol. 1907, 18, 426.

Thorium compounds are used to render the internal organs opaque to Röntgen rays (D. R. F. 223375, 1909).

Biological action of thorium.—Elemental thorium inhibits the growth of certain micro-organisms and algae without endangering the life of higher organisms (*Amphioxus*, *Zeitsch. Elektrochem.* 1911, 17, 816; *Arch. Sci. Phys. Nat.* 1911, [iv.] 32, 347); the salts inhibit the growth of cholera vibrio (*Compt. rend.* 1914, 159, 410-413).

Industrial application of Thoria v. GAS MANTLES. Gas mantles are generally woven in cotton or preferably ramie fibre, but artificial silk has also been employed, and formerly the thorium-cerium solution was added to the dissolved cellulose before it was spun into thread. The present practice, however, with viscose artificial silk is to impregnate the woven stocking just as in the case of ramie or cotton fibre. The rare earth nitrates may be replaced by the corresponding acetates or formates and, with artificial silk, the impregnated stocking is treated with ammonia or some volatile alkali such as hydrazine or tetraethyl-ammonium hydroxide in order to produce within the fibres the hydroxides of thorium and cerium. Hydrogen peroxide may also be employed as the precipitant. In either case, the stockings are washed free from soluble salts (ammonium nitrate, &c.) or acid; the head is hardened with a solution of magnesium, aluminium, zirconium, glucinum or chromium salt, and the mantle 'burnt off' and 'seasoned' as in the case of the ramie fibre.

From a kilogram of thorium nitrate 600 to 800 mantles can be made; hence each mantle contains about 0.5 gram of thoria.

Although in most instances the optimum effect is attained by mixing the thorium and cerium salts in such proportions that the mixed oxides of the mantle consist of 98.8 p.c. of thoria and 1.2 p.c. of ceria, yet owing to the yellow colour of the light produced by this amount of ceria in inverted mantles, it is customary in this form of illumination to reduce the proportion of ceria to from 0.5 to 0.7 p.c.

According to R. L. Swan (*J. Chem. Soc.* 1924, 125, 780) the catalytic activity of mixtures of ceria and thoria on the combination of hydrogen and oxygen at 450° reaches a maximum when the mixtures contain 1 p.c. of ceria (Welsbach mixture). The activity of pure thoria is the same as that of a mixture containing 9 p.c. ceria. The light-giving powers of these are also equal. The author considers that the Welsbach mixture represents the best illuminant obtainable from the two oxides in question. The ceria may act as a carrier of oxygen (*cf. A.* 1907, ii. 557) or as a promoter of the electronic emission from the thoria (*Chem. Soc. Abstr.* 1924, 126, ii. 400).

A pure thoria mantle gives no emission in the visible region of the spectrum and only a slight radiation of infra-red rays of short wave-length. A cerium dioxide mantle gives a maximum radiation at the extreme red end of the visible spectrum, the intensity at first diminishes in the infra-red region and then increases again for heat rays of longer wave-length. In this mantle there is, on the whole, a relatively considerable loss of heat by radiation, the temperature remains comparatively low and consequently the emission of light rays is only feeble.

In the Welsbach mantle containing 0.5 p.c

to 1.5 p.c. cerium dioxide, the emission of light is selective and attains its maximum in the blue region of the spectrum. On the other hand, the heat radiation is remarkably small, except for rays of comparatively long wave-length. Consequently the temperature attained by the mantle is comparable with that of the flame itself. The cerium dioxide colours the transparent ground mass of thoria so that an intense selective absorption is developed in the visible region of the spectrum and, providing that the amount of colouring oxide is small, this result is attained without any appreciable increase in the loss of heat by radiation and consequently without diminution in the intensity of illumination.

One hundred parts of thoria can hold in solid solution 6.7 parts of cerium dioxide, and as the mantle contains only about 1 p.c. of the latter oxide, it is entirely in the dissolved condition. Owing to this intimate mingling of the two oxides, a very small addition of cerium dioxide suffices to bring about the intense emission of light waves whilst the increase in heat radiation is too slight to act injuriously. If, however, the proportion of cerium is raised, the greater loss of heat by radiation leads to lowering of the mantle temperature and consequent diminution in luminosity. Cerium dioxide itself is stable in the Bunsen flame, but nevertheless the ignited mixed oxides, when treated with hydrochloric acid and potassium iodide solution liberate an amount of iodine corresponding with only a portion of the dioxide originally introduced into the mixture. This result suggests the possibility of some chemical combination between the cerium and thorium oxides which may be the chemical cause of the characteristic physical properties of the Welsbach gas-mantle (*cf. White and Traver, J. Soc. Chem. Ind.* 1902, 21, 1012; *Lewes, Chem. News* 1905, 26, 62; *Journ. Gas Beleuchtung*, 1903, 46, 787, 974; *R. J. Meyer and Anschütz, Ber.* 1907, 40, 2639). For the testing of incandescent mantles, see Coste and Powney, *J. Soc. Chem. Ind.* 1911, 30, 65.

RADIO-ACTIVITY OF THORIUM.

Thorium preparations, in general, exhibit radio-activity, yielding α -rays of similar intensity but greater penetrative power than those of uranium. The long range of these α -particles was discovered by Rutherford and Wood (*Phil. Mag.* 1916, vi. 31, 379-386), who state that they have greater velocity than any α -particles previously known. The β -rays from thorium are about one-tenth as intense as those from uranium, and have less penetrating power. The γ -rays are relatively feeble but very penetrating. It has been stated that the radio-activity of thorium from monazite is due to the uranium present in this mineral, and that minerals free from uranium yield inactive thorium (Baskerville, *J. Amer. Chem. Soc.* 1904, 26, 1642; Zorban, *Ber.* 1903, 36, 3911; 1905, 38, 557). On the other hand, minerals free from radium have been found to give helium and thorium emanation (Strutt, *Proc. Roy. Soc.* 1905A, 78, 88, 312; 1907A, 80, 56; Hahn, *Ber.* 1905, 38, 2371). After allowing for uranium, a constant ratio between the radio-activity and amount of thorium was found for thorium minerals in which, probably,

thorium and radio-thorium are in equilibrium. In thorium salts, where the radio-thorium is largely removed, this constancy does not exist. Boltwood has not succeeded in obtaining inactive thorium (Amer. J. Sci. 1906, 21, 415, and 433).

Thorium hydroxide precipitated by ammonia from a solution of a thorium salt has no emanating power and only a greatly diminished α -radiation. The filtrate retains the whole of the emanating power, and the minute residue obtained on evaporation and ignition possesses the radio-activity which the precipitate has lost. The emanating power and radio-activity of this product, thorium X, disappear in the course of a month, decaying to half their original value in four days. The precipitated thorium hydroxide recovers the properties just as fast as they

disappear from thorium X, and a second treatment of its acid solution by ammonia after one month leads to the separation of another quantity of thorium X having the same activity as the first fraction. Thorium X, a short-lived radio-active product of thorium, produces gaseous thorium emanation, and this in turn gives thorium 'active deposit,' which imparts radio-activity ('induced activity') to solid objects brought into contact with this disintegration product (Rutherford and Soddy, Chem. Soc. Trans. 1902, 81, 321, 837; Phil. Mag. 1902, 4, 370, 569).

Owing to the complicated nature of the disintegration changes the radio-activity of a thorium preparation is a complex function of its age. The sequence of these changes is indicated in the annexed diagram. All thorium emanations

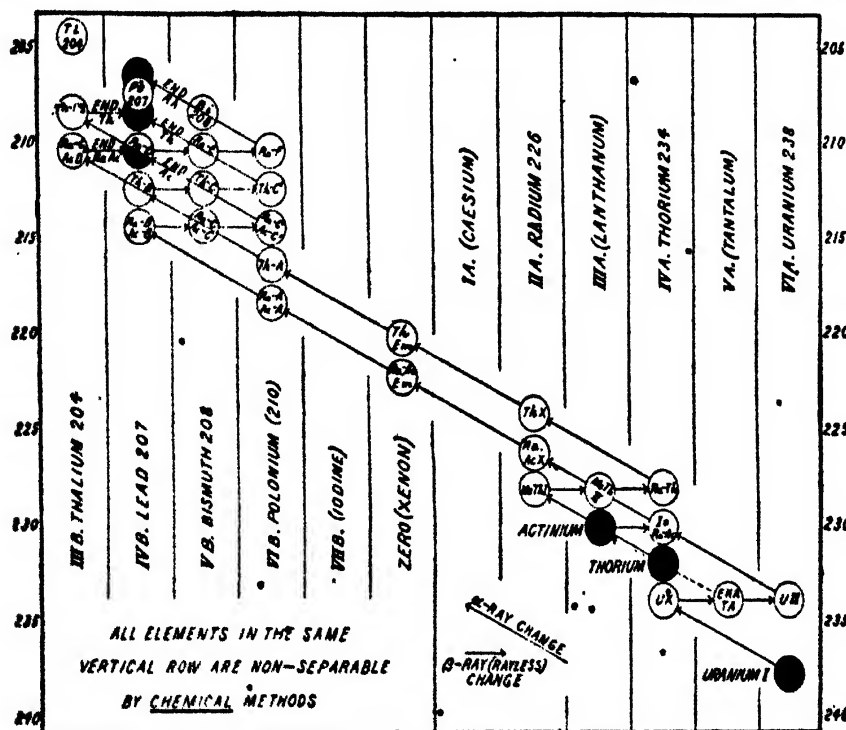


FIG. 1

are condensed at 5°C. (Fleck, Phil. Mag. 1915, 29, 337-362).

Mesothorium 1 is separated from thorianite by adding 26 grms. of barium nitrate to 1.5 litres of a slightly acid solution of 600 grms. of the mineral in nitric acid and by shaking the solution for an hour with excess of sulphuric acid when the sulphate of mesothorium 1 is co-precipitated with barium sulphate. The radioactive precipitate is reduced to sulphide by heating with carbon in a quartz crucible. Various methods are described for the reduction of this radio-active sulphate. Hahn (Ber. 1907, 40, 1462, 3304) recommends reduction with sugar carbon in a quartz crucible; Ebler (Eng. Pat. 1173, 1914), ignition with calcium carbide; and firing of a mixture of the dry sulphate and calcium hydride is suggested (Zeitsch. anorg.

Chem. 1913, 82, 149-158). The product is dissolved in hydrochloric acid. The lead is precipitated from this solution by hydrogen sulphide and traces of iron and thorium by ammonia. The radio-active chloride in the filtrate is crystallised out fractionally when mesothorium 1 is concentrated in the least soluble portions (Hahn, Ber. 1907, 40, 1462, 3304).

From monazite sand, mesothorium 1 is isolated by adding 0.1 p.c. of barium carbonate and heating the sand (400 grms.) with 800 grms. of concentrated sulphuric acid. The product is thoroughly mixed with cold water when the sediment contains practically the whole of the mesothorium 1 and radium. These two active components are concentrated from the barium sulphate precipitate by converting the product

successively into sulphide and chloride, and fractionating the latter from water when the mesothorium 1 accumulates in the least soluble crystals (Soddy, Eng. Pat. 25504, 1910; Chem. Soc. Trans. 1911, 99, 75).

In practice, the radioactive residues from monazite sand consist mainly of lead sulphate, silica, and rare earth phosphates. They may be boiled with a large excess of a mixture of caustic soda and sodium carbonate (10:1), the residue well washed, and the treatment with the preceding mixture repeated once or twice, when the silica and lead are almost completely removed and the barium, mesothorium, and rare earths left as carbonates. The residue is extracted with hydrochloric acid and the clear liquor precipitated with sulphuric acid. The crude radioactive barium sulphate may then be transformed into carbonate by boiling with excess of concentrated sodium carbonate solution several times in succession, with intervening washings (see Strong, J. Amer. Chem. Soc. 1921, 43, 440).

Another method for the separation of the radio-active constituents from monazite without the addition of barium salts is by the precipitation of these along with a small proportion of the thorium from phosphate solutions by dilution and boiling (U.S. Pat. 1084734, 1914; see also U.S. Pat. 1100743, 1914; D. R. P. 274874, 1913).

Mesothorium cannot be separated from radium by fractionation of the double barium salts, but in the fractional crystallisation of the picrates, bromates, and ferrocyanides from alcohol or acetic acid mesothorium separates before radium (Kunheim, D. R. P. 264901, 1912).

On account of this complete similarity of chemical properties all radium compounds separated from uranium minerals containing thorium contain mesothorium 1, and all mesothorium preparations include the radium present in the thorium minerals. In fact, technical mesothorium, produced from monazite sand, contains about 99 parts by weight of radium to one of mesothorium, but nearly 90 p.c. of the radiation it emits is due to the active products of mesothorium 1 (Hahn, Chem. Zeit. 1911, 35, 845).

Mesothorium 1 is rayless, and it disintegrates into mesothorium 2; its period of average life is 7-9 years, the period of half-change being 6-7 years (Phys. Zeitsch. 1918, 19, 257-263; J. Chem. Soc. Abs. 1918, ii. 347). It behaves like a metal of the alkali earths.

Mesothorium 2 reacts like a metal of the rare-earth series, and accordingly ammonia serves to precipitate it from solutions of mesothorium 1, a trace of zirconium salt being generally added to serve as a nucleus for precipitation (Hahn, Zeitsch. physikal. Chem. 1908, 9, 246; Russell and Soddy, Phil. Mag. 1911, [vi.] 21, 130). Two other disintegration products, radio-thorium and thorium X, are co-precipitated, but if the precipitation is repeated on the solution after one or two days the second precipitate will contain mesothorium 2, relatively free from radio-thorium. Mesothorium 2 has an average life period of 8-9 hours, the half-change period being 6-2 hours; it gives β - and γ -rays; the former are heterogeneous, the absorption coefficient

increasing as absorption proceeds; the γ -rays resemble those of uranium X.

Radio-thorium. Period of average life 1063 days (?), period of half-change, accurate to 1 p.c., 696 days. It is chemically identical with thorium, and is only distinguished from the latter by preparing it through mesothorium 1 and 2. Mesothorium 1 is readily separated from thorium, and when left to itself produces radio-thorium, which is separated by precipitating a solution of the two disintegration products with ammonia in the presence of a trace of zirconium salt. When first precipitated in this way the radio-thorium will contain mesothorium 2, but this decays completely in the course of 3 days, while the formation of the next disintegration product, thorium X, causes an increase in the radio-activity of the preparation over a period of 3-4 weeks. The emanating power increases with the growth of thorium X, but after a month the total activity and emanating power decay to zero.

Radio-thorium can be prepared by evaporating to dryness the nitric acid solution of the washed ammonia precipitate from solutions of thorium X, freed from barium, calcium, iron, and lead salts and phosphates. The residue is washed free from ammonium salts by a solution of sodium chloride free from carbon dioxide.

Radio-thorium preparations, especially when kept moist, are very suitable for demonstrating the properties of the thorium emanation. When the air in the tube containing a radio-thorium compound is blown between two darkened zinc sulphide screens with films turned inward, a brilliant luminescence is observed, and the decay and reproduction of the emanation can be thus illustrated (cf. Hahn, Ber. 1905, 38, 3371; Zeitsch. physikal. Chem. 1905, 51, 717; Phil. Mag. 1906, [vi.] 11, 793; Elster and Grittel, Chem. Zentr. 1906, ii. 302).

Radio-thorium emits α -rays which have a range of 3.9 cm. of air (Leslie, Le Radium, 1911, 8, 356).

Thorium X. Period of average life 5.35 days, period of half-change 3.7 days. Resembles radium, mesothorium 1, and the metals of the alkaline earths and remains in solution when thorium is precipitated with ammonia. The residue left on evaporating the filtrate gives on ignition a small amount of an intensely radioactive product, this activity being due to thorium X. If, however, thorium is precipitated by a carbonate or phosphate, thorium X is also rendered insoluble; the precipitate retains the initial radio-activity of the thorium compound, and when dissolved it exhibits the initial emanating power. The emanating power of a thorium solution is a measure of the amount of thorium X present (Zeitsch. anorg. Chem. 1909, 61, 338; 63, 197).

When fumaric or *m*-nitrobenzoic acid or pyridine is used to precipitate thorium both thorium X and thorium B are left in solution. In this way thorium hydroxide is freed from thorium X and its disintegration products. Four precipitations with *m*-nitrobenzoic acid give thorium hydroxide, having neither β -activity nor emanating power and a minimum of α -activity; the activity of this preparation then increases regularly without the initial decay characteristic of the precipitate obtained by

ammonia (Schlundt and Moore, *J. Phys. Chem.* 1905, 9, 682).

Other methods for the preparation of thorium X are the treatment with a solution of sodium carbonate of the radio-active lead sulphate obtained by the action of sulphuric acid in the presence of a lead salt, upon the minerals, dissolving the residue in hydrochloric acid, and precipitating the lead as sulphide, leaving thorium X in solution (*Chem. Zeit.* 1913, 37, 1105-1106); by the dialysis of colloidal solutions of thorium hydroxide prepared by digesting with a trace of thorium nitrate the washed precipitate formed by the action of ammonia on the nitrate when thorium X passes through (*D. R. P.* 278121, 1913); by extracting with a solution of common salt the filtered hydrated peroxide, disintegrated by standing, obtained by precipitating purified neutral solutions of radio-thorium with hydrogen peroxide (*D. R. P.* 279936, 1913).

Thorium X is more electro-positive than its successive products and cannot be separated from acid solutions by electrolysis or by the action of metals, only the thorium 'active deposit' being deposited. From alkaline solutions, however, all the active substances may be deposited electrolytically (von Lerch, *Monatsh.* 1905, 28, 899).

Thorium X exhibits an α -activity, the rays having a range of 5.7 cm. of air; it also emits feebly penetrating β -rays of low velocity, and in this respect differs from thorium and radio-thorium (Levin, *Phil. Mag.* 1906, [vi.] 12, 177).

For the action of thorium X on the maturation of eggs, the germination of seeds, and the growth of plants, see Averseng, Delas, Jaloustro, and Maurin (*Compt. rend.* 1924, 178, 1491; *Chem. Soc. Abstr.* 1924, 128, i, 796).

Thorium Y is described by Glaser (*Chem. Zeit.* 1913, 37, 477-478) as being obtained together with thorium X by the treatment of thorium minerals at 250°C. with twice their weight of concentrated sulphuric acid, stirring the cold product into 20 volumes of water, separating thorium, thorium X, and thorium Y from the filtered solution by dilution or neutralising with magnesia, dissolving the moist pre-

cipitate in sulphuric acid and pouring into water when the thorium Y remains undissolved.

Thorium emanation, period of average life 76 seconds, period of half-change 53 seconds, radio-active constant 0.0131 (sec.)⁻¹, α -activity, range of α -rays 5.5 cm. of air. This emanation, which differs from radium emanation in its short period and resembles it in showing α -activity, is most conveniently obtained from moist radio-thorium preparations; it is absorbed by charcoal at the ordinary temperature and is condensed on cooling, condensation starting at -120°, and being complete at -155°. The molecular weight determined by effusion is between 200 and 210, the coefficient of diffusion being about 0.1 (Leslie, *Compt. rend.* 1911, 153, 328). Thorium emanation, like radium emanation (niton) and actinium-emanation, belongs to the family of inert gases and is not absorbed or affected by chemical reagents. The induced radio-activity imparted to solid objects by thorium emanation lasts a few days, whilst that from radium or actinium emanation decays completely in a few hours (Rutherford, *Phil. Mag.* 1909, [v.] 48, 161).

Solid thorium nitrate and oxide have a lower emanating power than the hydroxide or carbonate, and in the latter case this phase of activity is further reduced by ignition. In these instances the molecules of emanation diffuse so slowly from the solid that the majority disintegrate within the substance and never escape. But when the thorium compounds are dissolved their solutions exhibit the same emanating power.

The amount of thorium present in a mineral may be quickly estimated by passing a steady current of air through the thorium solution and comparing the constant leak in an electro-scope produced by the stream of emanation with that brought about by a similar volume of a standard solution of thorium mineral (*cf.* Ramsay, *J. Chim. Phys.* 1905, [iii.] 617).

Thorium active deposit (thorium A, B, C₁, C₂, D, and E). For relative activities, see *Phil. Mag.* 1913, 25, 333-359. For investigation of initial charged condition, see Henderson, *Trans. Roy. Soc. Canada*, 1917, iii, 10, 151-167; *J. Chem. Soc. Abs.* 1917, ii, 351.

	ThA	ThB	ThC ₁ & ThC ₂	ThD
Period of average life	0.203 sec.	15.3 hrs.	79 mins.	4.5 mins.
" half-change	0.014 "	10.6 "	55 "	3.1 "
Radiation	α -rays	β -rays	2 α -rays	β - & γ -rays
Range of α -rays	—	—	{5.0 and 8.6 cm. of air}	—
Penetration power of β rays (mm. of Al, half absorption) —	—	0.05	—	0.441
" " γ -rays (cm. of lead, half absorption) —	—	—	—	1.5

Thorium A, the first product of thorium emanation, is very short-lived, but its existence is indicated by the appearance of the double scintillations on the zinc sulphide screen produced by the pair of α -particles emitted by the emanation. A distinct although very short time interval separates the two members of the pair (Rutherford and Geiger, *Phil. Mag.* 1911, [vi.] 22, 201, 621; *Zeitsch. physikal. Chem.* 1910, 11, 7; Moseley and Fajans, *Phil. Mag.* 1911, [vi.] 22, 69).

Thorium B, the second product of thorium emanation, is practically rayless except for a feeble β -activity. Consequently, a negatively charged wire exposed for a short time to a

powerful source of emanation (e.g. radio-thorium) has no very appreciable activity one second after withdrawal, but after a few hours acquires a powerful activity due to thorium C₁ and C₂.

On heating the active wire to red heat thorium B distils off without any appreciable effect on the activity of the wire. The inactive sublimate (thorium B) acquires an activity which, after reaching a maximum in 4 hours, decays with a half period of 10.6 hours (*Phil. Mag.* 1905, [vi.] 9, 628).

Thorium B is insoluble in chloroform and in methylene iodide. Both thorium B and thorium C₁ dissolve in aqueous solutions of salts,

hydroxides and acids, are difficultly soluble in boiling water and in organic solvents, but more soluble in potassium iodide solution (Phil. Mag. 1913, 25, 330-332).

Thorium C is removed from a solution of thorium active deposit by absorption with animal charcoal when thorium B remains dissolved. Thorium C is also deposited alone when the solution is electrolysed or shaken up with metallic nickel. Zinc, however, deposits both thorium B and C, but not thorium X.

Thorium C gives two sets of α -rays having different ranges, these being attributed to the presence in this active product of the two constituents thorium C_1 and thorium C_2 ; these products have not, however, been separated, and the two sets of rays are due to concurrent changes (Hahn, Phil. Mag. 1906, [vi.] 11, 793; Ber. D. physikal. Ges. 1909, 11, 55).

Thorium C_1 . When the thorium active deposit coating a plate or wire is kept in a vacuum at the ordinary temperature, the powerful α -ray disintegrations of thorium C and C_1 , one of which is the strongest known, cause a considerable proportion of thorium C_2 to 'recoil,' i.e. to become projected from the plate or wire on to surrounding surfaces of the vacuum space, these receiving surfaces being kept negatively charged.

According to von Lerch's rule the disintegration of radio-active elements is accompanied by a regular increase in the electro-negative character of the successive products. But to this rule thorium C_2 is an exception, as it dissolves more readily in acids than the other products, and is moreover more volatile than its generators, being completely volatilised at 700°C. from an active wire placed for 30 seconds in a Bunsen flame (Sitzungsber. Akad. Wiss. Wien. 1907, 116, [11a], 1443; 1909, 118 [11a], 1575; Zeitsch. physikal. Chem. 1911, 12, 273, 378). It can be separated by volatilisation from thorium C, which sublimes at 780°C. (Wood, l.c.).

Thorium C_2 is probably non-separable by chemical methods from thallium, and like this element is co-precipitated with potassium platinochloride (Chem. News, 1913, 107, 97). Barratt has found that thorium C undergoes dual disintegration into thorium C_1 , and thorium C_2 (Proc. Physical Soc. 1912, 24, 112).

Thorium C_2 , which emits only β - and γ -rays is the last active member of the series; its decay is regular and complete, and the ultimate product (thorium D) is regarded as an element indistinguishable chemically from ordinary lead.

Thorium-lead, which is the stable end product from thorium C_1 (α -ray change) or from thorium C_2 (β -ray change), has the atomic weight 208, and is an isotope of ordinary lead and of the lead (206) derived from radium.

The relationship existing between radio-active elements and the ordinary elements of the periodic classification is illustrated by the diagram on p. 41, in which can be seen the connection between the degradation products of thorium and the elements non-separable from these products by ordinary processes (Soddy, l.c.).

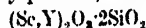
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Verneuil, La Chimie des Terres rares; Truchat, Les Terres rares; Rutherford, Radioactivity; Soddy, The Chemistry of the Radio-elements, 1911; Main Smith, Chemistry and Atomic Structure, 1924.

THORN APPLE v. DATURA.

THORON. A term given to the emanation of thorium. This gas is an isotope of radon and actinon, the emanations of radium and actinium respectively. A number of springs in the Pyrenees and in the Central Plateau of France have been examined to ascertain their content of radium and thorium emanations. The former occurs in various proportions in all the waters, but thorium emanation is found in traces only in those of the Central Plateau. Even in those cases in which thorium emanation is not detectable, it is probable that the water comes into contact with this emanation, but that the time elapsing between the termination of this contact and the appearance of the water at the outlet of the spring exceeds 10 minutes, which is the duration of the life of thorium emanation (A. Lepape, Compt. rend. 1924, 178, 931; Chem. Soc. Abstr. 1924, 126, ii. 295).

THORTVEITITE. A silicate of scandium with yttrium, dysprosium, and erbium



forming monoclinic prisms, reaching a length of 35 cm., of a greyish-green colour and somewhat resembling epidote in appearance. Useful as a source of scandia. It occurs in some quantity in pegmatite at Iveland and Evje in Sæterdalen, Norway, and is remarkable in being the only mineral containing scandium (analysis I.) as an essential constituent (J. Schetelig, Centr. Min. 1911, 721; Norsk Geol. Tidsskr., 1922, 6, 233; Vid.-Selsk. Skrifter, Kristiania, 1922, No. 1, 49). In the last paper is given a history of the element scandium).

A very similar mineral, as prismatic crystals 10 cm. long and 3 cm. across, was discovered in 1920, also in pegmatite, at Befanamo, Madagascar; this gave analysis II. (Boulanger and Urbain, Compt. rend. 1922, 174, 1442) with traces of Cl , Mn , Sn , Sb , and Pb . The figure for scandia includes about 0.5 p.c. of yttrium, neoytterbium, and lutecium. The mineral is only slightly attacked by hydrofluoric acid, or by fused bisulphates, but is decomposed by repeated fusion with sodium carbonate.

The Madagascar mineral being rather richer in scandia and with zirconia in place of yttrium-earths, it is regarded by A. Lacroix (Minéralogie de Madagascar, 1923, 3, 311) as representing an end-member of the thortveitite group, and for it the name *befanamite* is proposed.

	(Y, Di, Er) ₂								
	SiO_2	Sc_2O_3	O_2	ZrO_2	Al_2O_3	Fe_2O_3	FeO	Ign.	
I.	42.9	37.6	17.7	—	—	2.1	0.8	0.4	
II.	44.1	42.4	—	8.4	3.3	2.0	—	—	

L. J. S.

THROMBOPLASTIN. An extract from the brain of cattle, dissolved in common salt solution. Used as an hemostatic.

THSING-HOA-LIAO. A Chinese name for a cobaltiferous aluminium silicate used in the manufacture of porcelain; also applied to a cobaltiferous manganese ore used for producing a blue colour on porcelain.

THUJONE v. KETONES.

Probable presence of thujone in the essential oil of *artemisia herba alba*. This oil, $d_{40}^{20} 0.9257$, $n_D^{20} +3.88$, $n_D^{20} 1.4553$, contains 1.4 p.c. of free, and 7.39 p.c. of combined alcohols, calculated as $C_{15}H_{26}O$. The presence of camphor has been demonstrated, and that of thujone is probable (cf. Grimal, Chem. Soc. Abstr., 1904, ii. 605; E. Alinari, Annali Chim. Appl. 1924, 14, 109; Chem. Soc. Abstr. 1924, 126, i. 754).

THULITE v. ZOISITE.

THULIUM. Sym. Tm. At.wt. 169.4 (James and Stewart, J. Amer. Chem. Soc. 1920, 42, 2022). The erbium sub-group of the yttrium metals contains the three elements, erbium, dysprosium, and thulium; the compounds of the last of which have been hitherto studied only by few workers owing to difficulties of isolation.

Occurrence.—Thulium is a very rare element, the best sources being euxenite, sipylite (a columbite from Northern Norway), ytterspar (Norwegian xenotime) and samarskite. It occurs in small quantities in the yttrium earths from other rare minerals.

Separation. Cleve first indicated the existence of the rare earth, *thulia* (Compt. rend. 1879, 89, 478, 521, 708; Thalén, *ibid.* 1880, 91, 376), and Lecoq de Boisbaudran, by decomposing fractionally the nitrates of the yttrium group, discovered thulium fractions between those of erbium and ytterbium (Compt. rend. 1879, 89, 516). A separation of erbium and thulium has been effected by fractional crystallisation of the ethyl-sulphates (Urbain, Ann. Chim. 1900, [vii.] 19, 184).

According to Auer von Welsbach, spectroscopic examination indicates that thulium consists essentially of three elements. Of these three thulium I. and thulium III. cannot be isolated by the present methods of purification. The salts of the former absorb rays in the extreme red down to $\lambda 700$, and show characteristic lines between 2700 and 3270 (spark spectrum). Thulium III. exhibits a characteristic spark spectrum between 2800 and 3260. Thulium II. forms an almost white sesquioxide. Its salts are pale yellowish-green in daylight and emerald-green in artificial light, and exhibit the absorption spectrum hitherto ascribed to thulium. The oxides of those fractions which are richest in thulium II. and neo-ytterbium exhibit a characteristic phenomenon in the flame; before becoming actually incandescent the oxides give out a purple light for a short time. The spark spectrum shows many strong lines between 3400 and 3800 (Monahan, 1911, 32, 373). According to Eder (Sitzungsber. K. Akad. Wiss. Vienna, IIa, 124) thulium I. contains a new element, *danebium*; thulium II. has substantially the same spectrum as the original complex material, and *neo-thulium* is suggested as the name for the chief element present; thulium III. gave an arc spectrum containing a set of lines which are attributed to a new element, "*dubium*" (cf. Paulson, Physikal. Zeitsch. 1915, 16, 352).

The minerals containing thulium are decomposed by hydrochloric or sulphuric acid; the rare earth oxalates precipitated, ignited, and the resulting oxides converted successively into

oxalates and sulphates. The latter salts are heated with barium bromate in aqueous solution from which the rare earth bromates are fractionally crystallised. After 15,000 operations the absorption spectrum underwent no change.

Thulium bromate $Tm(BrO_3)_3 \cdot 9H_2O$, hexagonal prism, which has been obtained in considerable amount by repeated crystallisation of the more soluble portions of the rare earth bromates, is more soluble than erbium bromate, but less soluble than ytterbium bromate. Fractional crystallisation of the bromates of the yttrium earths gives a fairly rapid separation of thulium from its associates (C. James, Chem. News, 1908, 97, 61; 1911, 104, 73; J. Amer. Chem. Soc. 1910, 32, 517; 1911, 33, 1332).

Thulium salts are pale bluish-green, but their colour is readily masked by small quantities of erbium, the hue changing to yellowish-green, yellow, white, and finally pink as the amount of this impurity increases.

Thulium oxide (*thulia*), Tm_2O_3 , a dense white powder with a greenish tinge, is prepared by igniting the oxalate; it is the least basic of the oxides of the erbium sub-group and dissolves slowly in strong acids. It exhibits a reddish incandescence on heating.

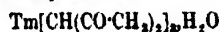
Thulium hydroxide is a white precipitate filtering readily even in the cold.

Thulium chloride $TmCl_3 \cdot 7H_2O$, deliquescent crystals very soluble in alcohol or water.

Thulium sulphate $Tm_2(SO_4)_3 \cdot 8H_2O$ is precipitated by alcohol from an aqueous solution of thulium chloride and sulphuric acid.

Thulium nitrate $Tm(NO_3)_3 \cdot 4H_2O$, deliquescent crystals obtained from solution in strong nitric acid.

Thulium oxalate $Tm_2(C_2O_4)_3 \cdot 6H_2O$, a greenish-white precipitate, soluble in aqueous alkali oxalates to form double oxalates.

Thulium acetylacetonate

crystallises from an alcoholic solution of thulium hydroxide in acetylacetonate; the absorption spectrum of this compound differs appreciably from that of the inorganic salts, nitrates, chlorides, &c. Other organic salts of thulium have been described by James and his co-workers.

Absorption spectrum, v. Cleve, *l.c.*, and Forsling, Bit. Sv. Vet. Akad. Handl. 1899, 24, 1, No. 7). G. T. M.

THUNDERITE. An explosive consisting of a mixture of ammonium nitrate, trinitrotoluene, and flour.

THURINGITE. A member of the chlorite group of minerals of some importance as an ore of iron. The best crystallised members of this group and those containing the least iron have the composition $H_2Mg_2Al_2Si_2O_{11}$, as in clinocllore and penninite. The magnesium is, however, isomorphously replaceable by ferrous iron and the aluminium by ferric iron; when this replacement is complete the formula would be $H_2Fe''Fe'''Si_2O_{11}$ with Fe 50.7 p.c. Depending on differences in composition and in physical characters, a large number of species and varieties have been distinguished by special names. Those forming distinct crystals or plates are grouped as *orthochlorites*, whilst those forming compact masses composed of minute scales or fibres are

called *leptochlorites*. Like the micas, the chlorites crystallising in the monoclinic system often with pseudo-rhombohedral forms; and they have a perfect micaceous cleavage parallel to the basal plane. The characteristic colour is dark green to blackish-green, hence the name, from $\chi\lambda\omega\pi\iota\varsigma$, a green stone. They are quite soft (H. 2-3) and often greasy to the touch; sp.gr. 2.6-3.5, depending on the amount of iron; decomposed by hydrochloric acid with separation of silica. They are of abundant occurrence as alteration products of silicate minerals of almost all kinds; and are found in igneous rocks, metamorphic rocks (e.g. chlorite-schist), and as beds in sedimentary rocks. In the last case they frequently present an oolitic structure (compare glauconite and greenalite). The following are the leptochlorites, all closely allied to thuringite, that have been worked as ores of iron.

Thuringite $H_2Fe''(Al,Fe'')_2Si_2O_4$ is compact with a fine scaly or granular structure and an olive-green to blackish-green colour; sp.gr. 3.15-3.19. It occurs as beds in clay-slates of Lower Silurian age near Schmiedefeld in eastern Thuringia (anal. I). The main ore-bed is 15-20 metres in thickness, and the ore, consisting of thuringite with chalybite and oolitic chamosite, yields 32-40 p.c. of metallic iron. Thuringite occurs abundantly amongst the iron ores of the diabase and schalstein zone between Sternberg in Moravia (anal. Ia) and Bennisch in Silesia. It is also met with in the Lake Superior iron mining district, and in the French Creek mines in Pennsylvania.

Chamosite or *Chamoisite* (anal. II) is compact or oolitic with a greenish-grey or greenish-blue colour; sp.gr. 3-3.4; Fe 28-37 p.c. It forms thick beds in strata of Jurassic age at Chamoson in Canton Valais, and also at the Windgällen in Canton Uri in Switzerland. A chamosite ore is also extensively mined in Silurian rocks at Nučič in Bohemia. Identical with chamosite is the so-called *berthierine* (anal. III, by P. Berthier, 1827), which occurs with chalybite in Jurassic strata at Hayanges in Dept. Meurthe-et-Moselle and in Lorraine, and which by its alteration gives rise to the important *minette* (q.v.) ores of this district. Another similar oolitic ore is the *bavilite* in the Lower Silurian rocks of Brittany and Normandy.

	I.	Ia. ¹	II.	III.	IV. ²	V. ³
SiO ₂	22.35	24.50	25.23	12.4	33.30	17.34
Al ₂ O ₃	18.39	18.45	19.97	7.8	4.37	—
Fe ₂ O ₃	14.86	11.23	—	—	44.33	43.05
FeO	34.34	31.20	37.51	74.7	—	30.27
MgO	1.25	2.86	4.39	—	1.73	—
H ₂ O	9.81	9.93	12.90	5.1	14.10	9.18

101.00 99.59 100.00 100.0 99.76 100.0

¹ Also MnO, 0.07; CaO, 0.93; P₂O₅, 0.44.

² Also MnO, 0.34; CaO, 1.22; P₂O₅, 0.37.

³ Also MnO, 0.16.

Stilpnomelane $H_2(Fe,Mg)_2(Fe,Al)_2Si_2O_4$ is present in the ores of the diabase and schalstein zone between Sternberg in Moravia and Bennisch in Silesia. From this district several other closely allied minerals have been described by F. Kretschmer (1905, 1906, 1918), including *moravite* $H_2(Fe,Mg)_2(Al,Fe)_2Si_2O_4$, and *stilpnochlorane* $H_2(Ca,Mg)(Al,Fe)_2Si_2O_4$ (anal. IV). The latter forms shining yellow scales and results from the alteration of thuringite; it is found in the iron mines at Gebitzgau near

Sternberg. *Viridite* $H_2Fe''Si_2O_{11}$, and *mackensite* $H_2Fe''Si_2O_{11}$, he regards as end-members of the thuringite series.

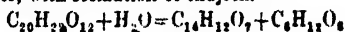
Cronstedtite $H_2Fe''Fe''Si_2O_{10}$ (anal. V) is found in some quantity in mineral veins at Kuttenberg and Frzibram in Bohemia, and in Cornwall. L. J. S.

THUS AMERICANUM v. RESINS.

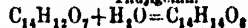
THUYA OCCIDENTALIS. *Thuya occidentalis* (Linn.).—In 1858 Rochleder and Kawaler (Wien. akad. Ber. 29, 10) isolated from the green portions of the *Thuya* (*Thuja*) *occidentalis* a glucoside *Thujin*, which, when hydrolysed, gave a yellow colouring matter *thujetin*.

Thujin $C_{20}H_{32}O_{12}$. The plant is extracted with alcohol, the extract when cold filtered from wax, and evaporated to a small bulk. The residue is diluted with water, a few drops of lead acetate solution added, the precipitated impurities removed, and the clear brown filtrate treated with lead acetate. The yellow lead compound is collected, extracted with dilute acetic acid, and basic lead acetate now added to the solution. The bright yellow precipitate is suspended in water, decomposed with sulphuretted hydrogen, the lead sulphide removed, the filtrate treated with carbon dioxide in order to free it from sulphuretted hydrogen and evaporated *in vacuo* over sulphuric acid. Crystals gradually separate, and these are crystallised repeatedly from dilute alcohol until when treated with ammonia a green coloration is no longer produced.

Thujin is described by these authors as citron yellow microscopic prisms sparingly soluble in cold water. The alcoholic solution becomes yellow on treatment with alkalis, whereas with ferric chloride a dark green coloration is produced. When *thujin* is digested in alcoholic solution with dilute hydrochloric or sulphuric acid it is hydrolysed with formation of glucose and *thujenin*, apparently an intermediate product, which readily takes up a molecule of water, with formation of *thujetin*—



Thujigenin.



Thujetin.

Thujetin $C_{14}H_{24}O_9$ forms yellow crystals, and is characterised by the fact that its alcoholic solution is coloured blue-green with ammonia, and green coloured by potassium hydroxide solution.

With lead acetate it gives a deep red precipitate. When *thujetin* is digested with boiling baryta water it is converted into *thujetic acid* $C_{14}H_{22}O_{10}$, which consists of yellow microscopic needles, sparingly soluble in water, readily soluble in alcohol.

Thujigenin $C_{14}H_{22}O_8$ crystallises in fine yellow needles, soluble in alcoholic ammonia, with a blue-green coloration.

The quantity of *thujin* which is present in the plant is very small; thus, from 240 lbs. Rochleder and Kawaler were successful in isolating a few grams only.

Perkin (Chem. Soc. Trans. 1914, 105, 1408), who re-examined this subject and employed methods almost identical with those of Rochleder and Kawaler, found that the glucoside corresponding to *thujin* possessed the formula $C_{21}H_{32}O_{11}$, melted at 183°-185°, and when

hydrolysed gave rhamnose and quercetin and was identical with the *quercitrin* of quercitron bark. The plant also contained a small amount of quercetin, and this also, prepared by the hydrolysis of the glucoside which, evidently corresponds to the thujetin of Rochleder and Kawaler, dissolved, in alkaline solutions with a pale green tint, but failed to give the blue-green coloration with ammonia described by these authors. During a preliminary investigation of this plant (Chem. Soc. Trans. 1899, 75, 829), the sample then examined gave a trace of yellow colouring matter soluble in alkalis with a strong green coloration, the acetyl compound of which after frequent recrystallisation melted at 205°-206°. It thus seems probable that the thujin of Rochleder and Kawaler consisted of quercitrin contaminated with a second glucoside, possibly that of myricetin. The quantity of this latter present in the plant may possibly vary according to its environment or with the season of the year.

THYMACEOL. Condensation product of acetone and *o*-thymic acid.

THYMATOL. Trade name for thymol carbonate.

THYME CAMPHOR *v.* CAMPHOR.

THYMEGOL. Trade name for the mercury potassium salt of thymol-*p*-sulphonate.

THYME OIL *v.* OILS, ESSENTIAL.

THYMIN *v.* PYRIMIDINES.

THYMOL *v.* CAMPHORS; also PHENOL AND ITS HOMOLOGUES.

According to Howards & Sons, Ltd., and John William Blagden (Eng. Pat. 200151) *m*-cresol is condensed with isopropyl alcohol in the presence of phosphoric acid at a temperature of 70°-90°. If the reaction temperature is higher (e.g. 150°), a condensation product melting at 114° and possessing antiseptic properties is obtained (J. Chem. Soc. 1923, 123, 124, i. 1006).

p-Cymene isolated from the crude oil obtained from the sulphite spruce pulp mill, after purification, is nitrated and the nitro-cymene reduced to cymidine by means of iron powder and hydrochloric acid. Sulphonation of cymidine gives a mixture of *o*- and *p*-cymidine sulphonic acids, which, by diazotisation and subsequent treatment with ethyl alcohol and copper powder, are successively converted into the corresponding diazocymenesulphonic acids and the same cymene 3-sulphonic acid, the sodium salt of which yields thymol on fusion with sodium hydroxide (Max Phillips and H. D. Gibbs, J. Ind. Eng. Chem. 1920, 12, 733-734; see also J. Amer. Chem. Soc. 1923, 45, 1489-1493).

Thymol in oil of thyme may be determined by extracting the phenols by repeated shaking with sodium hydroxide solution. On adding strong hydrochloric acid to an aliquot part of the extract the phenols separate. The thymol is obtained by crystallisation and weighed after collection and drying (Mastbaum. Anal. Fia. Qaim. 1922, 20, 501; J. Soc. Chem. Ind. 1923, 244 A).

THYMOLEN. Trade name for a mixture of naphthalene, camphor, and thymol.

THYMOLOFORM *v.* SYMMETRIC DRAUG.

THYMUS CAPITATUS OIL. The flowers and leaves of *Thymus capitatus*, grown in Sicily, yield on distillation about 1.5 p.c. of an oil,

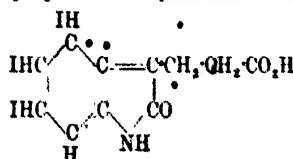
d_{15}^{20} 0.9582, n_D^{20} = 1.5106, n_D^{22} = -0.70°, which contains 73-84 p.c. by volume of phenols (carvacrol) and shows a corresponding high solubility in dilute alcohol. These results agree moderately well with those given by Pellini (Z. 1923, 858 A), and show that the figures given by Schimmel und Co. (Bericht, 1889, ii. 36) refer to an oil other than that of *Thymus capitatus* (F. C. Palazzo and C. Lutri, Annali Chim. Appl. 1924, 14, 103; J. Soc. Chem. Ind. 1924, 43 B. 537).

THYRESOL. Syn. for santalol methyl ether.

THYROGLOBULIN, THYROIDIN, THYROXIN *v.* THYROID GLAND.

THYROID GLAND. *Glande thyroïde*, Fr.; *Schilddrüse*, Ger. In 1891 Murray introduced the oral administration of thyroid gland in diseases where the natural secretion is defective (myxoedema, cretinism), and the subsequent success of the remedy has been one of the greatest triumphs of organotherapy. Baumann (Zeitschr. physiol. Chem. 1895, 21, 381) discovered the iodine content of the gland and obtained, by boiling with dilute sulphuric acid, an impure amorphous substance, iodothyron (thyroidin), containing 9-10 p.c. of iodine, and Oswald (*ibid.* 1899, 27, 15) separated a protein (thyroglobulin), also containing iodine.

The active constituent has been isolated by E. C. Kendall (J. Biol. Chem. 1915, 20, 501; Proc. Amer. Soc. Biol. Chem., J. Biol. Chem. 1917, 29, 29; Endocrinology, 1917, 1, 153; 1918, 2, 81; Proc. Amer. Physiol. Soc., Am. J. Physiol. 1918, 45, 540; J. Amer. Med. Assoc. 1918, 71, 871). It is obtained by hydrolysis of the gland with alcoholic sodium hydroxide and fractional solution in various organic solvents. It represents that half of the iodine containing substances of the gland which is insoluble in acids; the other half, soluble in acid, is also organic, but physiologically inert. Kendall has named the hormone thyroxin (from thyroxindol) and assigned to it the formula $C_{11}H_{15}O_2NI_2$ and the subjoined constitution:



Thyroxin forms crystals, m.p. 220°, sparingly soluble in alcohol, ether, water, acids and sodium carbonate, readily soluble in dilute sodium and ammonium hydroxides, with opening of the lactam ring. It is perhaps closely related to the important amino acid tryptophan and is extraordinarily active. On cretinism and myxoedema it has the full action of the entire gland, in daily doses of a fraction of a milligram. A dose of 10 mg. per day increases the basal metabolism of an adult by 30 p.c., and the total quantity present in the human body is estimated at 23 to 50 mg. The iodine content of the thyroid has generally been regarded as some measure of its activity. Hunt (Amer. J. Physiol. 1923, 23, 257) has recently found a close parallelism between iodine content and activity as tested by his acetonitrile method (see below), but on the other hand, Romeis (Arch. f. Entwicklungsmech. d. Organ. 1923, 50, 410)

prepared from thyroid a crystalline iodine-free substance, which accelerates the development of tadpoles. The estimation may be carried out by Baumann's process (fusion with sodium hydroxide and colorimetric comparison in chloroform solution; cf. Riggs, J. Amer. Chem. Soc. 1909, 31, 710; 1910, 32, 692; Seidell, *ibid.* 1909, 31, 1326). Hunter's method (J. Biol. Chem. 1910, 7, 321; Seidell, *ibid.* 1911, 10, 95) appears to be preferable and has been adopted by the United States Pharmacopoeia. One gram of the dried gland (corresponding to about 5 grms. of the fresh organ) is mixed in a nickel crucible of 125 c.c. capacity with 15 grms. of a mixture of anhydrous sodium and potassium carbonates and potassium nitrate in the molecular proportion of 1 : 1 : 2 respectively. Five grms. of the salt mixture is spread on top; the mass is fused, dissolved in 150 c.c. water in a half-litre conical flask and mixed with 50 c.c. of sodium hypochlorite solution containing 2.4 p.c. Cl by weight. Syrupy phosphoric acid, diluted with an equal volume of water, is added until the yellow colour of free chlorine appears. Then 10 c.c. of the phosphoric acid solution is added in excess, the solution is diluted with an equal volume of water and boiled down to 150 c.c. or for half an hour, to expel the excess of free chlorine. After cooling 10 c.c. of 1 p.c. potassium iodide solution is added, and the liberated iodine (corresponding to 6 times that originally present, which was converted into iodic acid) is titrated with N/200 thiosulphate, of which 1 c.c. = 0.01058 mg. iodine present in the gland. *Thyroideum siccum*, U.S. P., should contain 0.17-0.23 p.c. iodine. (= about 0.034-0.046 p.c. in the fresh gland) and should contain not more than 6 p.c. of moisture. It is also official in the B. P. Seidell and Fenger (J. Biol. Chem. 1913, 13, 517) state that the glands of the sheep, ox, and pig contain from June to November about three times as much iodine as in the rest of the year. Aldrich (Amer. J. Physiol. 1912, 31, 152) finds the ratio for these three animals as 5 : 7 : 9 respectively. The amounts found by Seidell and Fenger were for sheep, ox, and pig respectively 0.08-0.24, 0.03-0.33, and 0.16-0.44 p.c. of dry weight. They remark that a standard of 0.2 p.c. could only be obtained with sheep's thyroids in the United States during a small part of the year. In English sheep the amount apparently does not fall so much in winter.

The physiological estimation of the hormone is more satisfactory but complicated. Quantitative experiments on the rate of metabolism are best, but very laborious. In a simplified form they may be carried out on tadpoles, which, in a solution containing very little of the hormone, have their normal growth retarded and their metamorphosis (loss of tail and development of hind limbs) greatly accelerated (Gudernatsch, Arch. f. Entwicklungsmech. d. Organ. 1912-13, 35, 457; cf. e.g. Rogoff and Marije, J. Pharm. exp. Therap. 1916, 9, 57).

This method has been proposed for the commercial standardisation of thyroid preparations. Reid Hunt (J. Amer. Med. Assoc. 1907 [ii.] 240; J. Biol. Chem. 1905, 1, 33) finds that as little as 0.1 mg. of the gland may double the resistance of mice to poisoning by acetonitrile. On account of its effect on metabolism thyroid may be useful in reducing the weight of the constitu-

tionally corpulent, who are incapable of sufficiently oxidising fat. G. B.

THYROXIN. See THYROID GLAND.

TIEMANNITE. Mercury selenide, HgSe, crystallised in the cubic system with tetrahedral hemihedrism, and isomorphous with metacinnabarite (HgS). Compact granular material is more usual than crystals. Greyish-black colour with metallic lustre; sp.gr. 8.19-8.47; H. 2½. It occurs in some quantity with barytes, calcite, and manganese oxide in a vein in limestone near Marysvale in Utah; and large masses have been found in the mercury districts in Lake, Orange, and Santa Clara counties, in California. Other localities are near Clausthal in the Harz, and the Sierra de Umango in Argentina.

L. J. S.

TIERS ARGENT v. ALUMINIUM.

TIGER-EYE v. CROCIDOLITE AND QUARTZ.

TIGLIC ACID v. OILS, FIXED, AND FATS.

TIGLIC ALDEHYDE, TIGLIC ANHYDRIDE

v. *Guaiacum*, art. RESINS.

TIKITIKI. A preparation of rice-polishing extract used in the treatment of beriberi. It contains a high percentage of antineuritic vitamin, and is a cure for infantile beriberi. For a method of preparing it, see A. H. Wells, Philippine J. Sci. 1921, 19, 67 (in abstract J. Soc. Chem. Ind. 1922, 41, 77 A).

TIL or TEEL OIL v. SESAME OIL.

TILE ORE v. CUPRITE.

TILIACORA ACUMINATA (Miers). The dried powdered bark by exhaustive treatment with alcohol yields quercitol, fumaric acid, an alkaloid, *tiliacorum* C₂₂H₃₃NO₆, m.p. 260°-261° (decomp.), $\alpha_D^{20} = +105.3^\circ$, a phytosterol, a solid fatty acid, m.p. 47°, a mixture of unsaturated acids containing oleic and linolenic acids, with some linolic acid, a resin, and dextrose. Tiliacorum contains two methoxyl groups, but no methyl imide, or methylene oxide group; no acetyl or methyl derivative could be obtained. A solution of the alkaloid in sulphuric acid becomes first blue, and then green on treatment with oxidising agents (Van Itallie and Steinhauer Pharm. Weekblad. 1922, 59, 1381; J. Soc. Chem. Ind. 1923, 159 A).

TIMA. A medicinal preparation imported from Tampico as a remedy for phthisis. Is prepared as a syrup by boiling the fruit of *Parmentaria edulis* (DC.) with sugar, and mixing the product with almond oil (Arch. Pharm. [iii.] 107, 375).

TIMBER AND DRY ROT. E. H. Ellis (Chem. News, 1923, 127, 402) describes the fungus *Merulius lacrymans*, to which this disease is due, its method of growth and action upon timber, and the means adopted for its extermination. This fungus is rarely, if ever, found upon living trees, but is common upon worked timber, the term 'dry rot' referring to the condition of the wood upon which it grows and not to the infecting organism. Infection of the wood often occurs in the timber yard, but is rarely caused by the spores, which, although remaining alive for several years, appear to develop upon sound timber with difficulty. During dry weather the protoplasm of the fungal spores (mycelium) breaks up into small bodies (sclerites), which are easily scattered and readily germinate, thus leading to re-infection. Development of the fungus proceeds by the growth of a fine

network (*mycelium*) within the wood, followed by the well-known growth upon the surface, the form of which depends upon conditions such as moisture, temperature, &c. Various enzymes are produced by the *mycelium*, which cause the breakdown of certain constituents of the wood to water and carbon dioxide, whilst the lignin, tannin, and calcium oxalate remain as a spongy skeleton of the original timber.

Under favourable conditions the fungus is capable of penetrating mortar, thus spreading infection to distant wood. Various human diseases have been attributed to the growth of this fungus, but the impossibility of this is shown by the fact that 'dry rot' is killed at blood heat (98°F.). Infection of timber may be prevented by avoiding contact with infected material, the selection of well-seasoned timber, and storage of the wood both before and after use in dry and well-ventilated situations. In dealing with existing infection, timber may be impregnated with various antiseptics, among which the best are sodium fluoride, boric acid, magnesium silico-fluoride, cresote and tar, but the process is costly. Treatment with potassium or sodium dinitrophenates or dinitro-cresylates is effective, and kiln-drying of the wood is also recommended. In cases of serious infection all damaged timber should be removed, the exposed surfaces treated with formalin, followed by coating with an antiseptic, and precautions should be taken to avoid future access of damp (J. 1923, 29, 344; J. Inst. Brewing Abstr. 1924, 30, 123).

TIMBER FIRE-PROOFING. In the fire-proofing of wood the methods of impregnation are closely similar to those used in applying wood preservatives (see Chem. Trade Journal and Chem. Engineer, Oct. 5th, 1923, 39). The pressures applied will depend on the structure of the wood, as an excessive pressure will tend to crush the cells. Too high a temperature during drying may lead to brittleness. In order to assist penetration, an initial vacuum may be applied, followed by injection under about 170 lb. pressure. In the application of water-glass and its subsequent precipitation with hydrochloric acid, salt is left in the wood. To obviate this, it has been proposed to utilise pure silicic acid, prepared and impregnated by electro-osmotic methods (Eng. Pat. 101205 of 1917). Many fibres, such as kapok, have cuticles which are penetrated with difficulty by soluble salts. To facilitate penetration in such cases the material may be treated with alcohol or other volatile solvent or with a dilute solution of hydrofluoric acid (2 parts of the commercial acid in 100 parts of water). Coating with metal by electro-deposition is suggested as a method of fire-proofing aircraft linen without loss of tensile strength (Eng. Pat. 149745 of 1919).

For most practical purposes, the direct method of testing the efficacy of a fire-proofing treatment—that is, by applying a flame—should be sufficient. In certain cases, notably for aircraft fire-proofing, some method of testing the comparative protective action is necessary. Very little information is available, however, with regard to the inflammability of fire-proofed fabrics, although some results of comparative tests with unproofed materials have been made public (Aeronautical Advisory Committee

Report, No. 573 of 1918; Pharm. J. 1924, 112, 692).

Magnesium ammonium phosphate, which decomposes on heating into magnesium pyrophosphate and ammonia, has been patented by the Du Pont Company of America for reducing the inflammability of cellulose-ester and gil-varnish films. In the latter case the boiled linseed oil is incorporated with about one-third its weight of the phosphate (U.S. Pat. 1316881 of 1919).

For fire-proofing and preserving wood, the material may be impregnated with a solution of the double ammonium magnesium sulphate or with cuprammonium sulphate. In order to lower the melting-point of the magnesium sulphate, sodium or potassium sulphates may be added, preferably in quantity to form the eutectic mixture—that is, the mixture with the lowest melting-point (D. R. P. 306600 of 1914). Calcium sulphate or barium carbonate may be deposited in the body of the wood, the former by impregnation with ferrous sulphate followed by treatment with calcium chloride, the latter by treatment with a solution of barium sulphide and subsequent injection of gaseous carbon dioxide (U.S. Pat. 1346287 of 1920; Pharm. J. 1924, 112, 691).

TIMBO. The name of a narcotic medicine, the root rind of a variety of *Conchocarpus*. The rind appears in the form of tubes or rolls, is bright reddish-brown on the outside and yellowish on the inside. The outer and middle rind break off short, but the inner rind has a long fibrous fracture and the interior colour is whitish. It possesses a weak aromatic taste somewhat like cascarilla bark, but has no special odour. A cross-section shows an interrupted yellow zone near the outer side, whilst the inner rind is faintly streaked in radiating lines. Some of the cells contain crystals of calcium oxalate (Chem. Zeit. 11, 315; J. Soc. Chem. Ind. 6, 560).

TIN. Sym. Sn. At.wt. 118.71. Atomic number 50. According to Aston, ordinary tin is a mixture of isotopes—eight in number, and of atomic masses 120, 118, 116, 124, 119, 117, 122, 121. The average atomic weight, in proportion to the intensities of the lines of the positive rays, agrees well with the accepted value (Nature, 1922, 109, 813). The molecular weight of tin at different temperatures has been studied by Jouniaux (Bull. Soc. chim. 1925, [iv] 37, 67; Chem. Soc. Abstr. 1925, ii, 489). Tin was known and prized in the earliest historic ages, for it is mentioned without comment as one of the common metals in the days of Moses (Numbers xxxi. 22), and was an important commodity in the fair at Tyre; numerous bronze instruments of very early date have also been discovered in Assyria, and, particularly by Layard, in the ruins of Nineveh. Many of these bronzes are now preserved in the British Museum. The tin so employed was obtained by the Phœnicians from Cornwall and the Scilly Isles in this country, and from the mountains of Spain, and there is no evidence of the occurrence of tin in those countries in which, in ancient times, the metal was most largely used. Pliny appears to have been familiar with tin, and states that it occurs in grains, in alluvial soil, from which it is obtained by washing. These grains, the further

states, are black, and their metallic character can only be recognised by their great weight. Though tin was regarded by the ancients as one of the baser metals, its cost was greater in the days of Homer and Pliny than at present, for in the days of the latter of these writers an avoirdupois pound of tin cost 8s. 7½d. sterling, or about four times its present value. The uses of tin among the Romans were similar in many respects to those of the present day. It was chiefly employed in the form of an alloy with copper, on account of the hardness imparted to the alloy by a comparatively small proportion of tin, and some of the very earliest known bronzes agree closely in composition with those used for similar purposes at the present day. Tin was also used with lead by the Romans for the production of solder, and for tinning the inside of copper and brass vessels, in which art the Roman workmen appear to have attained considerable skill. Alloys containing more tin, corresponding somewhat to the modern *speculum metal*, were used by the ancients for mirrors, but the art of tinning iron does not appear to have been discovered until a much later date.

Occurrence of tin.—Tin occurs in comparatively few localities, never in the native state, and in but few forms of chemical combination. The most important one is *tinstone* or *cassiterite*, tin dioxide (SnO_2), which is met with in two principal forms, crystallised and massive. The crystals are of the regular prismatic or tetragonal system, isomorphous with those of rutile, and are frequently well formed and of large size. Tinstone in the usual or massive form is a dark reddish-brown or slaty-coloured very heavy mineral, which occurs in Cornwall in veins usually running nearly east and west, and in which the tin ore is associated with arsenical pyrites, copper sulphide, wolfram, and a great variety of other minerals. Tin usually occurs in plutonic or metamorphic rocks, such as granite, felspar, porphyry, or clay slate, but by the action of denudation on these older rocks grains of tinstone are frequently met with in the neighbouring alluvial deposits, and this variety of ore, which is of special purity and now almost entirely exhausted in this country, is known as 'stream tin.' The metal also occurs in small quantities as *tin pyrites* (SnS_2). The largest quantities of tin are now produced in the island of Banca ('Straits tin'). Smaller though considerable quantities are met with in Britain, Germany, Siberia, China, South Australia, New South Wales, Nigeria, and Bolivia. Among the newer sources of tin may be mentioned the Waterberg district, to the north of Pretoria, in the Transvaal, the present monthly output of which is valued at about £30,000, and is likely to increase. Cassiterite has been met with over an area comprising Helderberg, between Stellenbosch and Somerset West, and the Kuite River Mills in the Koeberg District of South Africa. The Malay States are the chief producer, contributing over 36 p.c. of the world's output; then follow Bolivia and the Dutch East Indies, with about 20 and 15 p.c. respectively. At present the production and consumption of tin appear to balance. Normally the United Kingdom imports about 35,000 tons of tin ore, about 8000 tons being from British possessions, and 40,000 tons of metal, which, with the excep-

tion of 2000–3000 tons, is derived from British possessions. The re-exports in a normal year are about 3000 tons of ore, and 40,000 tons of unwrought tin. The balance, about 32,000 tons of tin ore, together with the domestic production, which in 1913 was 8355 tons, was apparently sufficient to meet the domestic requirements of the United Kingdom. Few new sources of tin have been discovered in recent years, although it appears probable that the Belgian Congo is likely to become an important producer in the not far distant future. It would seem that unless really extensive deposits are discovered, tin will be one of the first base metals to be exhausted. The smelting of tin ore is concentrated in few hands, although the tin-smelting capacity of the world is well in excess of the annual supplies of ore. In this respect the Straits Settlements heads the list with a capacity of about 53,000 tons of metal, Great Britain following with a capacity of about 34,000 tons, and the United States with a capacity of 30,000 tons, the total world smelting capacity being about 175,000 tons per annum (Sir R. Redmayne, *J. Soc. of Arts*, 1923; *J. Soc. Chem. Ind.* April 27, 1923, 425). Promising reports are received in connection with tin mining in Texas. In parts of Nigeria tin occurs distributed over wide areas, but in relatively small proportions. The present world's output of tin is about 115,000 tons per annum.

Production of tin.—The metallurgy of tin is in its main features simple, but the mechanical preparation of the ore involves more skill and labour than is the case with any of the other common metals. So much, in fact, is this true that success in the extraction of tin frequently depends more upon the captain of the mine, who superintends the dressing of the ores, than upon the smelter. On account of the high price of tin, and the relatively high density of tinstone, it is found practicable to work ores which in the first place contain comparatively little tin, ores which contain only 0.5 p.c. of tinstone being sometimes profitably worked. The principle adopted in the mechanical separation of tinstone is very simply illustrated in the operation of 'vanning,' which is frequently used in Cornwall and elsewhere as an approximate test of the richness of an ore. A quantity of the crushed material is placed in a miner's shovel of special shape, known as a vanning shovel, water is added, and then by means of a circular motion which is imparted to the shovel by the hands, aided by a peculiar jerk of the wrist, the ore is ultimately almost completely separated from the earthy matter, and can be dried and weighed. On the large scale the ore is first picked and assorted, and then broken by suitable stone breakers and rolls. The roughly-powdered ore is carefully assorted, and then fed into a mill containing a battery of stamps, of which there are many varieties in use. Each stamp weighs 3 cwt. or upwards, the face of the stamp being either steel or chilled cast iron. By means of suitable cams on a revolving wheel the stamp is raised at regular intervals, and allowed to fall upon the ore which is contained in the box or coffer of the stamp. A supply of water flows through the boxes and escapes through perforations, carrying away the finely-crushed ore, while the larger pieces remain in the box to be further crushed by the stamp.

The finely powdered ore now passes to some form of buddle, or to a concentrating table, which more or less completely separates the earthy matter. Probably the simplest form of such apparatus, of which there is an endless variety, is the inclined plane with ridges or 'riffles' placed at right angles to its length. On such a plane the heavier particles naturally remain, the richer fragments being deposited principally at the upper part of the buddle, whilst the earthy matter, with some ore, passes away. But such a simple form of buddle is now seldom used, and a considerable number of improvements have been from time to time adopted. Thus the inclined plane is made movable, and either a jerking or a rocking motion is imparted to it, and this is found to give better results than the fixed form. But buddles of a circular shape have met with considerable favour in late years, one form (Borlase's) being a circular concave buddle fed from the outside and discharging the slimes from the middle; but the variety generally preferred in Cornwall is that of a very flat cone, the water and ore being distributed either by a revolving spout, near the apex of the cone, or by means of a smaller and more acute distributing cone. The waste liquid from the buddle is led into a succession of tanks or pools, where it is allowed to settle in order to recover the finer portion of the ore, which would otherwise be lost, and the slimes thus obtained are worked over again in order to recover the finely-divided tin ores.

In dressing tin ores it is important that they should not be too finely crushed, or the gangue will be removed with greater difficulty. The ore should be, as far as possible, separated into parcels, the fragments in each being of uniform size, and the method of treatment is varied with the fineness of the material; in no case should the ore be crushed more than is necessary to separate the matrix. These facts form the basis of all successful ore dressing.

Reduction of tin.—From the point of view of the tin smelter, ores of tin may be divided into two classes, first those of tolerable purity, which may be directly smelted in the furnace, and secondly a less important class of ores, which, from the fact that they contain notable proportions of copper, arsenic, sulphur, or tungsten, require to be further treated, after dressing, before smelting. Ores which contain arsenic or sulphur are roasted at a low temperature, usually in calciners with a bed which is mechanically rotated in a horizontal plane, and which is supplied with mechanical rabbles. The greater part of the arsenic and sulphur is thus removed. The mass is then withdrawn, and, after being exposed for some time to the action of the atmosphere, is washed to remove the oxide of iron and other lighter matters from the heavy oxide of tin. Ores which contain much tungsten are heated with sodium sulphate or carbonate in a reverberatory furnace, by which means soluble sodium tungstate is produced, and can be removed by washing from the unaltered oxide of tin. This process (Oxland's) is not carried on now to any considerable extent. The ore having been purified by one or other of these processes is ready for smelting in the ordinary way. The reduction of the metal from the ore is always accomplished by heating

with carbon, which operation may be performed either in a reverberatory furnace, as is the custom in this country, or in small blast furnaces such as are used to a limited extent in Germany. Shaft furnaces also are used in China, Sumatra, Nigeria, and by natives in many other localities.

Tin smelting in England.—The furnace employed for the smelting of tin in this country, and in fact pretty generally elsewhere, is a reverberatory, with a fireplace at one end and a stack at the other. At the front is a single working door, while at the back is a tapping hole which is closed during the smelting, but which when the operation is concluded serves to convey the metal into a 'float' or circular iron pot lined with clay. The bed of the furnace is about 18 ft. long by 9 ft. broad, and slopes to the tapping hole. The fireplace is about 2 ft. broad, and the firebridge is of firebrick and some 14 ins. high. The roof is low, and slopes uniformly from the firebridge to the stack.

The charge of ore, which weighs 20–25 cwts., is mixed with rather less than one-fifth of its weight of anthracite powder, and spread uniformly over the furnace bottom. If the ore is refractory, a little fluorspar or lime is added as a flux. The door is then closed and luted up, and the temperature gradually raised for 5–6 hours, when the door is opened, the mass rabbled, and a quantity of powdered anthracite or 'culm' is thrown on the surface of the charge. After heating for about another hour, and a further rabbled, the metal is tapped. Part of the slag produced is thick and is raked out of the furnace, while the remainder is more fluid, flowing out with the metal, and is called 'glass' by the smelter. The slag consists essentially of ferrous silicate, and as it frequently contains a considerable amount of tin it is melted again when the furnace is at liberty.

As tin is a valuable metal any considerable loss in smelting would result in commercial failure. The boiling-point of tin is high, in the neighbourhood of 2000°C., so the loss by volatilisation is very small. Practically the chief source of loss, in the smelting process, is in the slags. Tin oxide readily passes into solution in fused silicates yielding enamels. Hence the slag should be as small in quantity as possible, and should not be oxidised. The first requirement is met by employing ores of high concentration, and by mixing them so that the basic gangue of one will neutralise the acid gangue of another, so far as possible. Thus the use of fluxes is kept at a minimum, and the bulk of slag diminished. The slags are collected, and are generally smelted in a water-jacketed blast furnace, for the recovery of the tin they contain.

Small blast furnaces, which were previously used in Cornwall, have survived longer in southern Germany, and are also employed by the natives of India. The waste of metal is much greater than in the reverberatory furnace, whilst the cost of fuel (charcoal) is also greater than in England, but the tin obtained is stated to be of excellent quality.

Refining.—The refining process consists of two parts, a preliminary liquation, and the refining proper. The liquation is conducted in a furnace of similar shape to the reverberatory furnace above described, and about 10 tons are

operated upon at once. The temperature is carefully regulated so as just to melt the purer tin, which gradually flows away into a separate pot or 'kettle,' while the impurities, consisting of iron, arsenic, sulphur, and traces of many other elements, together with some 20 p.c. of tin, remain in the form of a hard, brittle, white, semi-metallic mass known as *hard-head*. For the composition and properties of hard-head, see Levy and Ewen, *Trans. Inst. Min. & Metallurgy*, 1908-9, 466. The purer metal which has collected in the kettle (which is heated by a small separate fire) is now refined by plunging billets of green wood under the surface of the melted tin. A quantity of gas is evolved from the wood, and violently agitates the metal, gradually separating a scum which contains the impurities originally present in the crude tin. The same result is sometimes attained by 'tossing' the melted metal in ladles from a height of several feet and allowing it to fall into the kettle; in this way the metal is also exposed to atmospheric influences, and a scum separates as before. The refined metal is sold as *grain*, *refined*, or *common tin*, according to its quality, though all tin met with in commerce has been more or less refined. For *refined tin* purer ores are employed, the refining is continued longer, and after poling the metal is allowed to stand some time, and only the upper or purer portions are used. The second or ordinary quality, when cast in suitable moulds, is known as *block tin*. A simple test of the commercial quality of tin is to melt the metal at a moderate temperature, and to pour it into an ingot mould. The ingot, if of good quality, should be smooth, bright, and rounded, and should retain this appearance on solidification; if impure it will have more or less sharp edges, and will 'frost' over on solidifying, while very impure metal will be tinged with yellow or purple, according to the amount and nature of the impurities. *Grain tin* is produced by heating blocks of refined tin to a temperature a little below the melting-point of the metal, at which point it becomes very brittle, and is broken either by dropping from a height or by a blow of a hammer. For further particulars of the properties and metallurgy of tin, see H. Louis, *Metallurgy of Tin*, London, 1911.

Electrolytic refining of tin.—After liquida-
tion, to remove iron, crude tin has been successfully refined on the large scale by electrolysis in solutions containing (a) 20 p.c. of hydrofluosilicic acid, 0.1 p.c. of sulphuric acid, and 6 p.c. Sn; (b) 5 p.c. of hydrofluosilicic acid, 8 p.c. of sulphuric acid, and 3 p.c. Sn; (c) 8 p.c. of sulphuric acid, 4 p.c. of cresol- or phenol-sulphonic acid, and 3 p.c. Sn; (d) 13.7 p.c. of sulphuric acid, 21.2 p.c. of crystallised sodium sulphate, and 1.5 p.c. Sn. The electrolysis is preferably carried out at 35° with a current of 10 amp. per sq. ft. at 0.3 volt. With electrolytes (a), (b), (c), which contain the tin as a stannous salt, an emulsion of 1 lb. of glue and 8 lb. of creosylic acid is added per ton of metal deposited, to assist in producing smooth deposits, and 0.3 p.c. of hydrochloric acid is added to bring about uniform corrosion of the anode and to make the slimes soft and porous. Electrolyte (d) contains the tin as stannic sulphate, and 0.2 p.c. of Congo aloes is added to obtain

a smooth deposit. The slimes from Bolivian crude tin containing 97 p.c. Sn usually assay about 20 p.c. Pb, 5 p.c. Cu, 3 p.c. As, 5 p.c. Sb, 20 p.c. Bi, and 30 p.c. Sn, together with 130 ozs. Ag per ton, and traces of Au. Two methods of treating this material have been used: the first involves fusion of the slime with sodium hydroxide under oxidising conditions to obtain a lead-bismuth-silver bullion, which is refined electrolytically, and a soda slag from which crude tin is again obtained by reduction. In the second process the slimes are melted and reduced to metal, which is cast into anodes: these are electrolysed in 18 p.c. hydrochloric acid, which dissolves 90 p.c. of the tin and bismuth, 45 p.c. of the antimony, and 35 p.c. of the copper. The bismuth is precipitated by crude tin and refined by fusion with soda and sulphur, and the tin is precipitated by lime. The slimes are smelted to give a base lead bullion, which is softened and desilverised (J. R. Stack, *Trans. Amer. Electrochem. Soc.* 1924, 45, 279; J. Soc. Chem. Ind. 1924, 43, B. 521).

Brands of tin. In 1911 a committee of the London Metal Exchange drew up a new form of contract for the purchase of tin. This provided for the recognition of two classes of tin: Class A. includes Straits or Australian tin of good merchantable quality, and also refined tin of good merchantable quality, assaying not less than 99.75 p.c. of tin. Class B includes common tin of merchantable quality, and assaying not less than 99 p.c. of tin. The official brands include the following: Straits, Australian, Banca, Billiton, English, German, and Chinese. In connection with this classification a number of brands and descriptions were assayed, and tabulated analyses prepared.

It will thus be seen that some of the best brands of commercial tin are of remarkable chemical purity.

Properties of tin. Tin is a white lustrous metal which exhibits a fibrous structure, and when bent emits a creaking sound owing to its crystalline character. When melted and allowed partially to solidify, and the still liquid portion poured away, needle-shaped crystals are formed in the remainder. The metal is deposited in tetragonal prisms when stannous chloride is decomposed by a weak electric current. Tin is capable of existing in different allotropic forms depending upon the temperature. At ordinary temperatures it is in a metastable condition, but on exposure to great cold it falls to pieces forming a coarse grey powder. Between 18° and 170° the stable form of tin is tetragonal, above 170° it is rhombic. Tin has a sp.gr. of 7.312 and melts at 232° (Heycock and Neville). It expands 2.8 p.c. during melting. The change of density of melted tin with temperature may be represented by the formula

$$d = 7.01 - 0.00074(t - 232)$$

(Hogness, J. Amer. Chem. Soc. 1921, 43, 1621). Tin suffers little change when exposed to air, either dry or moist, at ordinary temperatures. When melted it slowly oxidises to the dioxide. It is readily attacked by acids: hydrochloric acid converts it into stannous chloride with evolution of hydrogen, nitric acid forms meta-stannic acid. It dissolves in aqueous solutions

of the alkalis with evolution of hydrogen, forming meta-stannates.

For passive tin, see Steinerz (Z. Elektrochem. 30, 279, June, 1924; Sci. Abstr. 1924, 27, 832).

Uses of tin.—The manufacture of tin plates absorbs more tin than any other industry, and of this a separate account will be given. Tin is also largely used for alloying with copper to produce bronze, bell metal, and speculum metal, while in combination with other metals tin produces a number of useful alloys, to be afterwards described, among which may be mentioned pewter, Britannia metal, plumber's (or soft) solder, Queen's metal, type metal, fusible metal, &c. Though tin is comparatively brittle at ordinary temperatures, it becomes very malleable at about 100°, and can then be rolled into thin sheet or foil, for which there is a considerable application, and which was formerly much used, in the form of an amalgam, for the 'silvering' of mirrors.

Tin foil containing small quantities of aluminium gradually becomes brittle, owing to the slow oxidation of the aluminium. On account of its power of resisting atmospheric influences and the action of vegetable acids, tin is also used for the manufacture of pipes for brewers, distillers, and other purposes. For similar reasons lead pipes are sometimes tin-lined. Pots, pans, kettles, and other culinary utensils are frequently tinned inside. The process is very ancient, and extremely simple. The surface of the vessel to be tinned (which may be of copper, brass, or iron) is carefully cleaned and brightened, and a little ammonium chloride (patented for this purpose by John Bootie in 1768) is often rubbed over the surface. Some tin and a little powdered resin is now melted in the vessel, and is wiped over the surface with tow. By this means a skilful workman rapidly produces a uniform coating of tin, which resists considerable wear, and yet weighs, according to the experiments of

	Tin	Anti- mony	Arsenic	Lead	Bis- muth	Copper	Iron	Silver	Sul- phur
Banca tin	99.950	0.007	nil	trace	nil	0.018	0.045	nil	trace
Billiton	99.900	0.006	nil	nil	nil	0.023	nil	nil	nil
Penang	99.939	trace	0.013	trace	nil	0.016	0.028	nil	0.004
Singapore tin . . .	99.870	0.008	0.045	0.034	0.003	0.052	0.003	0.006	0.005
M. Bischoff	99.795	0.005	0.063	0.037	0.005	0.035	0.042	trace	0.008
Pyrmont tin	99.938	0.017	0.019	trace	nil	0.022	trace	nil	0.004
Irvine Bank	99.580	0.062	0.034	0.221	0.025	0.125	0.002	0.018	0.004
Williams Harvey & Co., No. 1	99.860	0.015	0.040	0.004	0.005	0.047	0.003	nil	0.006
" " " No. 2	99.560	0.166	0.037	0.162	0.007	0.050	0.005	trace	0.013
" " " No. 2a	99.350	0.245	0.065	0.223	0.015	0.042	0.016	trace	0.013
" " " No. 3	99.200	0.300	0.037	0.396	0.007	0.100	0.013	0.014	0.006
" " " No. 4	99.941	0.011	0.022	trace	0.001	0.020	trace	trace	0.005
Penpoll, No. 1 . . .	99.720	0.118	0.054	0.041	0.007	0.052	0.001	0.009	0.007
" " " No. 2 . . .	98.710	0.569	0.042	0.546	0.055	0.103	0.007	0.015	0.004
" " " No. 3 . . .	99.300	0.325	0.056	0.212	0.050	0.088	0.002	0.021	0.009
Redruth	99.160	0.178	0.053	0.177	0.017	0.445	0.014	0.006	0.008
Th. Goldschmidt, No. 1	99.860	0.004	nil	0.102	nil	0.043	trace	nil	trace
" " " No. 2 . . .	99.400	0.015	nil	0.425	nil	0.069	trace	nil	trace
" " " No. 3 . . .	99.150	0.122	0.046	0.143	0.112	0.352	0.007	0.003	trace
Chinese, No. 1 . . .	99.343	0.031	0.040	0.434	0.007	0.052	0.010	trace	0.011
Wing Hong & Co., No. 2	98.602	0.039	0.035	1.035	0.042	0.134	0.014	trace	0.011
" " " No. 3 . . .	95.280	0.381	0.050	3.995	0.020	0.106	0.028	0.018	0.008

Bayen, less than a milligramme per square inch of surface. No wonder that Pliny states, with surprise, that copper when tinned does not increase in weight! Tin salts are also used for tinning brass and copper wire, and as mordants in dyeing.

Alloys of tin. The alloys of tin are of great practical importance, and have naturally attracted considerable attention, although accurate information is still wanted in respect of many of their physical and other properties. For convenience of study the alloys of tin may be divided into two classes, the first in which the properties of the resulting alloy are entirely different from the mean of the constituents, while the second class includes those alloys some of the most important properties of which agree very closely with what might be anticipated from the properties of the constituent metals. The first class is typically represented by the alloys of copper and tin, which include the important alloys known as *brass*, *gun metal*, *bell metal*, &c.

Tin itself is weak, soft, readily fusible, and of a nearly white colour, while copper is strong, tough, moderately hard, and of a characteristic red colour. On adding tin to copper, however, in gradually increasing proportions a succession of alloys is obtained with properties which are utterly different alike from those of each other and from their constituent metals. Thus an addition of about 5 p.c. of tin to copper produces a tough strong alloy, which still retains a fairly characteristic copper colour, but which is much harder than copper, and is suitable for medals or coinage, but the hardening effect of tin is so great that already the practical limit has been reached for coinage purposes. On adding 5 p.c. more tin we have an alloy which is still harder, so much so that it has to be cast instead of being rolled or drawn, and the alloy possesses a rich yellow colour. With a little more tin an alloy suitable for the hardest bearings is produced, and with still more tin we have the alloy used for small bells, and which is

sonorous, but shows considerable brittleness when cold, but though it be worked at a low red heat. With still more tin an alloy suitable for the largest bells is obtained; brittleness is more marked, and the fracture is dull earthy grey, and it is only when the metal has been worked or burnished that a yellow colour is visible. But on continuing the addition of tin, which is one of the softest of the common metals, the alloys become more and more brittle, until with about 33 p.c. the alloy can easily be pounded in a mortar, and possesses a white colour, with a more or less pronounced blue shade. This alloy is thus utterly different alike from its constituents and from either of the other alloys previously mentioned. As examples of the second class of alloys of tin, in which the properties of the alloy are approximately what would be expected from the characters of the constituents, the combination with zinc or with lead may be taken. Tin and zinc unite in all proportions, and the colour, hardness, ductility, &c., of the alloys are what would be anticipated from a mixture of the two constituents. Tin and lead also unite in all proportions to form a series of alloys, all of which are nearly white in colour, and are soft, malleable, and readily fusible, like the metals themselves. Tin-lead alloys, however, furnish a characteristic illustration of the fact that the melting-point of mixtures or alloys is very commonly lower than the mean calculated from the melting-points of the pure substances. This rule is very generally observed, both in salt solutions, with mixtures of salts, and with mixtures of organic substances (Guthrie, *Phil. Mag.* [iv.] 59, 1, 206, 266; [v.] 1, 49, 354, 446; 17, 462; 6, 35). Common, or soft, solder is an alloy of tin and lead, the best proportions being very nearly 2 parts of tin to 1 of lead. The melting-point of this alloy, calculated from the melting-points of its constituents ($Pb=327^\circ$, $Sn=228^\circ$), would be 261° , but the lowest melting-point in this series of alloys actually observed is 180° (Turner, *B'ham. Phil. Soc.* [iv.] 318), and the composition of the alloy was very nearly 2 parts of tin to 1 of lead. A number of investigators have examined these alloys of tin and lead, including K  pfer, Pillichody, Laurie (*Chem. Soc. Trans.* 1889, 678), and more recently Rosenhain and Tucker (*Phil. Trans. Series A.* 1908, 89), and the results of the determination of the composition of the lowest melting-point alloy vary from about 60 to 65 p.c. of tin (62-93 p.c. tin, Rosenhain and Tucker). There appears to be no indication of a definite alloy of tin and lead in atomic proportions, though, on very slow cooling, there is evidence of the existence of a solid solution, at the lead end of the series. There is also an inversion at 150° with alloys containing 18-63 p.c. of tin. In addition to their use for solders the tin-lead alloys have an important application in the form of *paste*, the toughest and hardest variety of which contains about 3 parts of tin to 1 of lead. The hardness of lead-tin alloys is altered completely by prolonged re-heating of the alloy (C. di Capua and M. Arnone, *J. Soc. Chem. Ind.* 1924, 43, B. 560; Atti R. Accad. Lincei, 1924, 33, i. 293). Alloys of tin and antimony belong to the same class as those previously mentioned, and a mixture of 4 parts of tin with 1 of antimony is used for one

kind of type metal. Tin also enters into the composition of Britannia metal, the proportions being as follows (Greenwood), *Metallurgy*, i. 211):—

	Britannia metal			Queen's metal
	For spinning	For rolling	For casting	
Tin	94	90	84	75
Antimony	5	7	10	8.5
Copper	1	3	4	—
Bismuth	—	—	2	8 *
Lead	—	—	—	8.5

A Birmingham manufacturer's mixture for Britannia metals is as follows: tin, 1 cwt.; antimony, 12 lbs.; copper, $\frac{1}{2}$ lb.

Britannia metal has a somewhat considerable application on account of its white colour, and the fact that it takes a good polish and resists the influence of the atmosphere; its low conductivity for heat also renders it very suitable for some purposes. This manufacture was introduced by Jessop and Hancock about 1770.

Type metal varies considerably in composition, consisting essentially of antimony and lead; but for small type tin is commonly added, and in some cases considerable proportions of tin are employed.

The following illustrates the composition of type metal of excellent quality, and suitable for different sizes of type. It will be noted that large type is made of a softer and cheaper mixture.

	Tin	Lead	Antimony
Large type	7.5	78	14.5
Medium type . . .	9.0	73	18
Small type	14.5	57	28.5

From 1 to 1.5 p.c. of copper is also added in some cases to improve the wear of the type.

White bearing metals for heavy machinery contain the same constituents as type metal. At least 10 p.c. of antimony is required; with above 20 p.c. the alloy is brittle. The limit of tin, on account of price, is usually about 45 p.c. (Hague, *Bearing Metals*, South Staffs. Iron & Steel Inst. Jan. 1909; Hiorns, *Anti-friction Alloys*, Birm. Metallurgical Soc. Feb. 1909). For special purposes larger proportions of tin are employed, as shown in the following analyses (G. Hughes, *Non-ferrous Metals in Railway Work*, *Journ. Inst. of Metals*, Sept. 1911):—

	A	B	C
Tin	82.0	11.5	80
Antimony	14.0	13.5	10
Copper	4.0	3.0	10
Lead	—	72.0	—

Alloy B is a fairly typical soft bearing metal. A and C are harder, the former being used for bearings, &c., in steam locomotives, and the latter for high-class axle bearings on the pinion and commutator ends of electrical rolling stock.

Tin is also a constituent of the various fusible alloys, one of the best known being Wood's alloy, which consists of 4 parts of tin with 4 of lead, 8 of bismuth, and a little cadmium; it fuses at 63° .

The tin-lead-bismuth eutectic melts at 94° . It can be prepared by melting together 4 parts of tin, 8 of lead, and 13 of bismuth. The alloy with 4 of tin, 8 of lead, 10 of bismuth, and 4 of cadmium melts at about 71° .

Fusible alloys are used chiefly for taking rapid impressions of objects which would fre-

quently be injured by the use of metal melting at a higher temperature, and also for safety plugs in steam boilers, &c.

For the equilibrium of the ternary system bismuth-tin-zinc, see Sheikh D. Muzaflax (J. Chem. Soc. 1923, 123, 2341).

Hardness of tin-cadmium and tin-bismuth alloys.—The hardness of tin is increased by addition of cadmium to a maximum for about 6 p.c. of the latter. With further addition of cadmium, the hardness falls rapidly until the eutectic point is reached at 28 p.c. of cadmium, remains constant over the region 28-97 p.c. Cd, and then falls to the value for pure cadmium. This behaviour is changed markedly by annealing the alloys in paraffin wax at 150° for 330 hours, the two branches of the curve in the neighbourhoods of 0 p.c. and 100 p.c. of cadmium then revealing the solid solubility of each metal in the other; about 3 p.c. of tin dissolves in cadmium and about 8 p.c. of the latter in tin (cf. Bucher, A., 1917, ii. 211).

With tin-bismuth alloys the maximum hardness corresponds with the eutectic point, but annealing causes the disappearance of this maximum and renders the curve normal, the maximum hardness being then shown by crystals of tin saturated with bismuth, and the limit of solid solution being extended from 4 p.c. to 7 p.c. of bismuth (C. di Capua, Atti R. Accad. Lincei, 1924 [v.] 33, i. 141; Chem. Soc. Abstr. 1924, 126, ii. 414).

Tin-copper alloys. History.—Copper is one of the few metals which have been known from prehistoric periods, and, like silver and gold, is in the pure condition too soft and ductile for many useful applications. The ancients, therefore, prepared various hard copper alloys or bronzes, which were used for many purposes to which iron and steel are now applied. The elements added to give hardness were arsenic, iron, or, preferably, when obtainable, tin. A very ancient Egyptian knife-blade (1400 B.C.) examined by Dr. Percy (Metallurgy, i. 504) consisted of copper with 2.29 p.c. of arsenic and 0.43 p.c. of iron; such a material would, of course, form an indifferent cutting tool.

The Hindoos have for many centuries produced a variety of bronze for coins and statues, which was hardened by the presence of iron. Dr. Percy mentions an ancient Indian coin which contained 5.06 p.c. of iron, the remainder being copper (*l.c.*), while in the Birmingham Art Gallery there is one of the earliest known images of Buddha, which is believed to be 2500 years old, and which was found by Daniel Forbes to contain 91.50 p.c. of copper and 7.59 p.c. of iron. With the introduction of tin by the Phoenicians came the use of bronze in Egypt, Assyria, Greece, and all the important countries of the ancient world. Of these bronzes, numerous examples are preserved, and the composition recommended for various purposes was very similar to that which is used at the present day. Thus Pliny states (Thomson, Hist. Chem. i. 57) that the Romans made their pans for boiling from a mixture of 100 lbs. of copper and 3-4 lbs. of tin, while for statues to every 100 lbs. of copper, consisting of one-fourth old copper and three-fourths new metal, 12½ lbs. of tin was added. Brass was not known, or at all events was not in general use, until shortly before the

Christian era, and the references to brass which so frequently occur in the Old Testament have to do either with copper or bronze, and not with alloys of copper and zinc. See further on the early history of copper and copper alloys, W. Gowland, Presidential Address, Institute of Metals, 1912.

Constitution of copper-tin alloys.—Previous to the researches of Matthiessen, it was customary to regard alloys as examples of chemical combination, and most experimenters prepared and studied alloys of definite atomic proportions. An example of this method of working is to be found in the researches of Mallet on the tin-copper alloys (Brit. Assoc. Rep. ix., Construction of Artillery, p. 82). The remarkable change in properties which results when tin and copper are alloyed was used as an argument in favour of the view that definite chemical compounds were produced. The result of more recent investigations, however, tends to show that although in some cases definite atomic combinations actually do occur, still these are comparatively few (see C. H. Desch, Intermetallic Compounds, Journ. Institute of Metals, vol. i. 227); while the other alloys, which constitute the vast majority of those in use, are either solid solutions of a metal in an excess of one of the constituent metals, or are simply mixtures of the two or more metals present in the alloy. The equilibrium of the copper-tin series has been studied by Heycock and Neville, Phil. Trans. 202A, 1; Giolitti and Tavanti, Gazz. chim. ital. 1908, 38, ii. 209; Shepherd and Blough, J. Phys. Chem. 1906, 10, 630; Haughton and Turner, Jour. Institute of Metals, 1911, part ii.; Ishihara, Chem. Soc. Abstr. 1925, ii. 122; Stockdale, Chem. Soc. Abstr. 1925, ii. 973. For a discussion of the equilibrium diagram, see art. METALLOGRAPHY. In the tin-copper series there is good evidence of the existence of a definite alloy Cu₃Sn containing 61.64 p.c. of copper, while there is considerable reason to believe that Cu₅Sn, containing 68.18 p.c. of copper, also exists. Thus Calvert and Johnson (Phil. Trans. 1858), in investigating the conductivity for heat of these alloys, found a maximum conductivity corresponding to Cu₃Sn, and a minimum conductivity corresponding to Cu₅Sn. Some very interesting determinations by Riche (Compt. rend. 55, 1862, and more completely Ann. Chim. [iv.] 30, 361) show two maxima, corresponding to Cu₃Sn and Cu₅Sn. These experiments have also received strong support from the induction balance curve of Roberts-Austen (Phil. Mag. 1879, [ii.] 57), which shows two distinct breaks corresponding to Cu₃Sn and Cu₅Sn. The determination of relative electric conductivity by Lodge (*ibid.* 1879, [ii.] 554) also show a very distinct maximum at Cu₃Sn and a minimum conductivity corresponding to Cu₅Sn. Laurie examined these alloys from the standpoint of the electro-motive force produced in a standard cell, and concluded that there was very definite evidence of the existence of Cu₃Sn, but failed in this way to obtain any proof of the existence of Cu₅Sn (Chem. Soc. Trans. 1898, 109; 1899, 678).

The evidence in favour of Cu₃Sn is therefore exceedingly strong, while that in favour of Cu₅Sn, though not quite so complete, is still good, and at present there is hardly sufficient evidence

in support of any other atomic combinations. Further evidence on this point will be found in C. H. Desch's paper on Intermetallic Compounds, *Journal Institute of Metals*, 1, 1909, 227, above cited. These facts, when considered in connection with the known characters of the two alloys in question, give a key to the peculiar characters of the useful tin-copper alloys. The two definite alloys are white, hard, and brittle, and practically all the alloys used in the arts, except speculum metal, contain more copper than $\text{Cu}_3\text{Sn}=68.18$ p.c. Cu. Hence the useful bronzes may be regarded as mixtures of one of two definite alloys with an excess of a solid solution of tin in copper, and these tend to separate more or less completely during solidification. This separation is particularly marked with large castings rich in copper, as in *gun metal*, which was in former times largely used for ordnance. Microscopical examination shows clearly that at the copper rich end of the series of alloys the first constituent to separate out on cooling the fluid alloy is a solid solution of tin in copper. This forms a dendritic, or fir-tree like structure, giving cores which increase in tin from the centre outwards. This copper-rich solid solution is called the α constituent, and is relatively soft and ductile; as the proportion of tin increases harder constituents separate out, the first of them being designated by the symbol β . It is harder and more brittle than α .

Copper retains a maximum of 13.9 p.c. of tin in solid solution, but tin can retain only traces of copper. The compound Cu_3Sn exists in two modifications: the α -form is stable up to 676° , above which the β -form is the stable modification and melts unchanged at 720° . The existence of the compound Cu_3Sn has been definitely proved, and a new compound, Cu_4Sn_3 , has been found in and isolated from alloys containing more than 60 p.c. of tin. It is stable below the eutectic point at 225° in all alloys containing more than 61 p.c. of tin (cf. *J. Soc. Chem. Ind.* 1923, 42, 227A) (O. Bauer and O. Vollenbruck, *Z. Metallk.* 1923, 15, 119-125, 191-195; *J. Chem. Soc.* 1923, 124, ii. 640).

The production of bronze castings requires special precautions, which cannot be described here. For details, see Mallet On the Construction of Artillery, 1856; also Reports of the United States Chief of Ordnance, 1880, 126, 189; 1884, 369. These latter reports contain some important observations with regard to this variety of bronze. It is stated that the best proportion for such purposes is 91 of copper to 9 of tin. This is best cast in a mould or 'chill' of cast iron, and 100 tests of metal so prepared gave an average tensile strength of 21.9 tons per square inch, the maximum being 24.8 tons and the minimum 16.5 tons. It should be mentioned that these values are higher than those usually obtained in this country, where the metal is generally cast in sand moulds.

Composition of principal tin-copper alloys.—The following list is based on that given by Holtzapffel (*Mechanical Manipulation*, i. 270).

Tin, 0-5 p.c. A small quantity of tin is sometimes added to copper for engraver's purposes to give crispness. About 5 p.c. was used by the Romans for pans, and for ancient flexible bronze nails. A similar alloy is now used for some coinage and medals, often with

a little of the tin replaced by zinc; also for engineers' soft gun metal or 'brasses'.

7 p.c. Slightly harder alloy; suitable for mathematical instruments, &c.

8.5 p.c. Rather harder; fit for wheels to be cut with teeth.

8-12 p.c. Soft bronze statues of the ancients. These alloys are harder than the preceding, and mark the extreme limit for coinage purposes. Also used for brass ordnance, 9 or 10 p.c. of tin being preferred. Medium engineers' 'brasses' contain 10-12 p.c. of tin.

12-14.5 p.c. Hard bronze of the ancients, used for weapons and tools. These proportions are also used for engineers' hard bearings.

16 p.c. Soft musical bells.

18-20 p.c. Chinese gongs and cymbals.

20 p.c. Small house bells; Indian gongs.

22 p.c. Large house bells.

24 p.c. Limit for large church bells.

About 33 p.c. Speculum metal (v. Phil. Trans. 1840, 503).

About 66 p.c. 'Temper,' an alloy used for addition to tin and lead to harden pewter.

It has already been mentioned that the addition of a small quantity of tin to copper prevents it rolling well when hot, and the addition of a little more tin destroys its malleability when cold. Bronze is tempered by an exactly opposite process from that used in the case of steel, namely, the alloy is heated to redness and then rapidly cooled in water.

Admiralty bronze consists of 88 parts copper, 10 zinc, and 2 tin. It is a very useful and important alloy, which has received considerable attention in recent years. Its properties are largely influenced by temperature of casting and rate of cooling (see Carpenter and Flam, *J. Institute of Metals*, 1918, xix. 155).

For the majority of purposes bronze is melted in crucibles of fireclay or plumbago, the charge being about 90 lbs. For large castings a reverberatory furnace is often employed, though such work is sometimes performed by means of a large number of crucibles. It is recommended that the copper should be well melted and kept in fusion for some time before the tin is added, if strong castings are required. Founders also prefer to use some new metal in every charge, and not merely to re-melt scrap. The oxidation which takes place during melting removes some 3 or 4 parts of copper to 1 of tin; the result is, therefore, that the alloy, which contains about 9 parts of copper to 1 of tin, tends to get poorer in tin by remelting, and due allowance must be made for this loss, even though it may appear to be slight, as small differences in composition often exert a most important influence in tin-copper alloys.

Bronze bearing metal.—According to Dudley (*Jour. Franklin Inst.* 133, 81, 161; *J. Soc. Chem. Ind.* 11, 460), the following composition is very suitable for bearings for locomotives and similar purposes: copper, 77; tin, 8; lead, 15. The presence of lead in bearings very much diminishes the loss of metal caused by wear, and also reduces the local heating of the journals. Phosphor bronze and other varieties of bearing metal for similar purposes to the above often contain about 10 p.c. of lead, and the wearing properties of the alloy is chiefly connected with the proportion of copper and tin to lead. The presence

of tin is necessary in order to obtain a uniform alloy, as lead and copper alone do not unite well. With too much tin the alloy wears more rapidly and becomes more heated. The presence of phosphorus and arsenic gives solidity to the castings, but with suitable proportions of tin and lead, as above, alloys are obtained which wear even better than standard phosphor bronze with the following composition: copper, 79.7; tin, 10; lead, 9.5; phosphorus, 0.8 p.c.

Phosphor bronze is an alloy containing copper and tin in various proportions, and which also contains a small quantity of phosphorus, introduced in the form of phosphor tin. Occasionally small quantities of zinc or lead are also added. The phosphorus varies from a mere trace, added chiefly to ensure soundness in casting, to about 1.75 p.c. with hard alloys. The results of the analyses and mechanical tests of 99 samples of phosphor bronze, as received by the British Admiralty, have been given by A. Philip, Journ. Inst. of Metals, 1, 164, while the constitution and microstructure have been dealt with by O. F. Hudson and E. F. Law, Journ. Inst. of Metals, iii, 1910, 161. This alloy has met with considerable favour where special power of resisting wear (as with gearings and bearings for quick-running machinery) is required. Similar alloys containing manganese, which is added in the form of ferro-manganese, have also met with considerable application, and are known as *manganese bronzes*. **Silicon bronze**, made by the addition of copper silicide, is used for conductivity wire, though many of these so-called bronzes contain very little or no tin. They are usually alloys which closely resemble Muntz metal in composition, and contain about 60 p.c. of copper, 38 p.c. of zinc, and the remainder of specially added elements, such as manganese, and impurities.

The structure of a tin amalgam corresponding approximately with the formula $Hg_{25}Sn$ is found to consist, like that of tin bronzes, of large granules which are built up of a crystalline skeleton solidifying at a higher temperature and of a component still liquid at the ordinary temperature. The crystalline skeleton consists of acicular, tabular, and granular particles, which are comparatively loosely united and are composed of very small crystalline granules. Centrifugation of the amalgam allows of the separation of the liquid component from the crystalline skeleton (F. Hauser, Zeits. f. Physik. 1923, 13, 1 and 2, 1-6; Sci. Abstr. 1923, 26, 680-681).

Detection of tin and mercury by means of a spot test.—A black stain is produced if a mercuric chloride test paper is treated with one drop of a solution containing stannous tin and then with one drop of aniline. The stannous ion is the only cation in the five analytical groups that will reduce mercuric chloride to metallic mercury in the presence of aniline, and the test can therefore be used in the presence of any of the ordinary metals. If the tin is present in the stannic condition, it is first reduced to the stannous form by means of magnesium and hydrochloric acid. By using a test paper soaked in a solution of stannous chloride, the same reaction serves for the detection of mercury (Tananaev, Zeitsch. anorg. Chem. 1924, 133, 328; Chem. Soc. Abstr. 1924, 19, 571).

Dry assay of tin ores.—Hofman finds that Winkler's method of assaying black tin stone gives results averaging 65.96 p.c., or 1.88 p.c. too low, the figures disagreeing amongst themselves up to over 3 p.c. The process consists of reducing together 5 grms. each of cassiterite and cupric oxide with 15 grms. of black flux, 1.25 grms. of borax, and a little salt as a cover. A similar experiment is conducted without the cassiterite, and the copper obtained in the one case deducted from the alloy in the other gives the amount of tin. The following modifications of this method were tried: increasing the amount of charcoal, using chalk-lined crucibles, omitting the salt and increasing the potassium carbonate, and Rickett's modification of adding argol; but they all gave worse, and in some instances very variable, results.

The iron method—reduction with hematite, charcoal, and potassium cyanide or fluorspar—gave unsatisfactory results. The same may be said when a mixture of ferrocyanide and cyanide was used, and also when any of the Cornish methods were employed. So far, with fairly pure cassiterite only two methods have proved satisfactory, viz. the German and the pure cyanide methods. Hofman has attempted to prove which of these two methods gives the best results when the cassiterite is mixed with those minerals likely to be naturally associated with it. The minerals used were quartz, feldspar, mica, tourmaline, garnet, and columbite. Mixtures of the purified cassiterite ore with varying proportions of each of these minerals were assayed by both methods, the percentage of tin being calculated on the cassiterite ore present. The charges were so regulated that the flux in the German assay was always equal to three times the quantity of ore plus the mineral, and in the cyanide assay to six times the quantity. In the latter case 4 parts of cyanide were mixed with the ore; 1 part was used to coat the crucible bottom, and 1 part as a cover. In all cases the cyanide method gave more concordant, and less prejudicially affected, results than the other. The results of the German assays fluctuated greatly as the amount of mineral present increased. Thus, in the case of quartz and albite the results were lower as the quantity of mineral was increased, the respective figures being, with 37.5 p.c. of each mineral, 60.7 and 60.2 p.c.; the corresponding cyanide figures being 63.90 and 65.30 p.c. (the real percentage of tin was 67.84). The tin buttons, moreover, in the German assay with albite contained iron, while those by the cyanide process were free, the temperature of fusion being too low to cause decomposition of the albite.

With muscovite, tourmaline, garnet, and columbite the results with the German method were very unreliable, being sometimes too high and very ferruginous, and sometimes too low, varying from 82 p.c. with 50 p.c. of garnet to 46 p.c. with 44 p.c. of tourmaline. The cyanide method gave fairly good results in all the above cases, very little iron getting into the buttons, except in the case of garnet, when the result was 69.89 p.c., with 37.5 p.c. of mineral present. With the same quantity of muscovite, tourmaline, and columbite the assays were respectively 63.3, 64.7, and 66.0 p.c. Consequently, where anything like a true result is

required the cyanide assay is by far the most to be relied upon, and should be employed in cases of buying and selling, although in concentration works, where comparative results and large numbers of assays are required, the question of cost must be considered, and the cheaper German method might be adopted.

Hofman emphasises the importance of properly preparing the ore for assay, and states that the ordinary method of grinding the whole sample to a uniform size is not suited to the tin ores of the Black Hills, chiefly on account of the preponderance of mica. Hence a preliminary sizing is advantageous. The ore while being pulverised is screened through a series of sieves Nos. 20, 40, 60, and 80, the different-sized screenings being then washed. This method gives purer concentrates, and necessitates less loss of cassiterite, as the material has been washed without excessive grinding, which in the present process reduces the brittle cassiterite to a slime, while some of harder associated minerals are only converted into sand. The subsequent treatment of the concentrates mentioned in the first part of the paper is recommended, as the roasting renders the cassiterite more friable and more readily reducible, the assays in some cases showing a difference of 0.5 p.c. between the raw and roasted ores in favour of the latter (Part II., H. O. Hofman, Technol. Quarterly, 3, 261-280; J. Soc. Chem. Ind. 9, 1154; v. Rennic and Derrick, *ibid.* 1892, 662).

For analysis of tin ores by wet methods, cf. Craig, J. Ind. Eng. Chem. 1919, 11, 750; Analyst, 1919, 359.

The following figures, issued by the Imperial Mineral Resources Bureau, show the world's production of tin ore in terms of metal and the world's smelter production of tin in 1921:—

	Output of tin ore. Long tons.	Smelter output of tin. Long tons.
United Kingdom	679	14,000
Nigeria	5,057	—
Swaziland	234	—
Union of South Africa	720	—
Southern Rhodesia	—	4
India	1,362	172
Straits Settlements	1	41,917
Federated Malay States	34,490	—
Unfederated Malay States	1,611	—
Australia	2,650	2,985
Bolivia	18,804	60
Germany	—	4,000 ¹
United States	—	10,305
China	11,200	6,134
Siam	6,181	—
Dutch East Indies	26,911	—
Other Countries	900	500
	110,800	95,000

¹ Figures not available.

² Estimated.

In the volumetric determination of tin, stannous chloride solutions may be titrated directly with potassium bichromate, using diphenylamine sulphate as internal indicator, the end-point being marked by the development of a blue colour; or indirectly in a similar manner after addition of excess of ferrous chloride (J. G. F. Bruce, Chem. News, 1924,

184, 273; J. Soc. Chem. Ind. 1924, 43, B. 540; Analyst, 1924, 49, 402).

The small quantities of tin present in canned foods are determined volumetrically by titration with standard iodine after preliminary ignition to remove organic matter and precipitation as sulphide. A special apparatus is used in which the tin is reduced to stannous chloride by zinc and hydrochloric acid and titrated as such in an atmosphere of carbon dioxide. By means of an arrangement of three flasks and three 2-way taps the reduced liquid is blown by the carbon dioxide into another flask containing starch solution, the reducing flask is rinsed out by water saturated with carbon dioxide, and the wash-water driven as before to the main solution, which is then titrated with standard iodine, the solution being kept mixed by means of the gas content (E. J. B. Willey, J. Soc. Chem. Ind. 1924, 43, 70 T.; J. Soc. Chem. Ind. 1924, 43, B. 273).

COMPOUNDS OF TIN.

According to Paneth and Fürth (Ber. 1919, 52, [B] 2020) an alloy of tin and magnesium Mg₂Sn when acted upon by dilute hydrochloric or sulphuric acid evolves minute quantities of a gaseous hydride of tin which is decomposed on passing through a heated glass tube. The gas can be condensed by liquid air and re-evaporated without decomposition.

Oxides. A monoxide, *stannous oxide* SnO, and a dioxide, *stannic oxide* SnO₂, each of which gives rise to a distinct series of salts, are known, the former acting as a base and the latter acting as either base or acid. Oxides of the composition Sn₂O₃, SnO·3SnO₂, 2SnO₂·H₂O, SnO₂, and others have also been said to exist, but it is probable that, with the exception of SnO₂, they are mixtures of the other two oxides.

Stannous oxide SnO is obtained as an olive-brown anhydrous powder, when stannous oxalate is heated out of contact with the air; or as a white precipitate of the composition 2SnO·H₂O, with evolution of carbon dioxide, when stannous chloride and an alkaline carbonate or hydroxide are mixed in solution. If the precipitate is washed with air-free water, and the lixiviated product is heated in the absence of air, nearly pure dark grey stannous oxide is obtained (Enequist, Eng. & Mining J. 1895, 219; see also Hantzsch, Zeitsch. anorg. Chem. 1902, 30 289).

It may also be obtained as a bluish-black anhydrous powder by heating a mixture of 4 parts of stannous chloride with 7 of sodium carbonate, and lixiviating the resultant mixture of stannous oxide and sodium chloride (Sandall, J. pr. Chem. [i.] 254). The anhydrous oxide may also be obtained from the hydrated form as follows: (1) as a black powder by heating it out of contact with the air; (2) in minute cubes by digestion with acetic acid at 56°; (3) of a brilliant scarlet colour, which becomes brown on rubbing, by evaporating a dilute solution of ammonium chloride containing stannous chloride in solution until the chloride commences to crystallise (Fremy, Berz. J. 24, 133; 25, 172; Ann. Chim. [iii.] 12, 460); (4) as small black shining crystals, which, when heated to 258°, decrepitate and swell up, with production

TIN.

of soft olive-green laminae, by prolonged digestion with a weak solution of caustic potash at the ordinary temperature (Fremy, l.c.). A stronger solution dissolves the oxide and ultimately deposits it in crystals, the deposit from a solution of 4 parts of potassium hydroxide in 10 of water containing potassium stannate and tin, the former produced by absorption of atmospheric oxygen. Fremy also describes various red, black, brown, and other forms of this oxide.

The following method is given by Fraenkel and Snipischsky (Zeitsch. anorg. Chem. 1922, 125, 235): Stannous chloride is dissolved in the least possible amount of hot concentrated hydrochloric acid and sodium hydroxide solution added gradually until the solution reacts alkaline towards phenolphthalein; the resulting milky liquid is then kept boiling in a bath of saturated sodium chloride solution. In a few hours a blue lustrous powder is obtained which is washed and dried (J. Soc. Chem. Ind. 1923, 101 A).

Stannous oxide becomes incandescent, and forms stannic oxide, when heated in the air. It is violently oxidised by nitric acid, and other oxidising agents. Carbon or hydrogen reduces it to metal at a red heat. It dissolves in acids, with production of stannous salts, and in caustic potash or soda, but not in ammonia. The soda solution is employed in calico printing and dyeing under the name *sodium stannite*, and is prepared as described under *sodium stannate*.

Stannous oxide and tin salts are used as reserves under parapatraniline red and other diazo colours (Bull. Soc. Ind. Mulhouse, 1900, 45).

Stannous oxide is sometimes recommended for use in glass and enamel manufacture, but it is too costly, and the results are not very satisfactory.

A so-called *sesquioxide* Sn_2O_3 is obtained as a slimy grey precipitate by the action of recently-precipitated ferric hydroxide on a solution of stannous chloride (v. Fuchs, Kaestner's Archiv. für Chemie und Meteorologie, 23, 368; J. pr. Chem. 5, 318; and Berzelius, Pogg. Ann. 28, 443; Berz. J. 13, 110).

This substance is readily soluble in ammonia and in concentrated hydrochloric acid. It does not appear to form definite salts. Its hydrochloric acid solution acts like a mixture of stannous and stannic chlorides. An orange-yellow oxide of the composition $\text{SnO} \cdot 3\text{SnO}_2$ is obtained by digesting metastannic acid in cold aqueous stannous chloride (Fremy, J. Pharm. [ii.] 1, 344).

Hydrated stannous oxide, according to Ditte (Ann. Chim. 1882, [v.] 27, 145), is prepared by adding the hydroxides of sodium or potassium to a solution of stannous chloride, and was described as a brownish-yellow powder of the formula $\text{SnO} \cdot 2\text{H}_2\text{O}$ (cf. Schaffner, Annalen, 1844, 51, 168). According to Bury and Partington (Chem. Soc. Trans. 1922, 121, 1998) the more probable formula is $3\text{SnO} \cdot 2\text{H}_2\text{O}$. It is stable at 110° and slowly loses water on standing under water, forming stannous oxide.

Stannic oxide SnO_2 occurs as *cassiterite* or *tinstone*, varieties of which are known as *stream tin*, *wood tin*, *lead's eye*, &c. Daubrée (Ann. Mines, 20, 65) has pointed out that, with the exception of quartz, the minerals most frequently associated with tin ore are fluorine compounds.

Stannic oxide is obtained as an anhydrous

white powder of sp.gr. 6.7122 at 4° (Joule and Playfair, Chem. Soc. Trans. 1849, 1, 128) when tin is heated until it burns in the air. The powder is converted into microscopic quadrate crystals resembling the native oxide when heated in a current of hydrogen chloride (Deville, Compt. rend. 1861, 53, 161; see also Abel, Chem. Soc. Trans. 1858, 119). The oxide may also be obtained in trimetric crystals, and is therefore dimorphous (v. Daubrée, Pharm. Zentr. 1849, 821; Levy and Bourgeois, Compt. rend. 94, 1365.)

It has also been obtained in oblong and rhombic plates of sp.gr. 7.0096 and approaching the form of anatase (Emich, Monatsh. 1893, 14, 345).

Metallic tin may be heated electrically or otherwise to 1700° out of contact with air, and the resulting tin vapour is then burnt in a current of air or oxygen. The stannic oxide thus produced is said to be more homogeneous and in a better state of subdivision for enamelling than the ordinary oxide (Eng. Pat. 9231, 1900).

Stannic oxide is obtained from its ores or from dross, waste, &c., by heating the ore or waste with or without an admixture of coke, chalk, or dolomite and acting upon the liberated molten tin with hot air or oxygen (Fr. Pats. 392805, 392806, 1908; 370640, 1906; 409157, 409485, 1909; also Eng. Pats. 12910, 1899; 28565, 1908; U.S. Pats. 695939, 1912; 780984, 1905; 880873, 1908; J. Soc. Chem. Ind. 1900, 448; *ibid.* 1905, 197; *ibid.* 1908, 335; *ibid.* 1909, 21; *ibid.* 1910, 352; see also *ibid.* 1904, 1239; *ibid.* 1907, 696, 1094).

The dioxide may also be formed by electrolysis a solution of sodium chloride using a tin plate as anode and a platinum plate as cathode (Lorenz, Zeitsch. anorg. Chem. 1896, 12, 436).

Stannic oxide is reduced to metal when heated with hydrogen, carbon monoxide, carbon, potassium, or sodium (Doeltz and Graumann, Metallurgie, 1907, 4, 420). It dissolves in fused potassium disulphate, but separates from the mass when treated with water. When fused with sulphur, stannic sulphide is formed, with evolution of sulphur dioxide.

The anhydrous oxide is insoluble in acids, except in concentrated sulphuric acid, with which it forms a syrup decomposed by dilution, with precipitation of the oxide. It dissolves in aqueous or fused alkalis, with formation of stannates.

Treated with hydrochloric acid in presence of tin both stannous and stannic oxides form stannous chloride, and this is used as a method for the recovery of tin from the waste liquors of the dye house (Vignon, Textile Colourist, 18, 333; J. Soc. Chem. Ind. 1893, 762).

With chloroform stannic oxide chiefly reacts thus:



(Renz, Ber. 1906, 39, 249).

When heated with hypophosphorous acid over a Bunsen flame for 30 mins., *stannous phosphate* or *pyrophosphate* is formed; since these are readily soluble in hydrochloric acid, stannic oxide can thus be separated from silica which is not affected by this treatment (Dott, Pharm. J. 1906, 81, 585).

Stannic oxide, in the form of *pure powder*,

which is a mixture of tin and lead oxides, or a stannate of lead, is used as a polishing material for glass. To avoid any possibility of danger from the use of this powder it has been recommended to mix 1 part of putty powder with 2 of metastannic acid (Gueroult, *Compt. rend.* 1892, 115, 757). Stannic oxide is an important factor in the manufacture of glazes and of enamels, the latter assuming an intensely white colour on the addition of a small quantity of the oxide. It is also the best material known for making opaque glaze or glass, and is employed in glaze brick and tile manufacture (Enequist, *L.c.*; Burt, *Trans. Amer. Ceramic Soc.* 1902, 4, 139).

Tin oxide is also said to be useful for the purification of water (*J. Soc. Chem. Ind.* 1894, 56).

Perstannic oxide SnO_2 . W. Spring (*Bull. Soc. chim.* [iii.] 1, 180) has obtained a substance of the composition $\text{H}_2\text{Sn}_2\text{O}_7$, probably a hydrate of this oxide, by dialysing the turbid solution obtained by adding hydrated barium peroxide in excess to a solution of stannous chloride in hydrochloric acid, and evaporating the solution of the colloid on the water-bath.

Stannic acids. Two isomeric stannic hydroxides are known, each of which behaves as an acid and exists in various degrees of hydration between the limits H_2SnO_3 and H_4SnO_6 . They are both colloidal modifications of hydrated stannic oxide, only differing in the size of their particles, the α -acid consisting of relatively small, the β -acid of relatively large particles (Mecklenburgh, *Zeitsch. anorg. Chem.* 1903, 64, 368; 1912, 74, 207; 1914, 84, 121; see also Fremy, *Ann. Chim.* 1844, [iii.] 12, 466; *ibid.* 1848, 23, 335; Musculus, *Compt. rend.* 1867, 65, 961; Vignon, *ibid.* 1889, 108, 1049; *ibid.* 109, 372; Kleinschmidt, *Monatsh.* 1918, 39, 149; Kreis, *Schweiz. Chem. Zeit.* 1919, 389; Tian, *Compt. rend.* 1921, 172, 1402; Collins and Wood, *Chem. Soc. Trans.* 1922, 441).

Stannic acid, α - or ortho-stannic acid H_2SnO_3 , is obtained by precipitating stannic chloride with ammonia, or by addition of calcium or barium carbonate to a solution of stannic chloride in quantity insufficient to precipitate the whole.

It is also formed by treating an alkali stannate with a mineral acid (Kühl, *Pharm. Zeit.* 1908, 53, 49) and by electrolysis an alkali chloride, nitrate or sulphate solution, using platinum as cathode and tin as anode (Lorenz, *Zeitsch. anorg. Chem.* 1896, 12, 436), and by other methods (Engel, *Compt. rend.* 1897, 125, 851; Neumann, *Monatsh.* 12, 518; Coppadoro, *Chem. Zeit.* 1907, 31, Rep. 336).

Its composition varies with its mode of drying, and it is converted into anhydrous SnO_2 at $630^\circ\text{--}655^\circ$. It forms a gelatinous substance, or white voluminous, amorphous precipitate, slightly soluble in water and of acid reaction. When dried spontaneously, it forms translucent lumps, resembling gum arabic.

When boiled with phenosafranine in the presence of sodium sulphate, stannic acid forms an intense red lake; metastannic acid under the same conditions only forms a pale rose tint (Vignon, *Compt. rend.* 1891, 112, 580).

A colloidal stannic acid is known (*v. Graham, Phil. Trans.* 151, 213; Van Bemmelen, *Rec. trav. chim.* 7, 87; Schneider, *Zeitsch. anorg.*

Chem. 1894, 5, 83; *ibid.* 1900, 23, 111; Lottermoser, *J. pr. Chem.* 1899, [ii.] 59, 489; Biltz, *Ber.* 1902, 35, 4431). It can be prepared by the dialysis of an alkali solution of tin chloride or of a hydrochloric acid solution of potassium stannate. Colloidal stannic acid is the most important constituent of purple of Cassius (*v. GOLD PURPLE*).

Stannic acid forms a large and important series of salts, most of which are crystalline. The alkaline stannates are soluble, and may be prepared by dissolving the precipitated oxide in the alkaline hydroxide. The others are mostly insoluble, and are best obtained by double decomposition. The potassium and sodium salts are the only ones of technical importance. The stannates have been investigated by Fremy (*Ann. Chim.* 1844, [iii.] 12, 462; 1848, [iii.] 23, 393), Moberg (*J. pr. Chem.* [i.] 28, 230), Marignac (*Ann. de Mines*, [iii.] 15, 277), Ordway (*Amer. J. Sci.* [ii.] 40, 173), Ditte (*Compt. rend.* 1882, 94, 1114; 1883, 96, 701), and Bellucci and Parravano (*Atti R. Accad. Lincei*, 1904, [v.] 13, ii. 324, 339; *ibid.* 1905, 14, i. 457).

According to the last-mentioned authors they are isomorphous with the plumbates and platinates.

Sodium stannate Na_2SnO_3 , usually occurs in six-sided tables of the composition $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ (Moberg, Marignac, Ordway, *L.c.*), which are less soluble in hot than in cold water. According to Ordway, 100 parts of water dissolve 67.4 parts at 0° , and 61.3 parts at 20° .

According to Bellucci and Parravano, the water is present not merely as water of crystallisation but in a more intimate form, namely, as $\text{Na}_2\text{Sn}(\text{OH})_6$.

Crystals of the above composition are deposited from a hot alkaline solution, but the salt may also be obtained with 8, 9, or 10 molecules of water. The form crystallising with 9 molecules is said to be obtained in oblique rhombic prisms by recrystallising the commercial salt (Jonas, *Chem. Zentr.* 1865, 607); while, according to Haefely (Dingl. poly. J. 144, 66), crystals of the composition $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ are deposited from hot concentrated solutions of 1.3 sp.gr., but re-dissolve on cooling to a solution of 1.35 sp.gr., from which crystals containing 8 molecules of water are gradually deposited.

Copper is readily tinned by immersion in a solution of the salt.

Sodium stannate is largely used, under the name of 'preparing salt,' as a mordant in dyeing and calico-printing, the fabric being first passed through a solution of the stannate, and then through weak sulphuric acid, which precipitates the hydrated oxide on the fibres.

For preparing this salt on the large scale, the original processes patented by J. Greenwood, J. Mercer, and J. Barnes (*Eng. Pat.* 10757, 1845), J. Young (*Eng. Pats.* 12359, 1848; 12744, 1849), and Haefely (*Eng. Pat.* 603, 1854), are still used with some modifications. A number of other processes are mentioned in the list of patents relating to tin salts (*infra*).

The process of Greenwood, Mercer, and Barnes consists in heating 22 lbs. of caustic soda in an iron crucible until evolution of water ceases, and then adding 8 lbs. of sodium nitrate and 4 lbs. of sodium chloride, followed, when the mass is nearly fused, by 10 lbs. of feathered

tin, with constant stirring until deflagration ensues. The mixture then becomes white hot, and pasty, and is wholly converted into the stannate.

For preparing sodium 'stannite' a mixture of 4 lbs. of sodium chloride, 1 gallon (13.5 lbs.) of caustic soda, 1 lb. of sodium nitrate, and 4 lbs. of tin is heated in an iron crucible, and the dry powder finally obtained is stirred so long as ammonia is evolved.

Young's processes—most of which are described below—consist mainly in the preparation of the stannate directly from the ore, thus avoiding the cost of obtaining and re-oxidising the metal.

By one process the native or prepared oxide is boiled in an iron pot with a quantity, varying with the tin value of the ore, of 22 p.c. soda lye, the temperature being gradually raised to about 600°F., at which combination takes place. When the operation is completed, which is ascertained by removing a portion and seeing how much dissolves, the mass is cooled in another vessel and is dissolved, filtered, or decanted, and recrystallised or sold in solution.

In another process, the ore is heated to redness with one and a half parts of sodium nitrate in a current of steam with constant stirring. The stannate is produced, with evolution of nitrous fumes and nitric acid. The nitrate may be replaced by 1 part of salt, hydrochloric acid being then obtained as the by-product.

'Stannite' of soda is obtained by heating the metal with its own weight of caustic soda, with constant stirring, or by electrolysis of a concentrated solution of sodium hydroxide, using a rotating tin anode and a platinum cathode. The current must not be too strong, and the solution must be protected from oxidation by a stream of hydrogen (Goldschmidt and Eckardt, *Zeitsch. physikal. Chem.* 1906, 56, 385). The solution of the stannite may be used in dyeing and printing operations as it is, or it may be converted into stannate, with precipitation of tin as a black powder, by boiling.

The stannate may be obtained direct from the metal by heating a mixture of 20 parts of tin, 16 of sodium hydroxide, and 3 of manganese dioxide to redness, with constant agitation and free exposure to the air. The dioxide appears to act as a carrier of oxygen, and is obtained unchanged at the end of the operation.

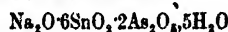
In another process, calcium stannate is obtained by roasting in a reverberatory furnace a mixture of the ore with slaked lime. The product is treated with sufficient hydrochloric acid to precipitate the tin as oxide, but not to redissolve any of it, and the precipitate is dissolved in boiling soda lye. The salt may also be obtained by boiling barium stannate, obtained similarly to the lime salt, with sodium sulphate, until all the barium is converted into sulphate.

Haeffely's process consists in the preparation of a solution of 'plumbate of soda' by dissolving 54 lbs. of red lead or 70-80 lbs. of litharge in a solution of 45 lbs. of caustic soda of 70°Tw. The solution is diluted, and 16 lbs. of tin is suspended in it while boiling, so that in 4 or 5 hours the lead is obtained as a deposit, which may be readily oxidised for re-use, while sodium stannate remains in solution.

The following process has also been employed (*Chem. Zeit.* 9, 851):—Ten boilers, arranged in horseshoe form, and each having a central tube, the lower end of which forms a perforated funnel, are almost filled with granulated tin, and six of them are charged with soda lye of 15°Bé. The liquor is drawn off from each, after a suitable amount of boiling, through a siphon passed into the central tube, and is passed from boiler to boiler until of 30°Bé., when it is allowed to settle in a tank. For preparing 'sodium stannate liquor' enough common salt is dissolved in the solution to reduce the proportion of tin to 5 p.c.; and for producing the solid the liquid is evaporated and calcined, and mixed with enough sodium chloride to reduce the tin to 42 p.c.

Sodium stannate is used in order to render cotton goods, such as flannelette, fireproof (W. H. Perkin). The flannelette is impregnated with a solution of sodium stannate of about 45°Tw., squeezed, dried on heated copper drums, passed through a solution of ammonium sulphate of about 15°Tw., in order to precipitate tin oxide, again squeezed, dried, and finished in the usual manner. The tin oxide is probably present in actual combination with the fibre, for the fireproofing is not destroyed by repeated washing with hot water and soap.

A sodium arsenio-stannate



occurring in shining needles, is sometimes used instead of the ordinary stannate, and is said to give brighter colours and to be more economical. It is prepared by adding nitric acid to a boiling solution of sodium stannate and sodium arsenate, and treating the resulting precipitate of $2\text{SnO}_2 \cdot \text{As}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ with excess of soda (v. Haeffely, *Dingl. poly. J.* 140, 290; J. Mercer and W. Blythe, *Eng. Pat.* 12807, 1849). In the latter process a sodium phospho-stannate is also employed for the same purposes. Another sodium arsenio-stannate



has been obtained by Prandtl (*Ber.* 1907, 40, 2133).

Potassium stannate K_2SnO_3 is obtained similarly to the sodium salt, and is sometimes employed in dyeing and calico-printing. It crystallises from spontaneously evaporated solutions in transparent oblique rhombic prisms of the composition $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ (Marignac, *Ann. de Mines*, [v.] 15, 277; Moberg, *J. pr. Chem.* [i.] 28, 230; Ordway, *Amer. J. Sci.* [ii.] 40, 173). It becomes anhydrous when heated to redness.

Potassium stannate is insoluble in alcohol, but dissolves in water to an alkaline solution, 100 parts of water dissolving 106.6 parts at 10° and 110.5 parts at 20° (Ordway, *loc. cit.*).

Cupric stannate CuSnO_3 has been employed as a green pigment. It is prepared for this purpose by precipitating sodium stannate with copper sulphate, or by addition of a solution of 118 parts of tin in *agua regia* to a solution of 250 parts of copper sulphate, with subsequent addition of sodium hydroxide in excess.

Chromium-tin compounds. A so-called chromium stannate or 'pink colour,' used for producing a blood-red colour in pottery glaze,

is prepared by heating a mixture of 10 parts of stannic oxide, 34 parts of calcium carbonate, 5 parts of silica, 1 part of alumina, and 3-4 parts of crystallised potassium chromate for several hours in a closed crucible. The red compound produced gives a fine rose-coloured product when washed with dilute hydrochloric acid.

A substance known as *mineral lake*, possessing a fine lilac colour, is used in colouring paper hangings and for oil painting. It consists of a mixture of chromium oxide and excess of stannic oxide, and can be prepared by igniting together 1 part of the former with 50 of the latter (Leykauf, J. pr. Chem. 1892, 19, 127), or by dissolving potassium chromate in 5 or 6 parts of water, and adding this solution to a solution of stannous chloride until precipitation ceases. The damp, washed precipitate is ground with half its volume of nitre, and dried, and the finely-powdered mixture is thrown in small portions into a crucible heated to redness and containing some potassium nitrate. After pouring off the supernatant fused salt, the pale-yellow residue is washed free from alkali, and is calcined at a strong heat in a luted crucible until it becomes dense and acquires the desired colour.

A series of 'pinks' have been prepared by moistening equal portions of calcium stannate or mixtures of tin dioxide and whiting with varying proportions of a solution of ammonium dichromate. The mixtures are then dried, fired, cooled, and washed with hot water. The products all contain a more or less constant quantity of chromium, and it is probable that they consist of the colouring agent, chromium oxide, resting on a base of stannic oxide (Leithbridge, Trans. Engl. Ceramic Soc. 1903-1904, 9; see also Hull, Trans. Amer. Ceramic Soc. 1902, 4, 230).

Stannates of many other metals and thio-stannates have also been obtained.

The powdery product of oxidation of tin with hot nitric acid, commonly described as metastannic acid, is a nitrate of metastannic acid, which on washing with water gives rise to metastannic acid as a secondary hydrolytic product. Metastannic acid obtained by the action of nitric acid (sp.gr. 1.40) on tin and careful washing with water, dried in air at ordinary temperature, has the composition $5\text{H}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$. It loses its water *in vacuo* over sulphuric acid. It is an amorphous powder, combining with hydrochloric and sulphuric acids with development of heat forming easily hydrolysable compounds. The action of hydrochloric acid on metastannic acid yields a *stannyl* chloride $5\text{SnO}_2 \cdot 2\text{HCl} \cdot 3\text{H}_2\text{O}$ or $\text{Sn}_2\text{O}_3(\text{OH})\text{Cl}_2$. According to Weiser (J. Phys. Chem. 1922, 26, 654), stannic and metastannic acids are not acids, but are hydrated stannic oxides, the composition and properties of which are determined by conditions of formation. There are no definite hydrates of stannic oxide. Hydrated stannic oxide adsorbs colloidal gold, silver, and platinum, forming purple masses, the most common of which is the purple of Cassius.

Application to purple of Cassius of Debye and Scherrer's X-ray method yields an impression, analysis of which shows that this substance does not contain gold in chemical combination, but consists of a mixture of colloidal gold and colloidal stannic acid (A. Huber, Phys. Zeits. 1924, 25, 35; Sci. Abstr. 1924, 27, 657).

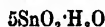
It is also obtained by the ready isomerisation of stannic acid, as when a hydrochloric or hydrobromic acid solution of the latter is allowed to stand (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 376).

It is insoluble in ammonia, except when freshly precipitated from a cold solution of a metastannate by an acid, but dissolves in alkaline hydroxides and carbonates, with formation of metastannates.

A colloidal metastannic acid is known (v. Graham, Phil. Trans. 151, 213; Van Bemmelen, Rec. trav. chim. 7, 87; Liebschutz, Chem. News, 1910, 102, 213; Kreis, Schweiz. Chem. Zeit. 1919, 389).

The meta- acid is said to have a tendering effect on silk fibres (Heermann, Färber-Zeit. 1908, 19, 318; Bayerlein, *ibid.* 1908, 18, 241).

The salts of metastannic acid appear to indicate that the acid has the formula:



The metastannates are difficultly crystallisable. When strongly heated, they decompose into stannic oxide and the base. Potassium metastannate $5\text{SnO}_2 \cdot \text{K}_2\text{O} \cdot 4\text{H}_2\text{O}$ is a strongly alkaline salt obtained by dissolving the acid in potash. It is precipitated from aqueous solution by a neutral alkaline salt or by ammonium chloride. Sodium metastannate



is a slightly soluble granular salt obtained like the potassium salt. A hard gummy precipitate of the composition $\text{Na}_2\text{Sn}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$ is obtained by addition of caustic soda to a solution of the above compound of hydrochloric acid and metastannic acid.

Thiometastannates are also known.

Perstannic acid $\text{HSnO}_4 \cdot 2\text{H}_2\text{O}$ is formed when stannic acid is treated with excess of 30 p.c. hydrogen peroxide and the mixture heated to about 70°. On heating to 100° it yields the acid $\text{H}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. The alkali stannates when similarly treated form the salts corresponding to these acids (Tanatar, Ber. 1905, 38, 1184). When concentrated alkali stannates are electrolysed at low temperature with a low current density they also form perstannates (Coppadoro, Gazz. chim. ital. 1908, 38, i. 489, and *l.c.*).

Salts of tin with oxyacids. These salts, although numerous, are of little technical importance, but a number of solutions containing them are used in dyeing and calico-printing. Stannous sulphate SnSO_4 is obtained as a crystalline powder by evaporating *in vacuo* a solution of tin or stannous hydroxide in dilute sulphuric acid. Stannic sulphate $\text{Sn}(\text{SO}_4)_2$ is obtained as a white salt, soluble in dilute sulphuric acid but mostly precipitated on dilution, by dissolving the hydroxide in sulphuric acid. According to Litte (Compt. rend. 1887, 104, 172), a solution of stannic hydroxide in warm dilute sulphuric acid (1-8) deposits, on concentration, first radiating needles, then rhomboidal lamellae, and finally hexagonal prisms, all colourless and all possessing the composition $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. He has obtained the same product by the action of sulphuric acid on metastannic acid. The crystals deliquesce to a clear liquid. The solution is decomposed, on dilution, with precipitation of the hydroxide. A number of double tin sulphates are known (Weinland and Kühl, Ber.

1906, 39, 2951; Zeitsch. anorg. Chem. 1907, 54, 244). *Stannous nitrate* $\text{Sn}(\text{NO}_3)_2$ is obtained by dissolving tin or stannous hydroxide in dilute nitric acid (R. Weber, J. pr. Chem. [ii.] 26, 121; Walker, Chem. Soc. Proc. 1893, 114; Jngel, l.c.; Kleinschmidt, Monatsh. 1918, 39, 149).

Metastannic nitrate $5\text{SnO}_2 \cdot 2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Sn}_2\text{O}_5(\text{OH})_2(\text{NO}_3)_2$ is prepared by the action of hot nitric acid on tin; the compound obtained from tin and cold nitric acid consists of a mixture of stannyl nitrate $\text{SnO}(\text{NO}_3)_2$ and metastannic nitrate.

A basic salt of the composition $2\text{SnO} \cdot \text{N}_2\text{O}_5$ is obtained as a white crystalline precipitate by adding a solution of sodium carbonate to the neutral salt in quantity insufficient for complete precipitation. It may also be obtained by digesting the normal salt with stannous hydroxide. It deflagrates at 100° , or on friction. *Stannic nitrate* $\text{Sn}(\text{NO}_3)_4$ crystallises in silky tablets from a solution of stannic hydroxide in nitric acid.

It is also formed by dissolving tin in 70 p.c. nitric acid (Montemartini, Gazz. chim. ital. 1892, 22, 384). Even at the ordinary temperature it slowly changes into the meta-salt, and for this reason the white bulky precipitate which it yields with aqueous sodium hydroxide may not dissolve completely in an excess of the reagent; at 45° the change in the stannic nitrate is so rapid that the solution suddenly gelatinises; the transformation is complete by prolonged heating at 100° .

The so-called 'nitrate of tin' or 'physic' used by dyers is a mixture of stannous and stannic chlorides (*v. Stannous chloride, infra*). A solution of tin in nitric acid is, however, also used in dyeing (*v. Crookes, Handb. of Dyeing and Calico Printing, 1874, 527*).

Stannous sulphide SnS is obtained as a tough, crystalline, bluish-grey fusible mass by heating tin with sulphur, or in crystalline scales by fusing the sulphide so obtained with stannous chloride and treating the product with dilute hydrochloric acid. The crystalline sulphide may also be obtained by heating the amorphous form in the electric furnace (Mourlot, Compt. rend. 1897, 124, 768). It is obtained as a brown powder, which blackens on drying, by precipitating stannous chloride with sulphuretted hydrogen.

Stannous sulphide is insoluble in normal ammonium sulphide, but dissolves in the yellow sulphide and in alkaline polysulphides (*v. Ditte, Compt. rend. 1882, 94, 1419*), and, with evolution of sulphuretted hydrogen and formation of stannous chloride, in hot hydrochloric acid. Hydrogen chloride acts similarly on the warmed, but not on the cold, sulphide (Ditte, *ibid.* 1883, 97, 42).

Stannous sulphide is sometimes soluble, at other times insoluble, in sodium hydroxide, the cause of this variation being unknown (Perkin, J. Soc. Chem. Ind. 1901, 425).

Pure stannous sulphide has m.p. 880° (Pélabon, Compt. rend. 1906, 142, 1137). It is slightly radioactive (Campbell, Proc. Cambridge Philos. Soc. 1906, 13, 282).

Orthorhombic crystals of stannous sulphide are occasionally met with in tin furnaces, and were supposed at one time to be an allotropic form of tin (*cf. Spencer, Min. Mag. 1921, 19, 113*).

Stannic sulphide SnS_2 cannot be prepared by simply heating tin and sulphur together, because the heat generated is sufficient to reduce the disulphide to monosulphide, but it may be so obtained when sufficient ammonium chloride or other volatile substance is present to moderate the action. Woulfe (Phil. Trans. 1771, 61, 114; also Gmelin's Handbook, 5, 79) describes a number of methods of preparing this compound, which is used as a bronze powder for bronzing articles of gypsum, wood, &c.

Various mixtures of tin chloride and sulphur, or tin, sulphur, and ammonium chloride, or tin amalgam or tin sulphide with sulphur and ammonium chloride, are heated in retorts or covered crucibles, at first gently for a few hours, then more strongly, but not quite to redness. On cooling the greater portion of the sulphide is at the bottom, but the purer and finer crystals are found sublimed at the top.

Crystalline stannic sulphide, sp.gr. 4.425, is often known as 'Mosaic gold,' *aurum mosaicum*, or *musivum*. For a reddish shade, 50 grms. of 50 p.c. tin amalgam, 25 of crystallised stannous chloride, 35 of ammonium chloride, and 35 of sulphur are finely powdered together and ignited gradually in a glass retort covered with asbestos, in the flame of a large blow-pipe, which is moved about periodically. During the operation the colour of the mass should be dark brown. If it becomes black owing to the formation of stannous sulphide, the flame should be lowered. For yellowish shades, 50 grms. of crystallised stannous chloride and 25 grms. of flowers of sulphur are employed. The yield is 57 p.c. of the theoretical (Langutt, Zeitsch. angew. Chem. 1897, 557). V. GOLD, MOSAIC.

When heated, stannic sulphide sublimes, with partial decomposition into sulphur and stannous sulphide. It dissolves readily in alkalis, but not in acids, except *aqua regia*. It fuses in a current of chlorine, and absorbs 6 molecules of the gas, forming a yellow crystalline compound of the composition $\text{SnCl}_4 \cdot 2\text{SnCl}_2$ (Rose, Pogg. Ann. 42, 517). When heated with iodine in a current of carbon dioxide it gives a brown, crystalline, fusible mass of the composition $\text{SnS}_2 \cdot \text{I}_2$ (Schneider J. pr. Chem. [i.] 79, 419).

The dirty-yellow precipitate obtained by passage of sulphuretted hydrogen through a solution of a stannic salt consists of a mixture of stannic sulphide and stannic hydroxide; this dissolves in alkaline sulphides, with formation of thiostannates (Kühn, Annalen, 1852, 84, 110), and also in alkalis and hydrochloric acid. Ditte (Compt. rend. 1882, 95, 641) describes several double sulphides or thiostannates and also seleniothio-stannates.

Hydrogen chloride or bromide convert the sulphide into the corresponding halide (Kelley and Smith, Amer. Chem. J. 1896, 18, 1096).

When stannic sulphide is allowed to remain in contact with ammonia, filtered, and the filtrate acidified, a white mass of an amorphous stannic sulphide is formed. It dissolves readily in ammonia to an orange-red solution, and becomes yellow on drying (Schmidt, Ber. 1894, 27, 2739; Chem. Zentr. 1907, i. 397; Materne, *ibid.* 1906, ii. 557; Lang and Carson, J. Soc. Chem. Ind. 1902, 1018). When dried in air it loses a little sulphur and becomes dark brown, hard, and brittle. This sulphide behaves like a

colloidal sulphide. Colloidal stannic sulphide has been obtained (Spring, Ber. 1883, 16, 1142; Schneider, Zeitsch. anorg. Chem. 1894, 5, 83; see also Biltz, Chem. Zentr. 1904, i. 1040).

Tin sesquisulphide Sn_2S_3 is obtained by gentle ignition of 3 parts of stannous sulphide and 1 of sulphur in a retort. It forms a yellowish-grey mass of metallic lustre (Antony and Niccoli, Gazz. chim. ital. 1892, 22, ii. 408). A sub-sulphide, Sn_2S_2 , of a grey colour, and crystalline, has been observed to occur (Epprecht, Chem. Zeit. 1915, 39, 341).

Stannous selenide SnSe is obtained with incandescence when selenium is heated with tin, as a light-grey lustrous body of crystalline fracture, not reducible by hydrogen. It is obtained as a dark-brown precipitate, which becomes nearly black on drying, by passing seleniuretted hydrogen into stannous chloride solution. It dissolves in alkalis and alkaline sulphides (v. Uelsmann, Annalen, 1860, 116, 124; Pélahon l.c.).

Stannic selenide SnSe_2 is obtained by passing seleniuretted hydrogen into stannic chloride solution as a yellowish-red precipitate which dries to a brown powder, soluble in caustic alkalis and alkaline sulphides, and forming stannous selenide when heated in hydrogen.

According to Little (Annalen, 1859, 112, 213), it is obtained as a tin-white, lustrous, easily-fusible mass, unaffected by hydrochloric acid, but readily decomposed by nitric acid, by heating tin in selenium vapour. Ditte (Compt. rend. 1882, 95, 641; *ibid.* 1887, 104, 174) describes some double selenides corresponding with the thiostannates (v. *Stannic sulphide*).

A telluride is also known.

Stannous chloride SnCl_2 is obtained in the anhydrous condition by heating tin in hydrogen chloride, or by heating a mixture of equal weights of 'feathered' (i.e. granulated) tin or filings and mercuric chloride; and in monoclinic prisms of the composition $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (O. Henry, J. Pharm. 12, 134) by evaporating a solution of tin in hydrochloric acid.

Stannous or stannic chloride may be obtained as desired by the following process: Stannous chloride, formed by the action of a solution containing chlorine on tin, is subjected to the action of a gaseous or fluid mixture containing free chlorine, hydrochloric acid, and air or oxygen (Young, J. Amer. Chem. Soc. 1901, 23, 119, 450). Stannic chloride is thus formed which when made to react with tin reforms stannous chloride (U.S. Pats. 810454, 810455, 810456, 810897, 1906; Df. R. P. 184484). For other methods, see D. R. PP. 176456, 176457, 181876, 188018.

The crystals melt at 40° , and at 100° lose most of their water, together with a little hydrochloric acid. When dried *in vacuo*, or over sulphuric acid, they become anhydrous.

The anhydrous chloride fuses at 249.3° to an oil which boils at $617-628^\circ$ (Carnelley and Carleton Williams, Chem. Soc. Trans. 1879, 563), or, according to Biltz and V. Meyer (Ber. 1888, 21, 22), at 606.1° . The anhydrous chloride is sometimes called 'butter of tin,' although that term is usually applied to the hydrated tetrachloride. Stannous chloride is soluble in water and alcohol. On dilution, the aqueous solution becomes turbid, from precipitation, with separation of hydrochloric acid, of a basic chloride

$2\text{SnO} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, which is also formed when the clear solution is exposed to the air. Mallet (Chem. Soc. Trans. 1879, 524) has observed a gelatinous deposit of the composition $\text{SnO}_2 \cdot \text{HCl}$, to which he has applied the term *chlor-stannic acid*, in a solution of stannous chloride after long standing. Donath (Rep. Anal. Chem. 7, 77) considers that this compound is produced, together with stannic hydroxide, by the action of light on aqueous stannous chloride.

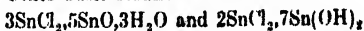
Keller (J. Amer. Chem. Soc. 1917, 39, 2354) found a crystalline deposit of $\text{SnCl}_2 \cdot \text{SnO}$, in cavities in a piece of tin found in an aboriginal cemetery in Florida.

R. Engel (Compt. rend. 1888, 106, 1398) has obtained a compound of the composition



which he calls *chlorostannic acid*, by passing chlorine over the hydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The crystals fuse to a clear liquid having the above composition, and depositing, when cooled to -40° , slender silky needles which melt at about -27° . According to Ditte (*ibid.* 1883, 97, 42), however, the liquid contains a chloride of the composition $\text{SnCl}_2 \cdot \text{H}_2\text{O}$, which is also formed by the action of concentrated hydrochloric acid on the chloride $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Other basic stannous chlorides are



(Carson, J. Amer. Chem. Soc. 1919, 41, 1969).

When stannous chloride is electrolysed crystalline tin can be obtained (Sapozhnikoff, J. Russ. Phys. Chem. Soc. 1905, 37, 153).

Stannous chloride forms crystalline double chlorides with the alkalis (v. Benas, Chem. Zentr. 1884, 957, forming salts of the composition $\text{SnCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$). Similar compounds are formed with NH_4Cl (Rimbach and Fleck, Zeitsch. anorg. Chem. 1915, 94, 139). It absorbs dry ammonia, with formation of a compound of the composition $\text{SnCl}_2 \cdot \text{NH}_3$, and also $\text{SnCl}_2 \cdot 2\text{NH}_3$ (Naumann, Ber. 1910, 43, 313).

A third compound, $3\text{SnCl}_2 \cdot 2\text{NH}_3$, is formed by the action of gaseous ammonia on stannous chloride between 120° and 300°C . It is a crystalline mass of reddish-brown colour, powerfully double-refractive, and appears to be the most stable of the compounds of ammonia and stannous chloride (Sofianopoulos, Compt. rend. 1911, 152, 865).

Stannous chloride is soluble in alcohol and in ether; the latter solution gives a brownish-red ring when added to hydrochloric acid containing 1/50 mgrm. of arsenious acid (Jong, Zeitsch. anorg. Chem. 1902, 41, 596).

Like other stannous salts, stannous chloride is a strong reducing agent and is employed as such, both for the reduction of organic and inorganic compounds. It is also used in the analysis of a number of substances (Henriet, Compt. rend. 1901, 132, 966; Weil, *ibid.* 1902, 134, 115).

A small quantity of stannous chloride is said to increase the yield of alcohol in fermentation processes; it also accelerates the revivification of the yeast sown in must, and cultures taken from the yeast so formed retain a similar property for a certain length of time (Gimel, Compt. rend. 1908, 147, 1324).

Stannous chloride and other stannous salts

are largely used in dyeing and calico-printing under the name 'tin-salts' or 'tin crystals' (Dreher, *Färber-Zeit.* 7, 145; Reisz, *ibid.* 221, 222; Binder, *Bull. Soc. Ind. Mulhouse*, 1900, 92; Paterson, *J. Soc. Dyers Col.* 1906, 22, 188; Coberti, *J. Soc. Chem. Ind.* 1899, 829).

Stannic chloride SnCl_4 was first prepared by Libavius in 1605, who obtained it by distilling a mixture of tin or its amalgam with excess of mercuric chloride; he termed the product *Spiritus argenti vivi sublimati*. It may also be prepared by the action of chlorine (Lorenz, *Zeitsch. anorg. Chem.* 1895, 10, 44; Beckmann and Geib, *ibid.* 1906, 51, 96); or phosphorus pentachloride on tin (Goldschmidt, *Chem. Zentr.* 1881, 489); or by the action of chloroform on stannic oxide (Renz, *Ber.* 1906, 39, 249). Technically, it is generally prepared by the action of chlorine or hydrochloric acid on tin-plate waste or tin waste residues from dye works and a large number of patents have been registered for this purpose (see *Fr. Pats.* 371067, 1906; 392615, 401125, 405851, 406300, 1909; Heermann, *Färber-Zeit.* 1907, 18, 34; *U.S. Pats.* 884756, 877261, 877248, 1908; 976990, 958986, 1910; *D. R. P.* 222838; *J. Soc. Chem. Ind.* 1907, 253; *ibid.* 1908, 100; *ibid.* 1909, 21, 1087; *ibid.* 1910, 424, 1105; see also *U.S. Pats.* 883140, 883141, 1908; *Fr. Pats.* 386594, 388089, 1908).

Stannic chloride may also be prepared by the action of sulphur dioxide upon stannous chloride in presence of strong hydrochloric acid

$$3\text{SnCl}_2 + \text{SO}_2 + 6\text{HCl} = 3\text{SnCl}_4 + 2\text{H}_2\text{O} + \text{H}_2\text{S}$$

(Smythe and Wardlaw, *Proc. Durham. Phil. Soc.* 1914, 5, 187).

The chloride distils over as a colourless mobile liquid, boiling at 113.89° at 760 mm. pressure (Thorpe, *Chem. Soc. Trans.* 1880, 37, 331), and solidifying at -33° to small white crystals (Besson, *Compt. rend.* 1889, 109, 940).

The liquid has sp. gr. 2.2788 at $0^\circ/4^\circ$ (Thorpe, *l.c.*), and, owing to its high refractive index, presents a very brilliant appearance.

When exposed to the air, it emits dense white fumes, and is finally converted into a crystalline hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Lewy, *Compt. rend.* 1845, 21, 369), which is also obtained, with evolution of heat, by mixing stannic chloride with one-third its weight of water. This hydrate is sometimes known as 'butter of tin,' or, by the dyers, as 'oxymuriate of tin.' Hydrates of the composition $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ are also known. For the sp. gr. of various solutions of this salt, see Heerman (*Chem. Zeit.* 1907, 31, 680).

On hydrolysis, it first forms the intermediate compound SnCl_3OH , and then stannic acid; by alcoholysis it gives the compound SnCl_3OEt (Pfeiffer, *Ber.* 1905, 38, 2466; von Biron, *J. Russ. Phys. Chem. Soc.* 1906, 37, 963).

Stannic chloride forms crystalline double chlorides, sometimes called *chloro-stannates* or *stannichlorides* with the alkaline chlorides (Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, v. 13, ii. 307; von Biron, *J. Russ. Phys. Chem. Soc.* 1904, 36, 489, 933; *ibid.* 1905, 37, 963, 994, 1036; Weimland and Bames, *Zeitsch. anorg. Chem.* 1906, 62, 250; Druce, *Chem. News*, 1918, 117, 193); thus, $\text{SnCl}_4 \cdot 2\text{KCl}$ and



the latter forming the 'pink salt' formerly much used by dyers.

Stannic chloride dissolves phosphorus and iodine, and mixes with bromine and carbon disulphide. It converts mercury into calomel, and is itself decomposed by nitric acid, with precipitation of metastannic acid. Among the substances produced by direct combination with other compounds may be mentioned $\text{SnCl}_4 \cdot 2\text{NH}_3$, a soluble volatile solid (Rose, *Pogg. Ann.* 16, 63); $3\text{SnCl}_4 \cdot 2\text{PH}_3$, a yellow fuming solid (Rose, *ibid.* 24, 159); $\text{SnCl}_4 \cdot \text{N}_2\text{O}_5$, a yellow amorphous mass; $\text{SnCl}_4 \cdot \text{SO}_2$, a white solid (Rose, *ibid.* 44, 320); $\text{SnCl}_4 \cdot \text{PCl}_5$ and $\text{SnCl}_4 \cdot \text{POCl}_3$ (Cassellmann, *Annalen*, 1852, 83, 257); $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$, a white crystalline compound (Coldridge, *Phil. Mag.* [v.] 29, 383, 480). A yellow crystalline substance $\text{SnCl}_4 \cdot 2\text{SCl}_2$, fusing below 30° , is obtained by the action of chlorine on stannic sulphide (Rose, *Pogg. Ann.* 42, 517).

When a cooled solution of stannic chloride in chloroform is treated with nitric peroxide, the compound $3\text{SnCl}_4 \cdot 4\text{NOCl}$ is formed (Thomas, *Compt. rend.* 1896, 122, 32), whilst if such a solution is treated with nitrogen sulphide dissolved in chloroform, red crystals of the substance $\text{SnCl}_4 \cdot 2\text{N}_2\text{S}_4$ are deposited (Davis, *Chem. Soc. Trans.* 1906, 1576).

Stannic chloride absorbs large quantities of chlorine at low temperatures, with considerable increase in volume and lowering of the melting-point (Besson, *Compt. rend.* 1889, 109, 940).

Stannic chloride is used in dyeing as a mordant, and silk is weighted with it before dyeing (Froenkel and Fasal, *J. Soc. Chem. Ind.* 1898, 148; *ibid.* 1904, 899). Its use for this purpose is said to have been discovered by the Dutch chemist, Drebbel, in 1630, who found that cochineal gives a permanent brilliant red dye in the presence of dilute stannic chloride.

A patent was taken out in England as early as 1748 by O. Pawl (Specification No. 630, 1748) for the use of tin dissolved in *aqua fortis*, with addition of ammonium chloride, for dyeing scarlet.

The older methods of preparing tin salts for this purpose, whereby tin is dissolved in excess of hydrochloric acid, and the solution is oxidised by means of chlorates, have the disadvantage of producing a very impure product. The mordanting and weighting is due only to the stannic chloride and the impurities tend to weaken the fibres, to make the latter more sensitive to light, and to bring about the gradual deterioration in the strength of the material. To avoid this, Sperry has devised a special apparatus whereby pure anhydrous stannic chloride may be prepared by the treatment of impure tin-bearing materials with ordinary commercial chlorine (*J. Soc. Chem. Ind.* 1908, 312, 404, 628, 749, 978; *Eng. Pat.* 389188; *U.S. Pats.* 882354, 887538, 883391. For Fig. and description of apparatus, see *J. Soc. Chem. Ind.* 1908, 313). From the pure stannic chloride thus prepared all the compounds of tin needed by dyers may be obtained in pure condition.

According to Fiehler and Müller (*Arch. Sci. phys. nat.* 1916, [iv.] 42 123), the weighting of silk by steeping it in a solution of stannic chloride is due to a true chemical combination between the stannic chloride and the fibroin and its component amino-acids, followed by hydrolysis

during the washing process. After the hydrolysis the stannic acid is precipitated in the silk and the fibroin is regenerated and is capable of taking up more stannic chloride.

A solution consisting of stannic and stannous chloride, obtained by dissolving tin in *aqua regia*, is used in the preparation of fuchsine under the name 'nitrate of tin' or 'physic' (see above).

It is now more usual, however, to employ the crystalline pentahydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

A solution consisting of stannous chloride, containing more or less stannous chloride, and used in dyeing under the name 'oxychloride of tin' or 'pink cutting liquid,' is prepared by adding 1 part of stannous chloride to $1\frac{1}{2}$ parts of nitric acid of sp.gr. 1.31 in portions, with constant stirring, to prevent boiling over from the violence of the action; or by dissolving 337 parts of stannous chloride in 300 parts of hydrochloric acid (20°Tw.), with the aid of a minimum of water, and adding gradually 58 parts of potassium chlorate.

In small quantities stannic chloride may be added to the sizing mass for cotton warps in order to prevent the too rapid decomposition of the size (Textile Colorist, 1893, 15, 7).

For the detection of tin in mordanted cloth, see Paterson (J. Soc. Dyers, 1906, 22, 189); Silbermann (Bull. Soc. chim. Mulhouse, 1906, 76, 357).

A rapid and delicate method for detecting sodium chloride in commercial stannic chloride, consists in precipitating the former with 99.5 p.c. alcohol saturated with hydrogen chloride (Heermann, Chem. Zeit. 1907, 31, 27).

Stannous bromide SnBr_2 is obtained in solution by dissolving tin in hydrobromic acid (Balard, Ann. Chim. [ii.] 32, 337). It may be obtained as an anhydrous, pale-yellow, crystalline mass by heating tin in hydrobromic acid vapour and re-distilling the product (Freyer and Meyer, Zeitsch. anorg. Chem. 1892, 2, 1).

According to Rayman and Preis (Annalen, 1884, 223, 323), it melts at 215.5° to a pale-yellow oily liquid, of sp.gr. 5.117 at 17° . According to Carnelley and Carleton Williams (Chem. Soc. Trans. 1879, 564), it melts at 259° , and boils at 617° – 634° .

A hydrate $\text{SnBr}_2 \cdot \text{H}_2\text{O}$ separates in needles of thin plates from the greenish solution of tin in warm concentrated hydrobromic acid. It loses its water in dry air, or when heated to 70° – 80° . It dissolves in a little water, but is decomposed by excess, with precipitation of a gelatinous precipitate (v. Benas, Chem. Zentr. 1884, 957). A hydrate $\text{SnBr}_2 \cdot 2\text{H}_2\text{O}$, crystallising in large monoclinic tables, is also obtained from the solution of tin in hydrobromic acid (Benas, l.c.).

Benas, Rayman and Preis have also described compounds of stannous bromide with potassium and ammonium bromides.

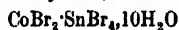
Stannic bromide SnBr_4 was discovered in 1826 by Balard (Ann. Chim. [ii.] 32, 337). It is obtained by adding bromine drop by drop to strips of tin, the temperature being kept between 35° and 59° (Lorenz, Zeitsch. anorg. Chem. 1895, 9, 366); or preferably, on account of the violence of the action with pure bromine, by gradually adding the tin to a solution of bromine in carbon disulphide, or by passing

the vapour of bromine over heated tin (Carnelley and O'Shea, Chem. Soc. Trans. 1878, 55).

Stannic bromide forms a white iridescent deliquescent mass, which, by distillation, is obtained in small, well-formed, highly lustrous crystals, melting at 30° and boiling at 210° (uncorr.) (Carnelley and O'Shea, l.c.), or at 203° (corr.) (Rayman and Preis, Chem. Zentr. 1882, 773), and having a sp.gr. of 3.349 at 3.5° (Rayman and Preis, l.c.).

It fumes in the air, and dissolves readily in water. The solution deposits stannic hydroxide on heating or after standing. A hydrate $\text{SnBr}_4 \cdot 4\text{H}_2\text{O}$ is obtained in colourless transparent, fuming crystals, by exposing the anhydrous bromide to moist air, or by dissolving in a little water and evaporating over sulphuric acid. Oxybromides $\text{Sn}_2\text{Br}_3\text{O}_{12}$, H_2O and $\text{SnBr}_3\text{O}_{10}$, H_2O , obtained from stannic bromide, and a compound $\text{SnBr}_2 \cdot 2\text{NH}_3$, obtained by absorption of ammonia by the warmed bromide, are also known (Rayman and Preis, l.c.).

Stannic bromide unites with ether to form a deliquescent crystalline body $\text{SnBr}_4(\text{C}_2\text{H}_5)_2\text{O}$ (Nickles, Compt. rend. 1861, 52, 809). By evaporating solutions of the mixed bromides, Raymond and Preis (l.c.) have obtained the following double bromides or stannibromides: $2\text{NaBr} \cdot \text{SnBr}_2 \cdot 6\text{H}_2\text{O}$, in pale-yellow, soluble crystals; $\text{CaBr}_2 \cdot \text{SnBr}_2 \cdot 6\text{H}_2\text{O}$, in slender deliquescent needles; $\text{MgBr}_2 \cdot \text{SnBr}_2 \cdot 10\text{H}_2\text{O}$, in pale-yellow, deliquescent tables; $\text{MnBr}_2 \cdot \text{SnBr}_2 \cdot 6\text{H}_2\text{O}$, in large, pale-yellow, deliquescent crystals; $\text{FeBr}_2 \cdot \text{SnBr}_2 \cdot 6\text{H}_2\text{O}$, in greenish, granular crystals; $\text{NiBr}_2 \cdot \text{SnBr}_2 \cdot 8\text{H}_2\text{O}$, in apple-green, granular, deliquescent crystals; and



in yellowish-red, deliquescent tablets (see also Leteur, Compt. rend. 1891, 113, 540).

Stannous iodide SnI_2 is obtained by dissolving tin in concentrated hydriodic acid. At the ordinary pressure solution is extremely slow, but it proceeds more rapidly in a sealed tube at 120° – 150° (Wöhler and Dünhaupt, Annalen, 1853, 86, 374). It may also be obtained in yellowish-red needles, slightly soluble in water, and readily soluble in solutions of alkaline chlorides and iodides, and in hydrochloric acid, by addition of potassium iodide in slight excess to a concentrated solution of stannous chloride (Warden, Pharm. J. 1897, 58, 61). The aqueous solution is decomposed by much water, with separation of hydriodic acid and a yellow, insoluble body the composition of which varies with the amount of water present (Personne, Compt. rend. 1862, 54, 216).

The formation of the iodide may be used as a delicate test for tin. One c.c. of the solution to be tested is treated with 0.5 c.c. of 5 p.c. potassium iodide solution and 0.5 of strong sulphuric acid added through a pipette reaching to the bottom of the test-tube. In presence of tin a yellow precipitate is produced at the plane of contact of the two layers (Heller, Zeitsch. Chem. 1922, 61, 180).

Stannous iodide melts at 316° (Carnelley and Carleton Williams, Chem. Soc. Trans. 1879, 564) and volatilises at a red heat. It absorbs dry ammonia, with formation of a white body having the composition $2\text{NH}_3 \cdot \text{SnI}_2$ (Rammelsberg, Pogg. Ann. 48, 169; Ephraïm and Schmidt,

Ber. 1909, 42, 3856). It unites with other metallic iodides, with hydrogen iodide (Young, J. Amer. Chem. Soc. 1897, 19, 851), and with stannous chloride.

Stannic iodide SnI_4 is obtained in yellowish-red octahedra by heating tin filings, preferably moistened with carbon disulphide or tetrachloride, with iodine to a temperature above 50° .

It has sp.gr. 4.696 at 11° (Bödeker, Die Beziehung zwischen Dichte und Zusammensetzung, &c., Leipzig, 1860), m.p. 146° and b.p. 295° (Personne, J. 1882, 172), m.p. 143° , b.p. 341° (corr.) (Emich, Monatsh. 1904, 25, 907). It sublimes at 180° .

It dissolves in carbon disulphide, carbon tetrachloride, alcohol, chloroform, and benzene. Water decomposes it into stannic hydroxide and hydriodic acid.

Its formation under certain conditions may be used as a delicate test for tin (Mazuir, Ann. Chim. anal. 1919, [ii.] 2, 9).

By the action of ammonia on stannic iodide, dissolved in carbon disulphide, a white substance $\text{SnI}_4 \cdot 8\text{NH}_3$, insoluble in water, is formed (Ephraim and Schmidt, l.c.).

Stannous fluoride SnF_2 is obtained in small, opaque, white, monoclinic tables of sweetish astringent taste, by evaporating a solution of stannous hydroxide in hydrofluoric acid.

Stannic fluoride SnF_4 is obtained in aqueous solution by dissolving the hydrated dioxide in hydrofluoric acid; or as a hygroscopic, white crystalline substance by the action of anhydrous hydrofluoric acid on stannic chloride (Ruff and Plato, Ber. 1904, 37, 673). It has sp.gr. 4.78 at 19° , b.p. 705° , but sublimes below this temperature. It combines with other fluorides forming a characteristic series of crystalline double salts, the *stannifluorides*, which are isomorphous with the corresponding fluorides of titanium, germanium, zirconium, and silicon (Marignac, J. 1859, 110; Emich, Monatsh. 1904, 25, 907; Ruff and Albert, Ber. 1905, 38, 55; Hall and Smith, Chem. Zentr. 1905, ii, 1462).

A number of mixed halogen compounds, such as SnCl_2Br , SnCl_2I_2 , SnBr_2I , &c., have been described (Besson, Compt. rend. 1897, 124, 683; Lenormand, J. Pharm. Chim. 1898, [vi.] 8, 249; *ibid.* 1899, 10, 114). According to Auger (Compt. rend. 1909, 149, 860), most of these compounds are only mixtures, thus, $2\text{SnBr}_2\text{I}_2 = \text{SnBr}_4 + \text{SnI}_4$, &c.

Phosphides.—Tin combines directly with phosphorus, forming a series of phosphides, which are used for the production of phosphor-bronze (Emmerling, Ber. 1879, 12, 155; Natanson and Vortmann, *ibid.* 1877, 10, 1460; Künzel, Dingl. poly. J. 1888, 270, 166; D. R. P. 103966; Stead, J. Soc. Chem. Ind. 1897, 206).

Tin phosphide Sn_3P_2 has a silver-white colour, crystallises in spangles, sp.gr. 5.18, and begins to dissociate at 480° .

The phosphide SnP is also a crystalline substance, sp.gr. 4.10. It has a metallic appearance, begins to dissociate into phosphorus and Sn_2P_3 at 415° , and is attacked violently by fuming nitric acid (Jolibois, Compt. rend. 1909, 48, 636). Other phosphides have also been described.

Tin hydride.—According to Vaubel (Chem. Zeit. 1924, 48, 351), a 5 p.c. solution of acetic

acid or a 1 p.c. solution of oxalic acid in contact with tin-plate containing rusty spots causes the evolution of tin hydride. The same effect is produced with pure tin in contact with metallic Fe , but the amount of hydride formed is much smaller. It is suggested that the formation of tin hydride in solution may account for cases of poisoning by eating tinned foods that show rust-spots (J. Soc. Chem. Ind. 1924, 43, B. 560).

Tin hydride is formed invariably when nascent hydrogen is liberated in the presence of tin; its production when tin is dissolved rapidly in hydrochloric acid accounts for the peculiar odour of the gas (Kastner, 1821).

The compound obtained by the action of tin hydride on silver nitrate solution has approximately the composition SnAg_4 .

During the dissolution of polished tin in hydrochloric acid, a black powder is deposited which dissolves only very slowly even in the concentrated acid; it is suggested that this is a peculiar modification of the metal which is produced by the reduction of stannous chloride by nascent hydrogen (W. Vaubel, Ber. 1924, 57, (B) 515; cf. Paneth and Fürth, Chem. Soc. Abstr. 1923, 124, ii. 41; 1924, 126, ii. 414; Paneth and Rabinovitch, Ber. 1924, 57, [B] 1877; Chem. Soc. Abstr. 1925, 128, ii. 59).

An unstable tin carbonate Sn_2CO_3 is also known (Deville, Ann. Chim. 1852, [iii.] 35, 4, 48; see also Moissan, Compt. rend. 1897, 125, 840).

Quadrivalent tin and trivalent arsenic in dilute sulphuric or hydrochloric acid may be completely separated by treatment with hydrogen sulphide after the addition of a little hydrofluoric acid. The separation is effected by treating the solution in a platinum dish with 2.5 c.c. of 48 p.c. hydrofluoric acid, heating for a few minutes, and when cold diluting to 300 c.c. The solution is then treated with a rapid stream of hydrogen sulphide for 30 minutes, when arsenious sulphide alone is precipitated. The separation is both rapid and quantitative (Le R. W. McCay, J. Amer. Chem. Soc. 1923, 45, 1187-1191; J. Soc. Chem. Ind. 1923, 42, 690 A.).

ORGANIC COMPOUNDS OF TIN.

Stannous acetate, oxalate, citrate, and tartrate are employed in dyeing and calico-printing, being generally prepared by addition of an alkaline salt of the acid to a solution of stannous chloride, or by dissolving the precipitated hydroxide in the acid. Liechti and Schwitzer (Mittheilungen des Tech. Gew. Museums, 1886, 41) have indicated the value of some of these as mordants (Platsch, Zeitsch. anorg. Chem. 1899, 20, 308; Rosenheim and Aron, *ibid.* 1904, 39, 171; Paterson, l.c.; Henderson, Orr, and Whitehead, Chem. Soc. Trans. 1899, 555).

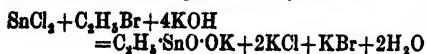
The ancient Egyptians are believed to have used basic tin citrates (prepared by the action of lemon juice or citric acid on tin), as a mordant, in dyeing the tapestries discovered in the tombs of Antinoë (Gillieron, Bull. Soc. Mulhouse, 1907, 77, 148). Basic tin citrate forms a very efficient mordant for yellow dyes on wool, giving pure intense colours.

Stannous formate is prepared by dissolving precipitated stannous hydroxide in dilute formic acid. It forms white anhydrous crystals, which decompose above 100° (Goldschmidt, Chem. Zeit. 1907, 31, 608).

Tin forms a number of alkyl derivatives of the type SnR_4 , $\text{SnR}^1\text{R}^2\text{R}^3$, &c. (Letts and Collie, Chem. Soc. Proc. 1886, 166; Pope and Peachy, *ibid.* 1903, 290; Polla, Ber. 1889, 22, 2915; Pfeiffer and Schnurmann, *ibid.* 1904, 37, 319; Werner, Zeitsch. anorg. Chem. 1898, 17, 99; Pfeiffer, *ibid.* 1910, 68, 102).

Methyl-stannic acid or **methyl-stannoxyllic acid** $\text{MeSnO}\cdot\text{OH}$ is formed when a mixture of methyl iodide, stannous chloride, and potassium hydroxide is allowed to stand for a day or two and the alkali is then removed by passing carbon dioxide into it. It can also be obtained pure by treating methyl-stannic bromide or iodide with ammonia. It is an odourless white powder, insoluble in water and organic solvents, but soluble in mineral and some organic acids, and in alkali hydroxides. With hydrobromic acid it yields **methyl-stannic bromide** or methyl stannibromide SnMeBr , m.p. 53° , which has also been obtained by other methods. The corresponding **iodide** or **iodoform**, MeSnI_3 , m.p. 86° , and the compounds SnMe_2Br_2 ; SnMe_2O ; SnMe_2SH and **methyl-stannichloroform**, m.p. $105^\circ\text{--}107^\circ$, b.p. $179^\circ\text{--}180^\circ$, have also been prepared (Pfeiffer and Lenhardt, Ber. 1903, 36, 1054, 3027; Pope and Peachy, Proc. Roy. Soc. 1903, 72, 7; Chem. Soc. Proc. 1900, 42, 116; Pfeiffer, Ber. 1904, 37, 4618; Shukoff, Ber. 1905, 38, 2691).

The potassium salt of **ethylstannic acid** is formed by the interaction of stannous chloride, ethyl bromide, and potassium hydroxide:



On treatment with dilute hydrochloric acid ethylstannic acid is formed as a white amorphous gelatinous substance, becoming yellowish-brown, transparent and horny on drying. For its salts, see Druce, Chem. Soc. Trans. 1921, 760).

The tin halogen compounds form a number of double compounds with aliphatic and aromatic amines (Cook, Amer. Chem. J. 1899, 22, 435; Richardson and Adams, *ibid.* 446; Slagle, *ibid.* 1898, 20, 633).

Pyridine stanni-iodide $(\text{C}_5\text{H}_5\text{N})_2\text{H}_2\text{SnI}_4$ is formed when an alcoholic solution of pyridine hydriodide is added to stannic iodide dissolved in alcoholic hydrogen iodide. It forms bluish-black glistening needles. The analogous **quinoline salt** $(\text{C}_8\text{H}_7\text{N})_2\text{H}_2\text{SnI}_4$ forms black needles. Both these compounds decompose gradually, liberating iodine (Rosenheim and Aron, Zeitsch. anorg. Chem. 1904, 39, 170). Similar chlorides, bromides and alkyl derivatives have also been prepared (Pfeiffer, Annalen, 1910, 376, 310; see also Hayes, J. Amer. Chem. Soc. 1902, 24, 360).

A number of other organic compounds of tin have also been prepared (Fischer, Monatsch. 6, 426; Werner and Pfeiffer, *l.c.*; Thiele and Dimroth, Annalen, 1899, 305, 102; Pfeiffer and Lenhardt, *l.c.*; Dillthey, Ber. 1903, 36, 925; Rosenheim and Levy, *ibid.* 1904, 37, 3662; Rosenheim and Schnabel, *ibid.* 1905, 38, 2777; Weinland and Bames, *l.c.*; Pfeiffer, Annalen, 1910, 376, 285; Druce, Chem. Soc. Trans. 1921, 755; Chem. Soc. Abstr. 1925, i, 798; Kraus and Gress, Chem. Soc. Abstr. 1925, i, 1394; Kraus, *ibid.* 1925, i, 1263, 1264; Vorländer, *ibid.* 1925, i, 1266).

According to Miak (Compt. rend. 1923, 176, 138) tin exists normally in the human organism; the liver has the highest content, followed by the stomach, kidneys, lungs, and brain. 0.03-0.04 grm. in 100 grms. of human viscera is not excessive in amount.

TINCAL v. BORAX.

TIN MORDANTS v. DYING.

TIN PLATES. *History.*—Although the art of tinning brass and copper was well known to the Romans (*v. supra*), the production of sheet iron coated with tin, or 'tin plate,' is of a considerably later period. The art was probably of German origin, and existed in Bohemia prior to 1620. About this time the manufacture was introduced into Saxony, and speedily developed into a thriving industry. Unsuccessful attempts, with which M. Réaumur was connected, were made to introduce the manufacture into France. About 1670 an English company was formed to start a tin-plate works in this country, and Mr. Yarranton was sent to Germany to learn the art. Works were started at Pontypool, and met with some success, but were stopped, owing to the grant of a patent for the manufacture to E. Hemming in 1691. Works were, however, once more started in 1720 at Pontypool, and these were gradually followed by others, particularly in South Wales, which gradually became the most important seat of the manufacture in the world. In the earlier processes of manufacture the plates were hammered by hand from iron made in the charcoal hearth, while the surface was cleaned from scale by immersion for several days in sour barley-water, instead of for a few minutes in dilute sulphuric acid, as at present.

In 1728, the *rolling* of sheets was introduced by Hanbury, of Pontypool, while sulphuric acid was substituted for barley-water in 1806. The rolling of tin plates as they leave the tin pot, which saves metal and improves the surface, was introduced by Morewood (who took out many patents for coating metals) in 1866, since which time a great variety of machines have been introduced for use in the tinning process.

Pickling, machines have superseded hand labour, while iron made in the old-fashioned open-hearth refinery (or puddling furnace for second qualities) has been generally replaced by steel. Siemens' steel was used about 1875, Bessemer steel about 1880, and basic steel was introduced a few years later (*v. P. W. Flower, Origin and Progress of the Manufacture of Tin Plates, J. Iron and Steel Inst.* 1886; C. Vogel, Stahl und Eisen, 29, 1097).

The M'Kinley Tariff, which came into force on July 1, 1891, led to a rapid development of the tin-plate industry in the United States, and a corresponding depression in South Wales. Other markets for Welsh tin plates were, however, gradually found, so that the industry has more than made up for the ground lost.

Production of tin plate.—The metal used for rolling into sheets was formerly, as above stated, wrought iron of special quality, which was made in refineries using only charcoal. At present very mild steel is employed, Siemens' steel being in most demand for this purpose. The bars are cut into suitable lengths, and each length is heated to redness, and then passed through 'chilled' rolls until its length is about

doubled; the plate is then folded across the middle, re-heated, and again rolled. The reheating, folding over, and rolling is repeated until a sheet of the proper thickness is obtained, sometimes as many as thirty-two thicknesses being rolled together as one piece in this way. The sheets are then cut to size with shears and separated, when they should part readily if the operation thus far has been successfully conducted. The 'rough black plates' so produced should be free from streaks or 'spilly' places, and should be uniformly coated over with a black scale of oxide. This is now removed by 'pickling' in warm dilute sulphuric acid for about 20 mins., and by subsequent washing and rubbing with sand and water. The sheets are next annealed in wrought-iron boxes, which are usually about 2 ft. square, but vary in size; the upper part is in the form of a bell for ready removal, and to prevent the entry of air the joint is stopped by being covered with sand. The annealing requires about 10 hours, and is conducted in a large furnace maintained at a cherry-red heat. The pots are then withdrawn and allowed to cool, after which the sheets are cold-rolled, to improve the surface and give the smoothness and uniformity which is necessary to produce a good tin plate. The cold-rolling renders the plates somewhat hard, and they are therefore annealed once more, usually in cast-iron pots, as it is not necessary in the second annealing to use so high a temperature or as long a time as in the first case. The sheets are now finally pickled in weaker sulphuric acid then was used in the previous pickling, and after being again rubbed with sand are immersed in water preparatory to tinning.

The tinning apparatus, or 'stow,' varies somewhat with the size and quality of the plates; with very large plates the bath of tin is contained in a basin-shaped pot, while for large sizes and ordinary qualities the plates are manipulated entirely by machinery during the tinning process.

The form of apparatus which was general in S. Wales until nearly the end of the nineteenth century, and which is still occasionally employed for purposes where a specially good tin plate is required to withstand atmospheric and similar influences, consists of five baths or pots, called respectively (1) the grease pot, (2) the tin-man's pot, (3) the washing pot, (4) the dipping pot, (5) the grease pot. Formerly two other pots were used, but these have been rendered unnecessary by the introduction of rolls. The grease pot contains melted grease, such as tallow or palm oil, and in this the sheets are dipped until all moisture has been removed and they are uniformly coated with grease. They are next dipped into the tin pot, which contains melted tin covered with a layer of grease, the latter being now usually replaced by a bath of zinc chloride or 'killed spirits.' The sheet now receives its first coating of tin, which, however, is not perfect, and to complete the tinning the sheet is dipped into the first compartment of the washing-pot, where it remains until a uniform coating is produced. The plate is now taken out and rapidly examined by the workman, who wipes over the surface with a brush, and to remove the marks of the brush rapidly dips the plate into the second compartment of the same

pot, which contains the best tin, and then transfers it to the grease pot, where it passes through a pair of rolls, which squeeze off the excess of tin and improve the surface. Formerly the plate remained for about 10 mins. in the grease pot, during which time the excess of tin drained off. The plate was afterwards transferred to the 'cold pot,' after which the lower part was inserted in the 'list' pot, which contains a little tin at a comparatively high temperature, and which rapidly removes the thick edge of tin which had accumulated at the bottom of the plate. The plates, after coating with tin, are then cleaned from grease, usually by rubbing with bran and finishing with the woolly skin of a sheep; they are afterwards separately examined for defects, and, after classification, are packed in the familiar flat wooden boxes and branded for market (*v. E. Trubshaw, J. Iron and Steel Inst. 1883, i. 252*).

For a description of the process of manufacture of tin plates in Germany, which does not materially differ from that above described, *v. Dingl. poly. J. 250, 231*.

For the method of tinning cast iron in Germany, *v. Schott, Stahl u. Eisen, 1919, 39, 119*.

In modern tin-plate works mild steel bars are reheated and rolled into 'black plates' by passing successively through two pairs of rolls for 'roughing' and 'finishing' respectively. In the United States sometimes only one pair of rolls is used; or two pairs of finishing rolls may be served by one pair of roughing rolls. The plates, after being separated, are pickled in diluted sulphuric or hydrochloric acid with the aid of pickling machines; they are then annealed under cover in iron or steel boxes, cold rolled, re-annealed at a lower temperature and again pickled, this time in weaker acid. The plates are then swilled in water and introduced, without drying, into the tinning machine. Of such machines there are various modifications. A typical form consists of two divisions connected with each other at the lower part of the pot which contains molten tin. The tin in the first division is coated with a tinning flux of zinc chloride, while that in the second division is covered with hot grease. The plate passes through the flux into and through the tin, emerging through the grease, and passing through rolls which remove the surplus tin, and give a smooth, bright, and even surface. For further details and drawings, see G. B. Hammond, *The Manufacture of Tin Plates, J. Iron and Steel Inst. 1897, 2, 24*; also papers by R. B. Thomas (*Proc. Inst. Mech. Eng. 1906, 499*) and T. L. Bailey (*J. Soc. Chem. Ind. 1918, 114 T*).

The occurrence of blisters in the thin sheets of steel used in the manufacture of tin plates is not infrequently a cause of considerable trouble. The origin of these has been studied by E. F. Law (*J. Iron and Steel Inst. 1906, 1, 134*), who concludes that oxidised steel will give rise to blistered sheets, and the defect is more likely to arise with Bessemer than with open hearth steel. Brittleness in sheets may arise from excess of sulphur or phosphorus. In metal of good chemical purity a peculiar form of weakness, sometimes called 'rectangular brittleness,' may result from annealing at an improper temperature, or for too long a time.

According to E. Mayer (*Stahl u. Eisen, 1918*

38, 900) there is no proof that molten tin really alloys with the iron, and the time of dipping is too short to admit of diffusion of the tin into the iron. A metallographic study of tinplate shows that there is always a sharp demarcation line between the tin and iron.

See also Chemistry in relation to Tinplate Manufacture (H. J. Bailey, J. Soc. Chem. Ind. 1923, 362). T. T.

TIN PYRITES v. STANNITE.

TIN SALTS or **TIN CRYSTALS**. *Stannous chloride* v. *Tin salts and oxides*, art. **TIN**.

TIN STONE. *Native oxide of tin* v. **CASSITERITE**.

TINTOMETER v. COLORIMETER.

TIN WHITE COBALT. *Smaltine, Cobalt arsenide* v. **COBALT**.

TIODINE. Trade name for thiosinamine ethylidide $C_2H_5 \cdot NH \cdot CS \cdot NH \cdot C_2H_5 \cdot I$ v. **THIOSINAMINE**.

TITANIC IRON-ORE v. ILMENITE.

TITANITE v. SPHENE.

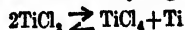
TITANIUM. Sym. Ti. At.wt. 48.1 (Thorpe); 47.9 (Baxter and Fertig, J. Amer. Chem. Soc. 1923, 45, 1228). Experiments to determine the ratio $TiCl_3 : 4Ag$ gave a mean value of 0.43957, the extremes being 0.43940 and 0.43967, which leads to the mean value 47.85 for the atomic weight of titanium, the extreme values being 47.89 and 47.78 (Baxter and Fertig, J. Amer. Chem. Soc. 1923, 45, 1228-1233; J. Chem. Soc. 1923, 124; Abstr. ii. 498). According to Aston, Titanium is simple. Titanium is not found in the free state, but occurs as oxide in three minerals of different crystalline form: *rutile*, *anatase*, and *brookite*. It is found as *titiferous iron ore* or *ilmenite* $(FeTi)_2O_3$, and in smaller quantities as *ephene* or *titanite* $CaTiSiO_5$, *perovskite* $(CaFe)TiO_3$, *schorlomite* $Ca(TiFe)SiO_3$, and *keilhaute* $CaY(TiAlFe)SiO_3$. It occurs in magnetic iron ores, and is thus frequently found in slags and pig iron; and in other minerals, in soils, clays, certain mineral waters, and in the sun's atmosphere (Barnes, J. Soc. Chem. Ind. 1896, 421; Hipsko, *ibid.* 1908, 901; Becker, Zeitsch. Kryst. Min. 1903, 38, 317; Hall and Smith, Chem. Zentr. 1905, ii. 1161; H. R. Adam, J. S. Afr. Chem. Inst. 1923, 6, 3). The presence of titanium oxide in clays considerably reduces their refractibility. Titanium is said to be diffused throughout all primitive granite rocks (Dieulauf).

It has also been found in human and in ox flesh and bone (Beakerville, J. Amer. Chem. Soc. 1899, 21, 1099); in the ash of many plants (Walt. *ibid.* 1896, 18, 402; Lippmann, Ber. 1897, 30, 3037); and in many peats (Beakerville, *l.c.* 402). It is more abundant in nature than has hitherto been supposed, but it is only within the last few years that the metal and many of its compounds have become important industrially.

Various titanium compounds have been suggested for use as pigments as far back as 1846. Ferro-titanium has been utilised in the iron industry since 1895, and titanium white, a pigment consisting essentially of titanium dioxide, is now being made.

Titanium can be extracted from its oxide by electrolyzing a solution of the latter in dry halogen salts of the alkaline earth metals heated to moderate redness. After cooling, the titanium is separated from the electrolyte by lixivation

with water and with dilute hydrochloric acid (Fr. Pat. 344096, 1904; J. Soc. Chem. Ind. 1904, 1098; cf. also Moissan, Eng. Pat. 3073, 1895; Sternberg and Deutsch, Eng. Pat. 18117, 1893; Borschers, U.S. Pat. 930344, 1909; J. Soc. Chem. Ind. 1909, 986). In a somewhat impure form it can be obtained by the reduction of potassium titanium fluoride with sodium (Weiss and Kaiser, Zeitsch. anorg. Chem. 1910, 65, 345). Very pure titanium has been obtained in moderately large quantities by heating pure titanium tetrachloride with about half its weight of sodium in a steel bomb to a low red heat (Hunter, J. Amer. Chem. Soc. 1910, 32, 330; Lely and Hamburger, Zeitsch. anorg. Chem. 1914, 87, 209), or by passing the vapour of $TiCl_4$ over sodium hydride. Also by heating the dichloride at 1100° in hydrogen:



Titanium in a very pure state is obtained by passing the vapour of the iodide over a heated tungsten filament. Thus obtained it is ductile (van Arkel and de Boer, Zeitsch. anorg. Chem. 1925, 148, 345; Chem. Soc. Abstr. 1925, ii. 1193.)

Titanium has the appearance of polished steel. It is hard and brittle in the cold, but can be readily forged when raised to a low red heat. It has sp.gr. 4.50 and melts at 1800° - 1850° (Hunter); see also Moissan (Compt. rend. 1906, 142, 673).

For crystalline structure (hexagonal), see Patterson (Physical Rev. 1925, [ii] 26, 56; Chem. Soc. Abstr. 1925, ii. 845).

It is less ductile than thorium, zirconium, or uranium, and can be obtained in rod-form only with special precautions, owing to its ready oxidisability.

Titanium burns in oxygen, in nitrogen, and in the halogens, dissolves readily in sulphuric or hot concentrated hydrochloric acid, more slowly in nitric acid, and decomposes steam at 700° - 800° .

Titanium readily forms alloys with various metals; some of those with iron having been employed for the manufacture of pencils for arc lights (Ladoff, J. Ind. Eng. Chem. 1909, 711).

Aluminium-titanium alloys with up to 30 p.c. of the latter metal contain hard crystals of the compound Al_3Ti , m.p. 1325° , and immiscible with aluminium (E. van Erckeleus, Metall und Erz. 1923, 20, 206.)

For Alloys with carbon and iron, see **TAMARU**, (Chem. Soc. Abstr. 1925, ii. 787).

Filaments of metallic titanium having a high melting-point and high resistance, and as used for incandescent electric lamps, are manufactured by treating titanic oxide with ammonia in the cold. The product is heated in a vacuum to 1200° , and is then mixed with an organic binding material such as a solution of casein in ammonia. The mixture is formed into threads and then heated in an electric furnace to 1300° . Finally the filament is subjected to the action of a high tension electric current in a vacuum (Trensen, Eng. Pat. 14652, 1906; J. Soc. Chem. Ind. 1909, 877).

Titanium is used in metallurgy, its addition to steel increasing greatly the transverse strength and elasticity of the steel (Ladoff, *l.c.* 642; Venator, Stahl und Eisen, 1910, 30, 889).

Its value in steel manufacture seems to be related to its power as a deoxidant. It is mainly applied in the form of Ferro carbon-titanium, containing from 15-20 p.c. Ti, and consisting of microscopic particles of titanium carbide held in a matrix of grey cast iron. When added to molten steel the matrix dissolves and the titanium carbide is diffused through the mass when it reacts on the oxygen, the titanium oxide acting as a flux for silicates and other slags. (For the effect of wear on titanium treated rails, see Comstock, J. Soc. Chem. Ind. 1915, 55.)

Aluminium-titanium alloys containing up to 30.7 p.c. of titanium consist of a mixture of hard, needle-shaped crystals of Al_3Ti in a softer ground mass of aluminium. The compound Al_3Ti melts at 1325° and forms neither eutectic nor solid solution with aluminium. Addition of titanium, in amounts not exceeding 1 p.c., to aluminium removes the combined nitrogen and oxygen, and consequently improves the tensile properties; at the same time, the resistance of the metal to attack by salt solutions and by organic acids is appreciably increased (cf. J. Soc. Chem. Ind. 1923, 721 A; Eugen van Erekelen, Metall. und Erz. 1923, 20, 206-210; J. Chem. Soc. Abstr. 1923, 124, ii. 569).

A protective coating on iron and steel is said to be formed by mixing a titanium ore with 10-50 p.c. of asphalt, and if the product is to be used as a paint, adding turpentine. These coatings can also be formed by heating the metal to be treated with a layer of titanic mineral mixed with carbonaceous material in a furnace for several hours (Johnson, Eng. Pat. 15500, 1893; J. Soc. Chem. Ind. 1893, 1046).

The arc spectrum of titanium has been analysed with the object of ascertaining the regularities of this spectrum. It is shown that two different sets of multiplets of six or seven lines occur. These sets have respectively the differences 170.1 and 2.167, and are similar to the multiplets of the alkaline-earth metals. There are also multiplets of eleven to thirteen lines, with differences 42.0, 62.3, 81.7, and 100.2, similar to the multiplets of manganese, chromium, and molybdenum. The majority of the lines classified belong to King's temperature classes I. and II., although a few belong to the classes III. and IV. (Astrophys. J. 1914, 39, 139). About 10 p.c. of the arc lines of titanium are thus classified. Long tables of the classification are given in the paper (C. C. Kieck and Harriet K. Kieck, J. Washington Acad. Sci. 19; J. Chem. Soc. 1923, 124, ii. 596; 1924, 126, ii. 510; see also Behner, Zeitsch. wiss. Phot. 1925, 23, 325; Chem. Soc. Abstr. 1925, ii. 1100; Crew, Chem. Soc. Abstr. 1925, ii. 335).

Compounds of titanium.—Titanium hydride appears to exist. When the gases from a titanium electrode are passed through a heated glass tube a deposit of titanium is formed as a black metallic mirror. The gaseous hydride is colourless and tasteless, and is condensed at the temperature of liquid air. Titanium forms four oxides. The monoxide TiO forms black prisms, obtained by heating the dioxide in the electric furnace, or with magnesium powder (Winkler, Ber. 1890, 23, 3658; Moissan, Compt. rend. 1892, 115, 1034; J. Soc. Chem. Ind. 1892, 923). The sesquioxide Ti_2O_3 (Moissan,

Compt. rend. 1895, 120, 290; Braun, Min. Mag. 1892, ii. 37) is obtained by strongly igniting the dioxide in hydrogen and allowing the product to cool in this gas. In sulphuric acid it forms a violet solution, this being the characteristic colour of all the solutions of trivalent titanium compounds. The corresponding hydroxide is obtained by digesting a solution of titanic acid in hydrochloric acid with metallic copper at 20° - 40° , or by treating the trichloride with alkalis. The sesquioxide and the corresponding salts are readily oxidised to the dioxide or the trioxide and their salts (Manchot and Richter, Ber. 1906, 39, 320, 488).

Titanium dioxide TiO_2 is the most important of the four oxides. It is trimorphous, occurring as the three distinct minerals mentioned above. It can be obtained by the decomposition of aqueous titanium chloride by ammonia or by fusing rutile with three times its weight of potassium carbonate.

Titanium oxide can be prepared by mixing crushed ilmenite or other titanium ore with carbon and heating to about 1800° . The resulting mass is crushed and the iron is removed by magnetic separation and treatment with acid (U.S. Pat. 921886, 1909; J. Soc. Chem. Ind. 1909, 657).

For the occurrence of titanium in Nile silt, see E. Griffiths-Jones (Analyst, 1923, 48, No. 568, 320).

The following results, expressed as percentage of TiO_2 , calculated on the silt dried at $100^\circ C$, were obtained:—

	Titanium dioxide. Per cent.
Nile silt collected from the river bank at Maadi, near Cairo	2.35
Silt from the River Atbara taken 10 miles upstream from the junction with the main river—	
No. 1, a grey silt of fine texture	2.2
No. 2, a coarse sand	1.3
Silt from Nile at Hassanat Discharge site about 5 miles upstream from the junction with the Atbara—	
No. 1, fine silt, brown in colour	2.4
No. 2, fine silt, grey in colour	2.55
No. 4, fine sand, brown in colour	1.7

Amorphous titanium dioxide is a white, tasteless powder which becomes lemon yellow when gently heated, and brown when ignited strongly. It has a sp.gr. 3.89-4.25. It is insoluble in water and dilute acids, resembles silicon dioxide closely in chemical properties, and when fused with alkalis or alkali carbonates forms the titanates.

Titanium dioxide finds application as a paint material and is extracted on the large scale from a variety of ilmenite found near Egersund, Norway. The concentrated ore containing 47.5 p.c. of titanium oxide is reduced to fine powder and mixed to a paste with concentrated sulphuric acid. On heating the mineral is converted into soluble sulphates of iron and titanium. On treating with water and heating nearly to boiling-point the titanic oxide is precipitated, dried, and calcined. The product is mixed with barium sulphate, carbonate and calcium phosphate, and comes into commerce as 'titanium white.'

Titanox consists of titanium dioxide precipitated upon a base of finely divided *blanc fixe*. In colour it is far whiter than white lead, but not quite so white as French process zinc oxide or the best grades of lithopone. Its hiding power is twice that of white lead and is the greatest of any white pigment. Its inertness towards varnish liquids enables it to be used in compositions that can be kept without danger of livering or thickening. 100 p.c. titanox in oil dries very slowly to a soft film, and a fair quantity of a metallic drier should be used, while for interior work an addition of about 30-50 p.c. of zinc oxide is advantageous, this causing it to give a firm dust-resisting film. Titanox appears to be very resistant to sunlight and to all atmospheric conditions and to hydrogen sulphide fumes. Experiments on rabbits showed that titanox is non-toxic and physiologically inert (H. A. Gardner, U.S. Paint Manuf. Assoc., Govt. No. 199, Feb. 1924, 256; J. Soc. Chem. Ind. 1924, 43, B. 303).

Green pigments containing titanium were first manufactured about 1861. White titanium pigments are now chiefly made in America and Norway, and are usually sold in two forms containing 65-90 p.c. and 25-35 p.c. TiO_2 , respectively. Ilmenite ($\text{FeO} \cdot \text{TiO}_2$, containing 51 p.c. TiO_2) is now the chief raw material used for these pigments, since it is cheaper than rutile (containing 90-98 p.c. TiO_2), which was formerly used. Pure white pigments are microcrystalline, and have sp.gr. 4.0 and refractive index 2.1-2.3. White titanium pigments are only soluble in the concentrated acids and alkalis, and are inactive towards the oils and pigments used in the paint and varnish industries. The resinates and linoleates of cobalt and manganese are particularly suitable siccatives for use with titanium paints, 0.2 p.c. of manganese or 0.03 p.c. of cobalt being recommended as suitable quantities. Paints containing titanium pigments are elastic and do not crack or scale after prolonged weathering. Titanium pigments have a high covering and oil-absorption power, and a ready-to-use paint contains 52-62 p.c. of white titanium pigment and 48-39 p.c. of oil (E. O. Rasser, Chem. Zeit. 1923, 47, 460-461; J. Soc. Chem. Ind. 1923, 42, 729 A).

The following volumetric method of estimating titanium in titanium pigments is not affected by other elements likely to be present, and is convenient when a number of samples have to be analyzed. The reagent used is prepared by dissolving 30 grms. of ferric ammonium sulphate in 360 c.c. of water containing 10 c.c. of sulphuric acid, adding permanganate solution drop by drop as long as the pink colour disappears, diluting to a litre, and standardising in terms of iron; 0.5 grm. of the pigment is mixed with 20 c.c. of concentrated sulphuric acid and 7 to 8 grms. of sodium sulphate in a 250 c.c. beaker, which is heated on a hot plate until fumes of sulphur trioxide are evolved and then boiled over a flame for 5 minutes or until solution is complete. The cold liquid is mixed with 100 c.c. of water and boiled, the barium sulphate and silica being filtered off and washed with 5 p.c. sulphuric acid solution. As reductor a 500 c.c. pyrex glass dispensing burette, 22 by 1 inches, is used. Into this is introduced a platinum gauze covered with a 1-inch mat of

fibrous asbestos supporting, in the order mentioned, a 1-inch layer of 10-mesh and a 6-inch layer of 20-mesh amalgamated zinc and a 5-inch layer of amalgamated stick zinc. The reductor is connected with a litre flask for receiving the reduced titanium solution through a 3-holed rubber stopper, which carries also an inlet tube for carbon dioxide and an outlet tube joined to the suction pump. The reductor is prepared by passing through it a little hot dilute sulphuric acid followed by hot water, sufficient of which is left to cover the zinc. The hot filtrate from the barium sulphate is now introduced, about 100 c.c. of water being drawn from the reductor into the original beaker to bring the solution to about the top of the zinc; the water withdrawn may be acidified with 10 c.c. of sulphuric acid and kept on a hot plate for washing after the reduction. The titanium solution is left in the reductor for 10 minutes, the receiving flask being meanwhile connected with the reductor and the air displaced by carbon dioxide. When reduction is complete the receiving flask is joined to the suction pump, and, with carbon dioxide still flowing, the reduced solution is drawn out and is followed by the acid washing liquor and three or four quantities of 100 c.c. of hot water, the zinc being kept covered. The suction is then gradually released and the flask disconnected, 5 c.c. of saturated potassium thiocyanate solution being added and the liquid titrated at once with the ferric ammonium sulphate solution until a brownish colour persists for at least a minute; the burette reading is to be corrected by an amount which each operator must determine by means of several blank tests. As the composition of titanium oxide is always very nearly 25 p.c. of titanic oxide and 75 p.c. of barium sulphate, the percentage of the pigment is obtained nearly enough for all practical purposes by multiplying the percentage of titanic oxide by four. If only an occasional estimation is to be made, the following gravimetric method is useful. The filtrate from the barium sulphate (see above) is treated with excess of ammonia and filtered, the precipitate being dissolved in hydrochloric acid (1:1) and again precipitated with ammonia. The precipitated titanium hydroxide is filtered off and washed with hot water, the filtrate being added to that from the previous filtration. The residue is dissolved in hydrochloric acid (1:1), the volume of the solution, which is received in a 500 c.c. beaker, being kept below 150 c.c. To the solution, heated to 50°C., ammonium hydroxide is added gradually until the precipitate formed just redissolves, ammonium carbonate solution being then added, drop by drop, until a slight permanent precipitate forms. This is dissolved in hydrochloric acid, and an excess of 2 c.c. of the acid (1:1) added, the solution being treated with sulphur dioxide gas or solution until it smells strongly, diluted to about 400 c.c. and boiled until only a slight odour remains. The liquid is filtered while hot, and the precipitate washed with hot water, dried, calcined at not lower than 900°C. for 30 minutes, and weighed as TiO_2 .

With a mixed pigment containing titanic oxide, 1 grm. is heated on a hot plate in a 400 c.c. pyrex glass beaker with 10 grms. of sodium sulphate and 40 c.c. of sulphuric acid (93 p.c.)

for 30 minutes, and then boiled for about 10 minutes, cooled, diluted to 300 c.c., boiled for 20 minutes, and filtered while hot. The residue is washed with 5 p.c. sulphuric acid solution; it contains silica, undecomposed silicates and all the lead and barium as sulphates. The hot filtrate, containing the titanium, iron, aluminium, zinc, and calcium, is treated with excess of ammonia, and filtered, the precipitate being washed with hot water, redissolved in hydrochloric acid (1:1), and again precipitated with ammonia. The precipitate is filtered off and washed with hot water, the filtrate being united with that from the first separation; if desired, this filtrate may be tested for aluminium and used for estimating the calcium and zinc. The precipitate is dissolved in dilute hydrochloric acid, and the titanium separated and estimated as described above, the filtrate being used for estimating the iron and aluminium (L. E. Barton, *Chem. Trade J.* 1923, 357, 358; *Analyst*, 1923, 48, 403).

For the volumetric estimation of titanium, see also Morley and Wood (*J. Chem. Soc.* 1924, 125, 518; *Abstr.* 1924, 126, ii, 351); Lundell and Jones (*J. Amer. Chem. Soc.* 1923, 45, 2620-2623; *J. Soc. Chem. Ind.* 1924, 43, B, 38).

Titanium oxide is used as a mordant, and in at least two cases it has an advantage over alumina; thus alizarin yellow produces with titanium as bright but a much faster colour than with alumina, whilst the scarlet obtained from alizarin orange on a titanium mordant is the fastest scarlet that can be obtained on wool.

For this purpose the titanium mordant must be freed from iron, and this can be done by dissolving freshly precipitated titanium hydroxide, containing iron, in tartaric acid, making alkaline with ammonia and precipitating the iron by the addition of the requisite amount of ammonium sulphide. The filtered solution is then warmed until most of the free ammonia has been expelled (Barnes, *J. Soc. Chem. Ind.* 1899, 15).

According to Sabatier and Mailhe (*Compt. rend.* 1910, 150, 823) the dioxide forms a very efficient catalyst in the esterification of acetic acid.

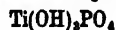
According to E. L. Nichols (*Physical Rev.* 1923, [ii] 22, 420), cathode rays but not ultra-violet light from an iron spark excite a very faint, orange-red fluorescence in titanium oxide, or, after fusion of the surface layer, a fine blue fluorescence, with rapid fatigue. A thin layer of the oxide, when heated, gave a very feeble greyish-blue fluorescence up to 425°, strong red from 425° to 677°, and strong yellow from 677° to 1000°. When the oxide is heated directly with an oxygen-hydrogen flame, two distinct phases are observed, according as the oxygen or the hydrogen is in excess (*cf.* Nichols and Wilber, *Chem. Soc. Abstr.* 1922, ii, 105; 1924, 126, ii, 81).

Like silicic acid, titanous acid forms a number of hydrates known as ortho- and meta-titanous acids (Wagner, *Ber.* 1888, 21, 960; Pfordten, *Annalen*, 1887, 237, 213; Tamann, *Zeitsch. anorg. Chem.* 1905, 43, 370; Bornemann and Schürmann, *Chem. Zentr.* 1910, ii, 1870). Many titanates are known. The two compounds $\text{Na}_2\text{TiO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{TiO}_3 \cdot 4\text{H}_2\text{O}$ described by Denzey in 1849 have been shown by Collenberg and Sandved not to exist (*Zeitsch. anorg. Chem.* 1923, 120, i; *Chem. Soc. Abstr.* 1924, 126, ii, 53).

Tetramethyl titanate prepared from methyl alcohol, sodium, and titanium tetrachloride crystallises at 210° and boils at 243° corr. at 52 mm. Tetraethyl-, tetraisopropyl-, and tetra-*n*-butyl titanates have also been prepared (Bischoff and Adkins, *J. Amer. Chem. Soc.* 1924, 46, 256; *Chem. Soc. Abstr.* 1924, 126, i, 259).

Chloro-acetate compounds of titanium have been prepared from TiCl_3 and acetic acid (Gina and Monath, *Zeitsch. anorg. Chem.* 1925, 143, 383; *Chem. Soc. Abstr.* 1925, i, 531).

Titanium peroxide TiO_2 (Classen, *Ber.* 1888, 21, 370) resembles hydrogen peroxide very closely in its reactions in solution. Faber (*Zeitsch. anal. Chem.* 1907, 46, 277) has prepared the hexavalent acetate and phosphate



both of which are stable at low temperatures, but, particularly the acetate, are explosive on heating. Hypertitanates of potassium and sodium have also been prepared (Melikoff and Pissarjewsky, *Ber.* 1898, 31, 678).

According to Billy (*Compt. rend.* 1921, 172, 1411) all salts of the oxide TiO_2 are really complexes of hydrogen peroxide and peritanic salts corresponding with the peroxide Ti_2O_3 .

Halogen compounds.—Titanium tetrachloride TiCl_4 can be obtained readily by passing dry chlorine over a mixture of the dioxide with carbon; by passing the vapour of chloroform over titanium dioxide (Renz, *Ber.* 1906, 39, 249), and by heating the latter with sulphur monochloride (Hall, *J. Amer. Chem. Soc.* 1904, 26, 1235; Bourion, *Ann. Chim.* 1910, [viii.] 20, 547; *ibid.* 21, 49), or by passing sulphur dioxide into a warm, strongly acid solution of titanium trichloride (Smythe and Wardlaw).

Titanium tetrachloride is best prepared from industrial ferro-titanium by treating the latter with hydrochloric acid to remove most of the iron. It is then levigated to remove titanous anhydride, and after drying the mass is introduced into a porcelain tube, heated to dull redness, and subjected to the action of a current of dry chlorine. The ferric chloride is separated by filtration, and the filtrate is fractionally distilled when the pure substance is obtained. It boils at about 136°, is colourless, and does not fume in air (Vigoureux and Arrivaut, *Compt. rend.* 1907, 144, 485).

The tetrachloride can also be prepared from rutile by igniting the latter with aluminium and then heating the mixture in a current of chlorine (Ellis; *Chem. News*, 1907, 95, 122).

It is a mobile, transparent, colourless liquid of sp.gr. 1.7604 at 0°/4° (Thorpe), which solidifies at -23° and boils at 136.4° under 760 mm. pressure (Thorpe). It is decomposed by an excess of water yielding titanous acid and combines with ammonia, forming a number of solid addition compounds (Rosenheim and Schütte, *Zeitsch. anorg. Chem.* 1901, 26, 239; Stähler and Wirthwein, *Ber.* 1905, 38, 2618). When the latter are extracted with liquid ammonia, dark yellow titanamide $\text{Ti}(\text{NH}_2)_4$ is formed. Titanous tetrachloride, like stannous chloride, yields a large number of crystalline compounds with other chlorides (Rosenheim and Schütte, *l.c.*; Ruff and Ipsen, *Ber.* 1903, 36, 1777). It is reduced to the trichloride by heating with aluminium, antimony, arsenic or tin in a sealed tube at 400°.

A solution in concentrated hydrochloric acid deposits, on evaporation in the cold over sulphuric acid, large, colourless, rhomboidal plates of $\text{TiCl}(\text{OH}) \cdot 2\text{H}_2\text{O}$, decomposed in moist air (Collenberg and Sandberg, *l.c.*).

Titanium trichloride TiCl_3 is formed when a mixture of titanium tetrachloride vapour with hydrogen is passed through a red-hot tube (Georges and Stähler, *Ber.* 1909, 42, 3200; Stähler and Bachran, *Ber.* 1911, 44, 2906), and can be prepared by electrolysis of a solution of the tetrachloride and then evaporating the solution to the sp. gr. 1.5 at $60^\circ\text{--}70^\circ$ (Spence, U.S. Pat. 723217, 1903; *J. Soc. Chem. Ind.* 1903, 495, 628; D. R. P. 154542). As prepared by the latter process, it forms violet crystals of the composition $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, which decompose into the tetra- and di-chloride on heating, the latter also being formed when the trichloride is heated in hydrogen (Georges and Stähler, *l.c.*). Titanium trichloride may be prepared by reduction of the tetrachloride by means of hydrogen, provided that the reaction products are quickly cooled and the hydrogen chloride is removed by means of metallic titanium. The trichloride so prepared consists of large violet crystals, which are fairly stable in the air. The reduction is not direct, but three reactions, $\text{TiCl}_4 + \text{H}_2 = \text{TiCl}_3 + 2\text{HCl}$; $\text{TiCl}_4 + \text{TiCl}_3 = 2\text{TiCl}_3$; $2\text{TiCl}_3 + 2\text{HCl} = 2\text{TiCl}_4 + \text{H}_2$, may proceed simultaneously (F. Meyer, A. Bauer, and R. Schmidt, *Ber.* 1923, 56, 1908–1914; *J. Soc. Chem. Ind.* 1923, 42, 1067 A). When titanium tetrachloride is heated with magnesium, zinc, aluminium, arsenic, or antimony it is reduced to trichloride, the reaction being accelerated by aluminium chloride. Phosphorus and sulphur reduce the tetrachloride only in presence of aluminium chloride. Reduction with aluminium and aluminium chloride in absence of air is the best method of preparing titanium trichloride. The trichloride can be sublimed at 425°C . at 1 mm. pressure. At 475°C . it decomposes into di-chloride and tetrachloride. Titanium dichloride is a black powder, stable at least to 600°C . in absence of air, but catching fire at once in moist air. It decomposes water immediately with evolution of hydrogen (O. Ruff and F. Neumann, *Zeitsch. anorg. Chem.* 1923, 128, 81–95; *J. Soc. Chem. Ind.* 1923, 42, 1220 A).

Investigation of the reduction of the tetrachlorides of titanium and zirconium by sodium amalgam, magnesium, zinc, aluminium, tin, arsenic, phosphorus, etc., has shown that reduction by aluminium at about 250° affords a convenient means for the preparation of the trichlorides, from which excess of tetrachloride and aluminium chloride can be removed by distillation. Titanium trichloride thus prepared is a bright violet, non-crystalline powder subliming at 425° / < 1 mm. to form dark violet, prismatic crystals; it is very sensitive to oxygen and moisture, and dissociates at 450° to form the volatile tetrachloride and a black residue of the dichloride, which is very reactive, takes fire in moist air, and decomposes water with evolution of hydrogen (O. Ruff and F. Neumann, *Zeitsch. anorg. Chem.* 1923, 128, 81).

The trichloride is a powerful reducing agent. It liberates sulphur from sulphurous acids, sulphates, and thiosulphates, and selenium from selenious acid, many metals, such as gold, silver

the platinum metals, mercury, and copper from solutions of their salts, and reduces nitric acid and nitrates to ammonia. It reduces ferric salts quantitatively to the ferrous condition, reacts with a gold solution like stannous chloride, producing colloidal gold, analogous to purple of Cassius, organic nitro compounds to amines, gives characteristic coloured precipitates or colorations with many organic acids or their salts. The intense violet coloration with solutions of alkali citrates is a characteristic and sensitive test, and can be employed in the analysis of many dyes (Knecht, *Ber.* 1903, 36, 166; Knecht and Hibbert, *ibid.* 1549; *ibid.* 1905, 38, 3318; 1907, 40, 3819; *J. Chem. Soc.* 1924, 125, 1537). This reducing property has also been made use of in cloth printing (D. R. P. 138503; *Frdl.* 1902–4, 477). Titanium trichloride forms double compounds with the chlorides of rubidium and caesium (Stähler, *Ber.* 1904, 37, 4405), and also with nitrogen sulphide (Davis, *Chem. Soc. Trans.* 1906, 1576).

The use of titanous chloride in the titration of iron is discussed by Brandt (*Chem. Zeit.* 1924, 48, 265, 270; *J. Soc. Chem. Ind.* 1924, 43, B. 469).

The standardisation of titanous chloride solutions, using the potentiometric method, has been studied by Zintl and Rauch (*Zeitsch. anorg. Chem.* 1925, 146, 281; *Chem. Soc. Abstr.* 1925, ii, 1003; see also Tomiček, *Chem. Soc. Abstr.* 1925, ii, 243).

A brown polymorphic modification of titanium trichloride, obtained by the action of the silent discharge on a mixture of hydrogen and the vapour of the trichloride, has been described by Böck and Moser (*Monatsh.* 1913, 34, 1825).

Titanium dichloride TiCl_2 , prepared as above, is a hygroscopic light-brown powder.

Titanium tetrabromide (Ruff and Ipsen, *l.c.*), and tribromide (Stähler, *l.c.*), the triiodide (Stähler, *l.c.*), tetra-iodide and the diiodide (Defaez and Copaux, *Compt. rend.* 1908, 147, 65), the tetra- and tri-fluorides (Ruff and Ipsen, *l.c.*; Ruff, Plato and Graf, *Ber.* 1904, 37, 673), and a number of alkali titanofluorides (Marchetti, *Zeitsch. anorg. Chem.* 1895, 10, 66; Piccini, *ibid.* 438; Ebler and Schott, *J. pr. Chem.* 1910, [ii.] 81, 552) have been prepared.

Titanium forms three sulphides TiS_2 , Ti_2S_3 , and TiS (Müller, *Chem. Zentr.* 1910, ii, 1195), and also a chlorosulphide.

Titanium sesquisulphate $\text{Ti}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is obtained when the metal is dissolved in dilute sulphuric acid. It is decomposed by heat and forms alums and double salts with the alkali sulphates.

The electrolytic reduction of many organic compounds is greatly facilitated by the addition of a small quantity of a titanium salt, such as the sulphate (D. R. P. 168273; *Frdl.* 1905–7, 115). Titanous sulphate is also recommended for detecting copper in dyed fabrics (Knecht, *J. Soc. Dyers*, 1904, 20, 97). The electrometric titration of chlorate, bromate, iodate, and ferricyanide with titanous sulphate is discussed by Hendrixson (*J. Amer. Chem. Soc.* 1923, 45, 2013; *Sci. Abstr.* 1924, 27, 53).

Titanous sodium sulphate $\text{Ti}_2\text{Na}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ is obtained by electrolysis of a solution containing titanic sulphate, sodium sulphate, and sulphuric acid. The electrolysis is carried out with a

low-current density in a lead-lined vessel, the solution being finally evaporated to a sp.gr. of 1.145, when the salt crystallises out.

It is a powerful reducing agent, and can be applied in the preparation of other titanous salts (Peter Spence and Sons, D. R. P. 149602, 1904).

Titanium disulphate $\text{Ti}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ forms double salts with the sulphates of the alkalis and alkaline earths (Weinland and Köhl, *Zeitsch. anorg. Chem.* 1907, 54, 253). A number of basic sulphates (Blondell, *Bull. Soc. chim.* 1899, [iii.] 21, 262; Roseheim and Schütte, *l.c.*) and titanousulphuric acid (Reichard, *Chem. Zeit.* 1904, 28, 16) have also been prepared. The preparation of solutions of titanyl sulphate TiOSO_4 is described by Weizmann and Blumenfeld (E. P. 209480, 210033; *J. Soc. Chem. Ind.* 1924, 43, B. 256).

Titanium forms a number of nitrides and also a chloro- and bromo-nitride (Ruff and Eiser, *Ber.* 1908, 41, 2250; *J. Soc. Chem. Ind.* 1908, 809; Ruff, *Ber.* 1909, 42, 900; Ruff and Treidel, *ibid.* 1912, 45, 1364). The mononitride Ti_3N_2 is a bronze yellow mass of sp.gr. 5.18, and is hard enough to cut rubies and diamonds (Moissan, *Compt. rend.* 1895, 120, 290).

According to Shukoff, however (*J. Russ. Phys. Chem. Soc.* 1910, 42, 40), titanium only forms solid solutions with nitrogen, but no definite compounds.

Titanium also forms a carbide (Shimer, *Chem. News*, 1887, 55, 156; Moissan, *l.c.*; and *Compt. rend.* 1897, 125, 839); a carbide of titanium, m.p. $3400^\circ\text{--}3500^\circ$ Abs. was prepared by Friederich (*Z. Physik.* 1925, 31, 813; *Chem. Soc. Abstr.* 1925, ii. 374); Titanium forms a cyanonitride $\text{Ti}(\text{CN})_2 \cdot 3\text{Ti}_3\text{N}_2$ (Wöhler, *Annalen*, 1850, 73; *ibid.* 34, 74, 212; Franck, *Chem. Zeit.* 1897, 21, 520; *J. Soc. Chem. Ind.* 1908, 809); and a silicide TiSi (Hönigsmid, *Compt. rend.* 1906, 143, 224; *J. Soc. Chem. Ind.* 1909, 249).

Soluble double pyrophosphates of titanium and alkali are prepared by mixing together alkali pyrophosphates and basic titanium sulphate (Barnes and Spence, *Eng. Pat.* 6329, 1906; *J. Soc. Chem. Ind.* 1907, 93).

Titanium phosphide TiP forms a brittle mass with a metallic lustre. It burns when heated in air, is a conductor of electricity, is insoluble in dilute and in concentrated alkalis and acids (Gewecke, *Annalen*, 1908, 361, 79).

Titanic acid forms crystalline *thiocyanates* of the type $\text{K}_2\text{TiO}(\text{SCN})_2 \cdot \text{H}_2\text{O}$ and double salts with pyridine ($\text{C}_5\text{H}_5\text{N}$), $\text{H}_2\text{TiO}(\text{SCN})_2$, and quinaline (Rosenheim and Cohn, *Zeitsch. anorg. Chem.* 1901, 28, 167).

Double fluorides of titanium, with some alkaloïds are described by Schaeffer (*J. Amer. Chem. Soc.* 1906, 30, 1863).

Complex azo-salts of titanium have been prepared by Mazzucchelli and Pantanelli (*Gazz. chim. Ital.* 1910, 40, i. 666). Other titanium organic compounds are described by Dilthey (*Ber.* 1904, 37, 588; *Annalen*, 1906, 344, 300), Rosenheim and Schnabel (*Ber.* 1905, 38, 2777), Grossmann (*Chem. Zeit.* 1906, 30, 907), Mazzucchelli (*Atti R. Acad. Lincei*, 1907, [v.] 16, ii. 265), Pantanelli (*Chem. Soc. Trans.* 1908, 1004).

The possibility of using titanium compounds in dyeing processes was first demonstrated by

Barnes in 1877. For the behaviour of titanio acid towards dyes, see A. M. Morley and J. K. Wood (*J. Soc. Dyers and Col.* 1923, 39, 100-106). The salts used are: the sulphate, chlorides, fluoride, oxalate, tartrate, lactates, and the double alkali derivatives of these salts. The salts for this purpose are obtained by the following process.

The ore is melted with sodium hydroxide and the mass is lixiviated with water; the residue is then washed free from alkali, dissolved in hydrochloric acid, and the solution is treated with alkali to precipitate titanium as hydroxide. The product is freed from iron by the addition of sodium sulphide, the precipitate washed and treated with sulphurous acid. It is then converted into titanium oxalate by treatment with ammonium oxalate and oxalic acid (Erban, *Chem. Zeit.* 1906, 30, 145; cf. also Dreher, *Eng. Pat.* 1835, 1903; *J. Soc. Chem. Ind.* 1904, 18; Spence, *ibid.* 1900, 246).

The *lactates* are conveniently prepared by dissolving titanio acid in hydrochloric acid and pouring the solution into a warm solution of an alkali or alkaline earth lactate (Dreher, *Farber-Zeit.* 1902, 13, 293; D. R. P. 149577; *Frdl.* 1902-4, 43; *J. Soc. Chem. Ind.* 1902, 988, 1245; 1903, 908).

The soluble salts of titanium, such as the oxalate, are very efficient fixing agents for the tannates of the basic colours, the results obtained being as good as, and in many cases better than, those obtained with antimony. For this purpose it is unnecessary to purify the titanium salts from iron (Barnes, *J. Soc. Chem. Ind.* 1899, 15).

Titanium tannate washed free from sulphate and chlorides, and dissolved in warm aqueous oxalic or tartaric acid, is an excellent dye for cotton, the shade varying with the sp.gr. of the solution. The solution of titanium tannate can also be employed as a further fixing and modifying bath after dyeing, the colours becoming faster and more yellow after such treatment. It also serves as an excellent fixing agent for the Janus colours which have been dyed substantively. Very good colours are also obtained with methylene blue, rhodamine, and aniline black (Barnes, *l.c.*; Kearns and Barnes, *Eng. Pat.* 8589; *J. Soc. Chem. Ind.* 1899, 491; Erban, *Chem. Zeit.* 1906, 30, 145).

A solution containing a titanium salt gives, with tannic acid, an orange precipitate; with gallic and pyrogallie acids, orange or brownish-yellow solutions; and with salicylic acid a pale-yellow coloration: a yellow to deep orange colour is also produced by hydrogen peroxide; these colours are imparted to wool when the latter is steeped in the hot solutions (Barnes, *J. Soc. Chem. Ind.* 1896, 420; 1897, 238; *Eng. Pat.* 5712).

The oxalate, tartrate, titanium sodium oxalate, titanium tanno-oxalate, titanium sodium sulphate, and titanous chloride can be used with good results in dyeing and mordanting silk. The titanium mordants are also useful in the chrome developing colours, and in the after treatment of silk previously dyed with anthracene yellow or brown or alizarin colours. For this purpose titanium potassium oxalate or titanium sodium sulphate are best used (Humb, *J. Soc. Dyers*, 1903, 19, 105; Barnes, *l.c.*; and *J. Soc. Dyers and Col.* 1919, 35, 58).

Titanium salts unite with the tannin matter of leather to form on the fibre a yellowish-brown titanium tannate, which is very fast to light and to the action of soap. On account of its cheapness, potassium titanium oxalate is the most applicable. It is exceedingly soluble in hot water and can be applied to tanned leather either in the dye-bath or with a brush. The mode of application and the previous and subsequent treatment of the leather depend on the quality of the latter, whilst the shade of colour obtained, which varies from bright yellow to a reddish-brown, depends on the nature of the tannage and on the amount of titanium salt used. The basic colours especially give much fuller and richer shades with titanium than without (Lamb, J. Soc. Chem. Ind. 1901, 1111; U.S. Pat. 722857, 1903; Dreher, J. Soc. Chem. Ind. 1902, 771; 1903, 294; 1904, 71; Eng. Pats. 9556, 1901; 27597, 1902; Stiansky, J. Soc. Chem. Ind. 1902, 1329; Erben, *l.c.*).

According to Barnes (*l.c.*) titanium tannate can also be used effectively as a pigment in water-colour drawings, the colour depending upon the conditions of preparation of the pigment and varying from brick-red to almost pure yellow. Titanium salts are also said to be employed in the manufacture of artificial teeth and in colouring porcelain (Ladoff, *l.c.*; Barnes, J. Soc. Chem. Ind. 1896, 421).

See A. H. A. Robinson on Titanium, Dept. of Mines, Canada.

The titration of triphenylmethane and azo dyes with N/20 titanous chloride solution is a satisfactory method for determining the strength of commercial dyes of these classes, and has been applied to the routine analysis of about 30 members of the former and over 100 of the latter class, giving results that could be relied upon to about 0.5 p.c. The concentration of sodium tartrate and of alcohol in the solution to be titrated and the temperature of titration can be varied within wide limits without materially affecting the results obtained. In the case of the azo dyes difficulty was encountered in the intense colour of the reduced solution, which masked the end-point of the titration. It was found that this colour depends to a large extent on the nature of the solvent, and that by a judicious choice of solvents a direct titration is possible. Details are given of a direct titration method and a black titration method for use with azo dyes. In the latter method the reduction products of the dye frequently serve as an indicator, but if not a 0.1 p.c. solution of reduced methylene blue may be added. Water, alcohol, acetic acid, and mixtures of these were used as solvents. The analysis of basic brown dye-stuffs was possible by the indirect method if the titanous chloride was added at room temperature. In the analysis of chrysoidines the temperature had to be kept below 70°C. to avoid decomposition and consequent low results (W. S. Calcott and F. L. English, Ind. Eng. Chem. 1923, 15, 1042-1044; J. Soc. Chem. Ind. 1923, 42, 1122A).

TITANIUM GREEN. Titanium ferrocyanide, prepared by adding potassium ferrocyanide to a solution of hydrated titanous oxide in hydrochloric acid, has been suggested as a substitute for Schweinfurth green and other arsenical

pigments (Elanier, Dingl. poly. J. 905, 130; Gentile, *ibid.* 140, 238).

TIZA. A local South American name for ulexite (*q.v.*).

T.N.T. Trinitrotoluene *v.* Explosives.

T.N.X. Trinitroxylene.

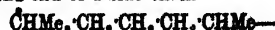
TOAD'S EYE. Native oxide of tin *v.* Tin salts and oxides, art. Tin.

TOAD VENOMS. Toads have long been known to be poisonous, and in the eighteenth century toadskins were employed as a remedy against dropsy. This application now only survives in China. A scientific basis for this therapy has been supplied by the isolation of the following crystalline active principles having a powerful digitalis-like action on the heart.

Bufotalin $C_{25}H_{35}O_8$, $C_{25}H_{35}O_8$, m.p. 148°, from alcohol, $2C_{25}H_{35}O_8 \cdot C_4H_9O_2$, m.p. 154°, from ethyl acetate. In each case the solvent of crystallisation is slowly lost in a high vacuum at 150°. On careful heating bufotalin sublimes at 225°-230°, $[\alpha]_D^{20} = +5.4^\circ$. This substance was first obtained in an impure form from the skin of the common European toad by Faust (Arch. exp. Path. Pharm. 1902, 47, 278), and was subsequently obtained pure by Wieland and Weil (Ber. 1913, 46, 3315; see particularly Wieland, Sitzber. bayer. Akad. Wiss. 1920, 329; Abstr. Chem. Soc. 1922, i. 199). Each toad skin yields about 10 mg. of bufotalin (and also 3 mg. of suberic acid). Of the six oxygen atoms, two are present as a lactone group, two as an acetyl group, and two are hydroxylic. Of the latter, one is capable of acetylation (which yields *acetyl bufotalin* $C_{27}H_{37}O_9$, m.p. 254°), the other can be oxidised to a ketone group (present in *bufatolone* $C_{25}H_{33}O_8$, m.p. 261°). *Tetrahydrobufotalin* $C_{25}H_{37}O_8$, m.p. 204°-205°, and *bufotalan* $C_{24}H_{35}O_8$, m.p. 198°-199°, have also been prepared, the latter by the removal of one molecule of acetic acid and of water by the action of concentrated hydrochloric acid on bufotalin.

Bufotalin is not present as such in the skin of the toad, but is a product of the decomposition of the actual poison bufotoxin $C_{26}H_{37}O_{11}N$, m.p. 204°-205°, hydrolysed by dilute acids to bufotalin $C_{24}H_{35}O_8$ and suberylarginine (Wieland and Alles, Ber. 1922, 55, 1789). Bufotalin differs from bufotalan (above) by having four double bonds, and being yellow.

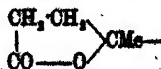
The carbon skeleton of bufotalin, apart from the acetyl group, consists of 24 carbon atoms, with four rings, and the same arrangement is believed to be present in the bile acids. Moreover, cholic acid has been shown by Windaus and Neukirchen (Ber. 1919, 52 [B], 1915) to differ from cholesterol by having an isopropyl group at the end of a side chain



which in cholic acid is represented by



In bufotalin this side chain is probably further oxidised to β - γ -lactone



Bufotalidin is a second crystalline toxic substance from the European toad, $C_{25}H_{35}O_7$. With alcohol of crystallisation it melts at 178°.

and after heating in a high vacuum at 228°-230°; it is probably oxybufotalin.

Bufo $C_{12}H_{14}O_4$, m.p. 217°-218°, $[\alpha]_D^{20} = +11^\circ$, occurs in the secretion of the parotid gland of the large Central-American toad *Bufo* *agui* (together with nearly 7 p.c. of adrenaline), and was isolated by Abel and Macht (J. Pharmacol. expt. Ther. 1912, 3, 319). According to Shimizu (*ibid.* 1916, 8, 347) it is also present in the Chinese drug 'senso.'

Bufo *agui* is used for the preparation of an arrow poison by South American Indians.

Wieland considers that the formula for bufagin may require alteration to $C_{17}H_{22}O_4$, which is that of the methyl ether of bufotalin. The above toad venoms are pharmacologically similar to digitalis and strophanthus (*q.v.*). Digitoxigenin is, according to Cloetta (Arch. exp. Path. Pharm. 1920, 88, 113), $C_{24}H_{38}O_6$, and strophanthidin (=cymarigenin, *see art.* STROPHANTHUS), has 23 or possibly 24 carbon atoms. All these heart poisons from animal and vegetable sources seem to be related to cholesterol and the bile acids. G. B.

TOBACCO. The botanical order of the *Solanaceae* includes many well-known plants which are extensively cultivated because certain portions of them are of great utility to the human race. The tuber of the potato and the fruit of the tomato are food substances of great value and of almost universal consumption. Other genera of the order, however, afford instances of cultivation simply for the production of foliage; the dried leaves of the thorn-apple (*Datura Stramonium* (Linn.)) are sometimes smoked as a remedy for asthma. The most important plants of this class, however, belong to the genus *Nicotiana*, and their dried leaves are known as tobacco. The etymology of the word 'tobacco' is somewhat obscure; the geographical origin assigned to it by tracing it either from Tobago, an island in the West Indies, or from Tabasco, an island in the Gulf of Mexico, is probably incorrect. When the Spaniards first visited San Domingo they found that the natives used a peculiar contrivance for inhaling the smoke of burning tobacco leaves. This instrument was called a 'tabaco,' and was shaped like a Y with the arms so close together that they could be inserted up the nostrils, and it is highly probable that the word tobacco thus originated.

Upwards of 40 species of the genus *Nicotiana* have been described, but many of them are simply modifications resulting from the influence of soil and climate on the chief species, *Nicotiana Tabacum* (Linn.), the most important member of the genus, is a fine plant, indigenous to America, where it grows from 6 to 9 ft. high. The stem is slightly viscous, and the leaves, which are oblong or lanceolate in shape, are attached alternately, and surround the stem in the form of a spiral (of which the ninth leaf overhangs the first, the tenth the second, and so on). The distance between the leaves is usually about 2 ins. Characteristic soft downy glandular hairs cover the stem and the under surface of the leaves, and these are of great service in the identification of tobacco by the microscope. The flowers have funnel-shaped corollas, about 2 ins. long, of a rose or pinkish colour, and are produced in large terminal clusters; the seed

pods have two valves, and the seeds are very small and numerous. Modifications in the type have resulted in the production of several varieties of this species, differing chiefly in the size of their leaves. The two principal groups now recognised are *Nicotiana Tabacum*, var. *macrophylla*, or 'Maryland tobacco,' comprising stalked and stalkless forms, and *Nicotiana Tabacum*, var. *angustifolia*, or 'Virginia tobacco.' The finest growths of Cuba, Manila, and Turkey (including Latakia), are now attributed to a form of the stalked Maryland tobacco. Under the name of Shiraz tobacco, *N. persica*, a very fine variety, is cultivated in Persia; but the plant is probably a form of *N. Tabacum*, obtained by cultivation of seed derived from a Brazilian variety. Of the remaining species, *Nicotiana rustica* (Linn.) is the most important. It is of hardier constitution and dwarfer habit than the preceding species, and the flowers are also of a lighter colour. It is cultivated largely in Germany, Hungary, and in the East Indies, and includes the common Hungarian and Turkish varieties.

The use of tobacco for smoking purposes is supposed to have originated among the North American Indians. When America was first discovered, and afterwards when fresh portions of the continent were explored, the practice was found to be prevalent among all the native tribes, and its introduction into Europe very soon followed. The plant was first cultivated in Spain early in the sixteenth century, and was introduced into France and Italy about the year 1560. It attained considerable fame as a medicinal herb, and was at first regarded with universal favour. Sir John Hawkins is said to have brought plants home in 1565, but Sir Walter Raleigh, who learned the uses of the plant from Mr. Ralph Lane, Governor of Virginia, probably first introduced its cultivation. The habit of smoking soon became general, but this use of the plant met with a considerable amount of opposition, not only in England, but also throughout Europe. Nearly the whole of the early literature on the subject was written in an antagonistic strain. Kings' counterblasts, Popes' anathemas, Sultans' decrees and even violent punishments failed to check the growing habit, and plantations sprang up, not only in the New England States, but also all over the United Kingdom. In the year 1604 the tax on the imported article was raised from 2d. per lb. to 6s. 10d. per lb., and English planters were forbidden to produce more than one hundredweight of the leaf. Shortly afterwards the pre-emption of tobacco was made a royal monopoly, and the King enjoined the plucking up of all tobacco found growing in England and Ireland. In the years 1652, 1660, and 1663, Acts were passed prohibiting the cultivation of tobacco in England and Ireland, and these Acts were extended to Scotland in the year 1782. The prohibition as regards Ireland was removed in the year 1779, but was subsequently reimposed in the year 1831. Notwithstanding these measures, the cultivation of tobacco in England did not really cease until the year 1785, when some planters in the vale of York were imprisoned and fined the sum of £30,000. The restrictive legislation as regards Ireland was repealed in 1907, and for Great Britain in 1910.

Culture.—The tobacco plant, though essentially tropical, can, with suitable modifications in the cultural details, be grown successfully in temperate climates. It is cultivated for commercial purposes in the United States, Cuba, Mexico, Brazil, Paraguay, the Dutch Indies and North Borneo, Australia, India, China, Burmah, the Philippines, Persia, the Transvaal, Rhodesia, Nyassaland, the Levant, Greece, Hungary, Germany, Russia, France, and Holland, and is grown on a small scale in the United Kingdom. In Spain and Egypt its cultivation is prohibited. Cigar leaf is grown in Cuba, the East Indies, North and South America, Rhodesia, and Germany; tobacco for pipe smoking in the United States, the Levant, Germany, the Transvaal, Nyassaland, Australia, China, Java; tobacco for cigarettes in the United States, the Levant, Greece, Persia, and other countries. In the United States, several types of leaf are grown, of which the principal are the Seed Leaf and Florida varieties of Cuba and Sumatra tobacco for cigars; White Burley; the Heavy Shipping or dark tobacco of Kentucky, Virginia, and Maryland; the Yellow tobacco of Carolina and Virginia; and the Perique of Louisiana. A spangled type of yellow tobacco is grown also in Ohio. Seed Leaf requires a strong, highly-manured soil, which will promote a rapid growth, so that the plants may be harvested when expansion of the leaves ceases, and the process of granulation and secretion of the gummy substances begins. White Burley flourishes in a highly fertile disintegrated limestone. Heavy Shipping tobacco thrives best on ferruginous clayey soils. Yellow tobaccos need a sandy porous, sterile soil, to which just sufficient fertilizers (superphosphate, potash, and nitrogenous) have been added to promote summer growth; in the autumn the plant's declining vitality causes the leaves to turn more and more yellow until the tint desired is reached, which is afterwards fixed in the curing process. Perique is grown on low-lying lands, black with humus, in the swampy districts of Louisiana. Climate has a great influence on the flavour, but the texture of the leaf depends largely on the nature of the soil in which the plant grows. The northern varieties, for example, planted in the Southern States gradually change in character; the plants ripen earlier and the leaves assume a lighter colour, diminish in size, and increase in thickness and sweetness. * Special attention must be paid to the fertilizers used to ensure that the proportions of ammonia, potash and phosphoric acid most suitable for the type of leaf are employed. Too much ammonia darkens the colour of the leaf and increases its nicotine-content, while too little ammonia retards the growth. Alkaline materials encourage the growth of certain fungoid diseases, especially root-rot, and lime is therefore much less used than was formerly the case.

The seed is sown in February, March, or April, in seed beds, composed of a light friable soil prepared some time beforehand, and a brush heap is burned on the ground prior to sowing to destroy harboured insects. The young plants are raised either in hot beds, or in cold frames protected by plant-matting, according to the locality. In the three months from April to June, when the plants are about 8 ins. high,

they are transplanted into well ploughed soil, thrown up in ridges; and if the weather is dry, they are watered in. A space of from 1½ to 3 ft. is allowed between each plant in the rows, which are made from 3 to 4 ft. apart. The constant removal of suckers from the plants ('suckering'), frequent harrowing of the soil, and destruction of weeds and insect pests are necessary. In Turkey and other Eastern countries, where small leaves are desired, and the buds and flowers are also used, 'topping' is not practised, but the larger growths of the United States, &c., usually require this treatment when the first bloom begins to show. Ten to a dozen leaves in the case of Heavy Shipping tobacco, and 16 to 18 leaves in the other varieties, are allowed to remain on the stem, and the increase in leaf surface may be as much as 50 p.c., when compared with leaves of normal size. Seed Leaf requires from 2 to 3 weeks after this operation to ripen, yellow leaf and Burley take a month, and Heavy Shipping tobacco 2 or 3 weeks longer. An abnormal amount of organic matter accumulates in the cells of ripe tobacco leaf, owing to the 'topping' and 'suckering' of the plant. The continuous accumulation of nicotine, oxidising enzymes and acids which takes place in the cells finally causes the chlorophyll granules to acquire a yellowish colour. The change from the normal deep green tint of the leaf is very noticeable to the experienced eye, and indicates that the time for harvesting has arrived. Another sign of ripeness is that the leaf becomes brittle, and snaps when bent between the fingers on account of the great increase in its starch contents. The constituents of the cells having fulfilled their functions are at this stage going back to the stem to be transferred thence to the upper leaves, to be used for other purposes in the economy of the plant. Compared with the young leaf, the ripe leaf has a density half as high again, and contains about 2½ times as much matter soluble in boiling water. The curing of tobacco is a skillful operation, involving much more than the simple drying of the leaf. Its object is to promote by favourable conditions the important changes in composition which are brought about by enzyme action on the surplus food material stored in the ripened leaf. Until this is accomplished, it is necessary that the life of the leaf, which may persist for several days after harvesting, should be preserved. Any actions which tend to kill the leaf prematurely are to be avoided, e.g. breaking or bruising the leaf, freezing or very rapid drying. The methods of curing are fully described in Farmer's Bulletin, No. 573 of the U.S. Department of Agriculture, 1916. White Burley and Seed Leaf are air cured in houses that can be ventilated at will: this operation requires from 6 to 8 weeks. An alternating change from the moist to the dry condition of the leaves takes place according to atmospheric conditions as the curing proceeds. Yellow leaf is cured by artificial heat, distributed by fires in air-tight barns. The temperature is maintained at 80° to 90°F. for 16 to 36 hours for the leaf to acquire the proper colour, the heat is then raised by 5° to 10° at a time, about every 2 hours, to 115° to 120°F., and maintained at this point until the leaf is properly cured. The curing of the stalks is then effected by raising the temperature hourly by 5° to 10°

to about 180° to 175° F. The whole operation takes about three days. Heavy Shipping tobacco is hung on scaffolds or in barns for some days to become yellow, and the curing is completed by open log-fires, kindled directly under the tobacco and gradually increased in size. In India, Ceylon, and other Eastern countries, sun-curing is sufficient. Where resort to artificial heat is necessary, it is essential that the increase of heat should be at first very gradual, as the object is not so much to dry the leaf as to fix as far as possible its qualities as regards colour, strength, elasticity and flavour. A high initial temperature causes the leaf to dry rapidly and retain its green colour, whereas by slow drying the tint produced will vary from shades of yellow to brown. The proper fixing of the colour of the leaf is of great financial importance to the curer. The leaves, except those of the yellow varieties which are harvested as they ripen, are not usually removed from the stems prior to curing. Perique tobacco undergoes a special process of curing. After the leaves in the drying-houses have acquired a brown tint they are twisted into rolls containing about 30 leaves; these rolls are packed into boxes holding about 50 lbs. and heavy pressure is applied; the rolls are then slightly opened out and exposed to the air to aerate the exuded juices and, when these are re-absorbed, again subjected to pressure. This operation is repeated daily for about 10 days, and at longer intervals for some 3 months, with the result that the tobacco acquires a glossy black colour, and a rich characteristic spirituous odour. In Florida, cigar leaf is now grown from Cuba and Sumatra seed, but success has been achieved only by making considerable changes in the ordinary methods of cultivation. The plants are placed closer together, about 14 ins. apart; the Cuban varieties are topped high, but the Sumatra kinds are allowed to bloom. Each plant yields from 18 to 30 suitable leaves which are primed off as they ripen. The discovery that plants shaded by trees were far superior to those grown in the open fields, led to the adoption of artificial shading, which has also been tried with success in Cuba, Porto Rico, and Connecticut.

Preparation for the market involves the grading, fermentation, and ageing of the tobacco, and is usually managed by the packers and not by the farmers. There are three methods of fermentation; the sweating in bulk, the natural sweat after packing in cases, and the forced sweat in case; but the first is generally used, as it can be more easily controlled. The natural sweat of Seed Leaf is conducted in large wooden cases, each holding about 300 lbs. of leaf; a space of about half an inch is allowed between the boards, through which the air enters and the moisture escapes. In the autumn the leaves are pressed tightly into the boxes, which are then stored in the warehouse in tiers until the sweat occurring in the following summer is finished. The temperature is maintained fairly uniform, and the loss of weight during the process amounts to from 10 to 14 p.c. White Burley and Heavy Shipping tobacco are allowed to sweat in bulk for a short time before being primed, or forced into hogheads by pressure; the hogheads are large enough to hold from 1500 to 2000 lbs. of tobacco leaf.

Yellow tobaccos are also bulked down for a month or two to fix the colour, and are afterwards packed loosely. Cuba, Sumatra, and other cigar tobaccos are carefully graded according to colour, &c., and are fermented in large bulks, varying from 3000 lbs., for the light varieties to 15,000 lbs. for the dark varieties of leaf. The fermentation is allowed to proceed for from 6 to 8 days, and the heaps are then re-made, the outside portions being placed in the centre. The operations are conducted in rooms heated by steam pipes to about 165° F., but if the temperature of the heaps is allowed to rise much above 140° F. the enzymes present are liable to undergo oxidation with consequent deterioration in the quality of the tobacco.

Home-grown tobacco. In the year 1886, owing to the agricultural depression in this country, efforts were made to remove the restrictions then existing on the home cultivation of tobacco, and permission was obtained to try experimental growings in several selected localities. These experiments were repeated in the following year, and were sufficiently satisfactory to justify the opinion that tobacco could be grown successfully as a farm crop in the British Isles. Experiments under the auspices of the Department of Agriculture in Dublin were started in Ireland in the year 1900. In the year 1904, the cultivation was commenced on a commercial scale, and in the year 1907 the statutory restrictions were repealed. The Department continues to furnish all possible assistance to the tobacco growers, and annual reports on the progress of the experiments are published in its journal. A total area of about 200 statute acres was devoted to the cultivation of tobacco in the year 1914, as compared with 20 acres in the year 1904. The crop of 1914 yielded about 160,000 lbs. of marketable tobacco. During the war the area under tobacco cultivation was greatly reduced, but in 1922 about 35,000 lbs. of tobacco were raised from 50 acres planted by 46 growers. Cultivation has been tried successfully in the following counties: King's County, Louth, Meath, Kilkenny, Wexford, Tipperary, and Limerick. The experimental tests which have been carried on for several years gave promise that satisfactory roll and plug pipe-tobaccos could be produced from such hybrid varieties of leaf as 'Copper King,' 'Blue Pryor,' and 'Kentucky Black,' also 'Irish Gold' for cigarette tobacco. These varieties were found, however, to suffer from root-rot, a condition which does not obtain in the Italian hybrids 'Skiky,' and 'Turcoriah,' which have since been tried for pipe and cigarette use respectively. The influence of the cool, moist climate favours the production of large thin leaves which are somewhat deficient in gum, resins and aroma; but these defects have to some extent been overcome by prolonging the ripening season, during which the leaf gains in body. Irish leaf is for the most part used for blending with unfermented dark American tobacco of the Western type, and recent experiments have been directed chiefly to the raising of small crops of heavy dark varieties by working farmers. The Irish climate, however, favours the production of tobacco such as is grown in northern countries, all of which is fermented. The crop of 1922 has been treated thus with satisfactory results. The acquisition

for success are deep cultivation, a fine soil, and fields protected from cold winds by high hedges or other means. As regards manures, the initial growth is found to be more rapid when farmyard manure is supplemented by artificial manures. The largest yield is obtained on uplands, when manures containing a large proportion of phosphates are used; potash is more effective for moorlands. Nitrogen and phosphates have a tendency to produce a coarse leaf; with potash a smooth leaf is obtained, and the burning qualities are improved, but the growth is somewhat retarded. In consequence of the minute size of the seed, about 300,000 to the ounce, the plant is forced to rely unusually early on external nourishment. The seeds are sown in glass-covered hot-beds some time between the middle of March and the middle of April, and the plants are transplanted at the latest by June 1st. The usual cultural details are followed: insect pests, on the whole, are not so troublesome as they are abroad, but the cool, moist climate greatly increases the tendency to produce suckers. 'Topping' of all the varieties, except Turkish, is usually practised. Ripening is hastened by the 'topping' and 'suckering' operations, but the usual indications, change of colour, curling of the edges of the leaf, &c., are less manifest under Irish climatic conditions. Harvesting lasts from about the end of July to mid-October, according to whether the leaves are primed off as they ripen, or whether the whole plant is harvested with the leaves still attached to the stem. The practice of allowing the plants to wilt in the open air on scaffolds which are capable of being protected from heavy rains, has been found very valuable. Air-curing, supplemented by suitable artificial heat at critical periods, has proved to be the best method for most classes of tobacco. The subsequent preparation of the leaf for the market involves the usual operations of grading or sorting, fermentation in bulk, and ageing, after the tobacco is packed. A statute acre of land yields on the average about 1000 lbs. of tobacco at a cost of from £20 to £60.

The enactments against the growth of tobacco in Scotland and England were repealed by the Finance Act of the year 1909-1910, and from 1911 to 1913 a rebate of one-third of the duty was allowed on home-grown tobacco. Grants have since been made by the Development Commissioners and the Board of Agriculture with the object of promoting experimental work on the culture of tobacco which has been undertaken in 27 counties in the United Kingdom under the auspices of the British Tobacco Growers Society. Thirty-three acres were planted in the year 1913, in addition to 80 acres cultivated by private growers. In the year 1915 duty was charged upon nearly 33,000 lbs. of tobacco grown in England, and upon 2000 lbs. grown in Scotland; but no tobacco has been grown in Scotland since 1916. The Ministry of Agriculture have also undertaken experiments on the growth and after-treatment of tobacco on government-owned land in Norfolk. In 1923 about 14,000 lbs. of leaf were obtained from 18 acres under cultivation in Hampshire. Since 1918, however, there has been a marked decrease in the areas under tobacco cultivation in the United Kingdom, Northern Ireland, and the

Irish Free State. Growers contended that the rebate of one-sixth from the duty allowed by law in 1919 in the case of home-grown tobacco was not sufficient to allow of tobacco being grown at a profit. A Government Committee appointed by the Treasury to inquire into this question reported in 1923, Cmd. 1983, that though a limited number of agriculturists might derive some benefit from some measure of assistance to the industry of tobacco growing in this country, they came to the conclusion that the nature and extent of that benefit were not such that the committee could recommend any further expenditure of public funds over and above the help already given by Imperial Preference. The principal grounds on which the committee's conclusions were based are as follows:—

(1) Even allowing for the improvements which might be effected in British grown tobacco as the outcome of further experience, they could not anticipate that anything more than a low-grade article would be grown generally in Great Britain.

(2) There is accordingly no prospect of tobacco being grown on a large scale so as to compete successfully with foreign tobacco, except under a preference such as the industry now enjoys; and the amount of such a preference will always be liable to alteration (apart from the automatic decrease which a reduction of duty would bring about).

(3) Competing overseas products would always have the advantage of more suitable climates and of cheaper labour, and it cannot be assumed that Great Britain will have a monopoly of improvement.

(4) The crop is not suitable for smallholders, owing to the heavy capital expenditure required, the uncertainty of the quality and amount of the yield, and the interval which must elapse before a return on the outlay can be expected.

(5) Except on a limited area of land, the crop does not offer such a prospect of effecting a general improvement in the system of agriculture nor so remunerative a substitution for existing crops, as would justify some considerable outlay in bringing about its establishment.

Provision is made for remission of duty on such home-grown tobacco as is used for the preparation of tobacco extract for insecticidal purposes. An approved denaturant must, however, be added to the extract before it is allowed to pass out of revenue control.

Composition.—The tobacco plant contains a large number of substances common to the vegetable kingdom, chief among which are cellulose, starch, albuminoids, saccharine matters, resins, chlorophyll, and many organic acids. On the character and proportion of these organic substances depend largely the uses to which the several varieties of tobacco are put. Freshly-cut green leaves contain from 80 to 90 p.c. of moisture: the normal percentage in the leaf when ready for the market is from 12 to 14 p.c., but in the finer grades of cigar and other leaf 20 p.c. is not uncommonly found. The amount of nicotine, the characteristic constituent of tobacco, varies from about 1 to 10 p.c.: thick-leaved varieties contain more than those with thin leaves, and the top leaves of a plant are richer in nicotine than those at the base of the

stem. Schloßing has shown that the amount present in the leaves increases as growth proceeds: from leaves of the same kind collected on May 25, August 27, and September 25, he obtained 0.79, 2.27, and 4.32 p.c. of nicotine respectively. Dark, heavy tobaccos contain considerably more nicotine than the light coloured varieties. The use of large quantities of nitrogenous manures favours the production of nicotine in the plant. Java leaf contains from 1 to 2 p.c., Havannah, Maryland, Manila, and Turkish from 2 to 4 p.c., Virginia and Kentucky up to 7 p.c., while some heavy French varieties contain as much as 10 p.c. of nicotine. The organic acids present in tobacco are chiefly malic, citric, oxalic, and pectic; acetic acid is sometimes found in fermented leaves. Some proportion of these acids exists in combination as acid salts and gives an acid reaction to the cell-sap. The malates, owing to their hygroscopic properties, are said by Behrens to exercise a considerable influence on the 'life' of the leaf by preserving its elasticity and softness. The changes in the colour of the leaf which occur during the curing process are concomitant with considerable changes in the chemical composition, brought about partly by the etiolation of the chlorophyll granules, and partly by the subsequent oxidation of the sap contents of the dead cells. The acidity of the leaf, and the proportions of soluble albuminoids, and of starch also markedly diminish. Further changes of a complex character occur in the sweating process. The nicotine which exists in the leaf in combination with various organic acids is partially liberated, and part of it and of the amino bodies and albuminoids also, are eliminated. The nitric acid and ammonia-content should be little affected, but excessive fermentation favours the production of ammonium salts. Experiments by Dr. Loew of the United States Department of Agriculture, supplemented by those of Oosthuizen and Shedd, have proved that various soluble ferments or enzymes exist in the tobacco plant during its growth, and their researches have thrown light on the considerable influence enzymes exercise on the changes which occur during the ripening, curing, and fermentation stages. Invertase, diastase, emulsin and reductases have been identified in the tobacco seed, and in the leaf, not only during all stages of its growth, but also after the completion of the curing process. Oxidases have been found to be present in the growing leaf, but after the 'topping' operation they gradually diminish in quantity until maturity is reached, and almost entirely vanish during the 'curing' process. Starch is converted into sugar early in the curing stage by the action of diastase, but may disappear at a later stage, probably through the action of the oxidases present. Proteolytic ferments accomplish a considerable reduction in the amount of 'fat' or protein in the leaf, and reductases exercise a reducing influence on the nitrates and nicotine content of the leaf. Considerable loss of weight occurs during the curing and fermentation periods, amounting to as much as 15 p.c. in the later stages alone, of which about a quarter is solid matter. The retardation of enzyme action by unfavourable conditions in the curing and fermentation processes adversely affects the

flavour and aroma of the tobacco. Many attempts have been made to isolate and identify the bodies which impart the aroma to tobacco, but they have so far proved unsuccessful. At one-time the source of the aroma was believed to be the so-called tobacco-camphor, or nicotianin, a crystalline volatile substance obtained by the steam distillation of fermented tobacco; but experiments have shown that it is not always associated with nicotine in tobacco leaf, as was supposed. The theory of Suchsland, that the distinctive aromas which characterise the different types of tobacco are due to the action of specific bacteria during the sweating process, has not been substantiated by other observers. The formation of the aromatic substances is believed to be due largely to the influence of enzyme action, whereby elimination or breaking down occurs, especially in the nicotine, amino-bodies and other nitrogenous constituents of the leaf, during the fermentation stage. It is well known that a high nicotine content in a cigar is often associated with a poor aroma, and that if the leaf has a high protein content the quality of the aroma is especially liable to be deteriorated by imperfect curing. The deficiency in aroma which is characteristic of bright yellow leaf is no doubt due to the destruction of the enzymes which occurs in consequence of the high temperatures required during the curing stage of this class of tobacco. The aromatic matters of tobacco are soluble in water, and more or less so in alcohol, and are readily dissipated by heat. The odour developed in smoking a cigar may be due partly to the mere volatilisation of the aromatic products of the sweating process and partly to the destruction of certain constituents. Nicotine, ammonia, carbon monoxide, pyridine, trimethylamine, butyric acid, and traces of nicotianin, hydrogen cyanide, formaldehyde, and hydrogen sulphide, in addition to water and carbon dioxide, have been found in tobacco smoke. Kissling recovered from the smoke of two different samples of burning tobacco, each containing originally 3.75 p.c. of nicotine, 27.8 and 52.0 p.c. of the nicotine, while the quantity in the unconsumed portions of the tobacco increased to 4.5 and 5.9 p.c. respectively.

Armstrong and Evans (Brit. Med. J. 1922, (1), 992) found that the amount of carbon monoxide varied with the rate of smoking. Cigarettes smoked normally yield a smoke containing 0.6 to 0.8 p.c. carbon monoxide, pipe-tobaccos from 0.7 to 1.14 p.c., and cigars from 6 to 8 p.c. As regards cigars the results are little affected by make or quality, closeness of packing and rate of smoking being the determining factors.

The table on p. 82 of the analyses of certain kinds of tobacco serves to show the wide differences in the composition of various typical varieties. It is compiled from the results of analysis of many kinds of tobacco, which were made in the Inland Revenue Laboratory under the direction of Dr. James Bell.

The amount of ash found in tobacco varies greatly, and when calculated on the dry leaf ranges from about 10 p.c. to as much as 25 p.c., or even more. The lowest amount is found in the light varieties used for making cigarettes, and the greatest amount in leaf intended for making snuff. The ash of tobacco invariably

PERCENTAGE COMPOSITION OF TOBACCO DRIED AT 100°C.

Constituents	Manilla	Vir- ginia Ripe	Vir- ginia Bright	Turkey	Havana	Latakia	Ken- tucky	German	Java	China
Nicotine	3.00	3.86	2.20	0.90	3.98	1.17	4.59	3.22	3.30	2.50
Malic acid (anhydride)	10.72	9.06	4.17	4.90	12.11	9.07	11.57	12.04	6.04	7.46
Citric "	3.94	3.09	1.00	1.90	2.05	2.40	3.40	2.89	3.30	1.53
Oxalic "	3.72	1.58	1.72	1.38	1.53	1.98	2.03	2.51	3.38	3.91
Acetic "	0.36	0.80	0.35	0.14	0.42	0.36	0.43	0.34	0.22	0.31
Tannic "	0.30	1.34	6.32	3.39	1.13	2.33	1.48	0.68	0.51	3.13
Pectic "	10.63	7.72	7.51	9.62	11.36	6.25	8.22	10.23	10.13	7.48
Nitric "	0.43	0.43	0.14	0.05	1.32	0.76	1.88	0.37	0.23	—
Cellulose	11.73	10.38	12.64	9.72	15.76	10.00	12.48	14.48	11.82	7.98
Starch	—	—	1.73	6.28	—	0.69	—	—	—	1.54
Saccharine matter	—	—	14.59	12.07	—	1.46	—	—	—	12.93
Ammonia	0.30	0.05	0.03	0.05	0.49	0.10	0.19	0.32	0.23	0.04
Insoluble albuminoids	11.27	14.29	4.68	5.30	9.75	7.25	8.10	6.62	9.53	4.49
Resins and chlorophyll	7.51	5.21	3.41	7.90	5.15	6.62	1.99	2.13	6.45	6.02
Fatty substances	2.04	1.07	2.27	0.49	1.03	1.12	2.28	0.89	0.81	0.25
Soluble extractive matter rich in Nitrogen	8.34	16.24	13.47	13.24	7.74	18.97	13.90	8.10	10.39	14.35
Indefinite insoluble matter	9.45	12.93	12.41	9.71	8.68	14.94	13.10	12.56	15.20	12.61
Mineral matter	16.26	11.95	11.36	12.90	17.50	14.53	14.36	21.72	18.46	13.42

contains potash, lime, magnesia, iron-oxide, alumina, soda; carbonic, silicic, sulphuric and phosphoric acids, and chlorine. The potash, which exists in the tobacco mainly in combination with the organic acids, may be present to the extent of fully 30 p.c. of the total amount of the ash. The amount of lime present is generally lower than that of potash: magnesia and silica rank next, while the amounts of soda, alumina and iron oxide are relatively small. Lithia and manganous oxide are occasionally present in very small quantities. The combined chlorine varies from a mere trace to as much as 15 p.c. of the total amount of the ash (*cf.* Roberts, Analyst, 1918, 254).

The following table shows the percentage composition of the ash of the several kinds of tobacco enumerated in the preceding table.

The leaves of tobacco contain more magnesia and silicic acid, and less alkali, phosphoric acid and chlorine than the stalks. The nitrates are confined almost entirely to the stalks and stems of the young plant, and decrease in amount as the plant comes to maturity: analysis of cigar-stalks from Missouri and Connecticut showed from 0.5 to 0.75 p.c. of nitrates, as against 0.15 p.c. found in cigarette leaf. Home-grown tobacco as a rule contains a considerably higher percentage of ash than is present in similar varieties grown abroad: this circumstance is probably accounted for by the use of manures either in excessive quantities or of unsuitable character, especially when large quantities of combined chlorine are present.

Good burning qualities in tobacco are associated with a high percentage of ash, rich in

PERCENTAGE COMPOSITION OF ASH.

Constituents	Manilla	Vir- ginia Ripe	Vir- ginia Bright	Turkey	Havana	Latakia	Ken- tucky	German	Java	China
Percentage of ash on dry tobacco (excluding sand)	21.40	14.96	12.32	12.92	21.40	18.18	17.98	25.88	18.80	14.76
Potash	16.25	34.16	22.19	14.51	11.83	19.57	16.78	—	14.06	14.44
Potassium chloride	6.45	2.53	7.01	19.29	12.68	4.06	2.41	24.98	19.61	3.73
Soda	0.54	0.86	1.46	0.54	0.81	0.55	0.66	—	0.67	0.41
Sodium chloride	—	—	—	—	—	—	0.60	—	—	—
Lime	33.26	18.90	21.70	22.54	33.06	34.69	29.51	35.66	23.30	31.09
Calcium chloride	—	—	—	—	—	—	—	5.89	—	—
Alumina	0.22	0.29	0.89	0.76	0.76	0.68	0.19	0.43	1.79	0.97
Iron sesquioxide	0.18	0.40	2.44	0.43	0.45	0.55	0.32	0.23	0.84	1.10
Magnesia	7.22	6.74	12.44	9.21	5.29	5.53	6.78	6.45	8.68	12.70
Silica	1.59	1.55	0.57	2.06	1.97	2.03	4.94	0.86	6.16	3.38
Phosphoric anhydride	3.32	3.23	4.72	6.39	4.17	3.62	3.36	5.19	6.67	5.11
Sulphuric "	4.47	4.32	8.29	5.29	4.34	3.67	5.07	3.47	7.94	4.63
Carbonic "	25.90	27.02	18.29	19.07	25.54	25.05	29.58	19.25	11.34	22.24
Percentage of sand on dry tobacco	0.60	0.95	1.28	1.80	1.80	0.22	5.26	0.94	1.72	2.18

lime and potash salts: chlorides, except in the presence of much potash and lime, have a decidedly retarding effect on the combustion, but silicates, phosphates and sulphates have a beneficial effect. Albuminoids hinder, but cellulose promotes the good burning qualities of tobacco; while nicotine appears to be an unimportant factor. The comparative burning qualities, estimated by the time of glowing of the kindled leaf, vary from about four seconds in yellow varieties to as much as 175 seconds in Pennsylvania cigar-leaf.

Tobacco is analyzed as regards organic and inorganic constituents by the usual methods described in text-books dealing with agricultural and quantitative chemical analysis. Special processes applicable to tobacco are described in the report on the culture and curing of tobacco in connection with the 10th United States Census of 1880. The percentage of moisture is liable to be under-estimated if the drying-oven is not maintained at a temperature of 100° . The ash should be re-carbonated by the addition of strong solution of ammonium carbonate, and subsequently dried before ascertaining the weight. A convenient method for the estimation of nicotine in tobacco is that of Kissling, which is as follows: Take 20 grms. of tobacco, finely powdered and dried at a temperature not exceeding 60° , grind it up in a mortar with 100 c.c. of alcoholic solution of soda (6 grms. of NaOH dissolved in 40 c.c. of water and then made up to 100 c.c. with absolute alcohol). Transfer the mass to a Soxhlet extraction apparatus and extract for 3 hours with sulphuric ether. Remove as much of the ether as possible by careful distillation, mix the residue with 50 c.c. of a 4 p.c. solution of soda, and distil in a current of steam. The flask containing the nicotine extract should be connected with the condensing apparatus by means of a tube having a safety bulb, and the distillation conducted rapidly and in such a manner that when 200 c.c. of the distillate have been collected not more than 15 c.c. of liquid remain in the distilling flask. Titrate the distillate with decinormal H_2SO_4 , using lacmoid or litmus paper as an indicator. By using a series of test papers and noting the burette-reading against each, the exact point of neutralization can readily be ascertained when the papers are dry.

The method of Bertrand and Javillier, based on the precipitation of the nicotine as the silicotungstate, may advantageously be employed when the nicotine distillate also contains ammonia. A gravimetric adaptation of their process has been described by R. Spallino (Gazz. chim. ital. 1913, 43, 482-486). Five grms. of tobacco are placed in a Kjeldahl flask with 20 c.c. of water and 3 c.c. of 10 p.c. soda solution, and the mixture steam-distilled to a bulk of 500 c.c. To 100 c.c. of the distillate are added 10 c.c. of dilute HCl, and 10 c.c. of a 12 p.c. solution of pure potassium silicotungstate, and the mixture well stirred and allowed to stand for 2 hours. The precipitate is filtered through a tared Gooch crucible, washed with water acidulated with HCl, and ignited at a red heat. The residue has the composition $12\text{H}_2\text{O}, \text{SiO}_2$, and its weight multiplied by the factor 0.1136 gives the quantity of nicotine in one gram of the tobacco.

The method of Kissling is for the determination

of nicotine in tobacco smoke. Popp and Contzen (Chem. Zeit. 1922, 46, 1001) found that the total nicotine in eight kinds of cigar and pipe tobacco varied from 0.31 p.c. to 2.21 p.c. The smoke from these tobaccos contained from 0.20 p.c. to 1.05 p.c. of nicotine. See also Analyst, 1923, 33. According to H. Rhode (Zeitsch. Untersuch. Nahr. Genussm. 1923, 45, 112-115), the five brands of tobacco examined contained from 0.68 to 2.37 p.c. of nicotine calculated on the dry substance. When the samples were smoked in a pipe, attached to an aspirator with an intermittent action, from 15.4 to 28.8 p.c. of the total quantity of nicotine was found in the smoke. The amount of the alkaloid present in the smoke was not proportional to that in the tobacco itself (Analyst, 1923, 48, 568, 334).

Various methods of estimating nicotine in tobacco and tobacco extracts have been critically examined by Rasmussen (Zeitsch. anal. Chem. 1916, 55, 81; Analyst, 1916, 208), who found that the polarimetric method of Koenig as well as the silicotungstic method of Bertrand and Javillier, and the method of Kissling above described, gave accurate results; whilst Keller's method and that of Toth were less accurate, and those of Ulex, Degrasie, and Thoms were untrustworthy. This investigation has been carried further by Shedd in the Journal of Agricultural Research (Washington D.C.) 1923, 961-970. In the recovery of nicotine by the distillation method he used solid sodium hydroxide and found that, unless the bulk in the distilling flask was maintained at from 15 to 25 c.c., extreme difficulty was experienced in distilling off all the nicotine, especially when derived from tobacco. On the other hand, when 2 grams of soda were added to liberate the nicotine, higher results were obtained from the distillate by precipitation than when less quantities of alkali were used. He attributes the difference to the presence of some other volatile substance, produced by the action of the strong alkali on the small bulk in the distilling flask, which is precipitated by silicotungstic acid. For these reasons he suggests that instead of using the distillation method, the ether extract of the nicotine obtained by the Soxhlet extraction, after careful reduction in bulk, should be extracted in a separator with cold dilute hydrochloric acid (1:4) from 4 to 6 times. The extracts are bulked and an aliquot part, representing about 0.25 gram of tobacco extract, or from 1 to 2 grams of tobacco, is taken and diluted to 400-500 c.c. with water. Sufficient dilute hydrochloric acid—at least 3 p.c. is required—is added to show an acid reaction with methyl orange before precipitation. For this purpose he uses a 12 p.c. solution of silicotungstic acid having the specific formula $\text{SiO}_2, 4\text{H}_2\text{O}, 12\text{WO}_3, 22\text{H}_2\text{O}$. The factor for converting the weight of the ignited residue to nicotine is 0.114. The details of the method are as follows: Five grams of finely powdered dry tobacco, or 1 gram of tobacco extract (about 40 p.c. grade), is moistened with 25 c.c. of alcoholic sodium hydroxide solution (6 grams of sodium hydroxide in 40 c.c. of water and 60 c.c. of 90 p.c. alcohol). The extracts 5 c.c. of soda solution is used and the mixture made into a moist paste with calcium carbonate. The sample is extracted for 3 hours with ether in a Soxhlet extractor, and the

taken that the temperature of the cooling jacket does not rise above 20°C. and that the volume of solvent in the extraction flask is never less than 25 c.c. After extraction, the excess of ether is removed, but the volume remaining must be sufficient to keep the whole of the extracted matter in solution. The ether extract is transferred to a separating funnel, the flask being rinsed with ether and finally with hydrochloric acid (1:4), and shaken with from 4 to 6 10-c.c. portions of hydrochloric acid (1:4). The formation of emulsions can be avoided by adding 1 c.c. of alcohol. The washings are filtered through glass wool into a 100 c.c. graduated flask. When tested portions of the washings no longer give a turbidity with silico-tungstic acid reagent, the whole volume is made up to 100 c.c., an aliquot portion equivalent to 1 to 2 grams of tobacco is diluted to 400-500 c.c., and sufficient hydrochloric acid (1:4) added to ensure that at least 3 c.c. of it is present in 100 c.c. of the solution; 1 c.c. of silicotungstic acid solution is then stirred in for every 0.01 gram of nicotine supposed to be present. After stirring for 3 to 5 mins. the precipitate appears crystalline and settles readily. The solution is allowed to remain for 18 to 24 hours and filtered, preferably through a Hirsch or Buchner funnel. The precipitate is washed with hydrochloric acid (1:1000), dried, and transferred—with the paper to a platinum crucible. After heating until all carbon is removed the crucible is finally ignited for not more than 10 mins. over a Teclu or Meker burner. The weight of the residue $\times 0.114$ gives the weight of nicotine in the aliquot portion taken. The silicotungstic acid reagent is a 12 p.c. solution of the acid $4H_2O \cdot SiO_2 \cdot 12WO_3 \cdot 22H_2O$. The other silicotungstic acids do not give a suitable crystalline precipitate with nicotine (O. M. Shedd, J. Agric. Res. 1923, 24, 961-970; J. Soc. Chem. Ind. 1923, 42, 1150A).

Manufacture.—In several European countries, among which may be mentioned France, Spain, Italy, Austria-Hungary, and Turkey, the manufacture of tobacco is a State monopoly. In Canada, the United States, Germany, Holland, and other European countries the manufacture is in private hands. In the United Kingdom, tobacco is subjected to a heavy import duty, but a rebate of one-fourth is allowed on tobacco grown in the British Empire. Certain legal restrictions are imposed, which, however, chiefly affect the manufacturers of the commoner kinds of tobacco. The only substance allowed by law to be used in the manufacture of tobacco is water. The use of olive oil is permitted in spinning and making up roll tobacco, and essential oils are allowed for flavouring purposes. The finished article must not contain more than 32 p.c. of moisture, and if it is roll tobacco, not more than 4 p.c. of olive oil. The leaves of plants other than tobacco may not be employed, nor any preservative except acetic acid. Essential oils for flavouring purposes may be added to snuff, and the addition is allowed of the carbonates, chlorides and sulphates of sodium and potassium, ammonium carbonate, and of 1 p.c. of lime in the form of lime-water. The snuff, when dried, however, must not contain more than 26 p.c. of alkaline salts nor more than 13 p.c. of the oxides of lime and magnesia, inclusive of the amounts naturally

present in tobacco. More latitude is allowed in the manufacture of tobacco in bonded factories: the addition of foreign leaves is not permitted, but any suitable sweetening or flavouring matter may be used. Sugar, honey, liquorice, glycerin, gum, salt, and logwood are the ingredients most commonly used for this purpose in the manufacture of this kind of tobacco, which is known as Cake- or Cut-Cavendish, and is manufactured chiefly for exportation. If intended for home consumption, this tobacco is required to be enclosed in a specially designed Customs' wrapper to distinguish it from the ordinary article, and it is subjected to a higher rate of duty. The sale of cigarettes containing sweetening matter is not permitted.

Tobacco leaf is imported into this country either entire or with that portion of the mid-rib removed which cannot be used in manufacturing, in which case it is called 'strips', and assessed at a slightly higher rate of duty. Apart from fluctuations due to war-time conditions, the proportion of 'strip' tobacco imported is steadily declining, having fallen from 39 p.c. in the year 1907 to 30 p.c. in the year 1925. Over 85 p.c. of the raw material comes from America, and about 6 p.c. from other foreign sources, chiefly the Levant, Dutch Indies, China, and Japan. Empire-grown tobacco secured preferential tariff treatment in 1919, and in 1925 the rebate of duty allowed was increased from one-sixth to one-fourth. About 8 p.c. is now imported, chiefly from India, Nyasaland, Rhodesia, Canada, and North Borneo. The principal kinds of foreign tobacco used are Virginia, Kentucky, Western, Burley, Ohio, Perique, Havannah, Japan, Java, China, Sumatra, Borneo, Turkish, and Latakia. The more tender varieties, such as Turkish, are packed carefully in bales leaf upon leaf, but hogsheads are the usual packages employed: the leaves are packed either in layers or in bunches of ten to a dozen leaves, bound round with another leaf and known as 'hands.' Price, colour, texture, burning qualities, aroma, and body or drinking power, that is, ability to absorb and retain moisture without becoming too wet, are all factors which influence manufacturers in selecting tobacco.

Imported leaf, although apparently dry, usually contains from 10 to 20 p.c. of moisture, but 14 p.c. may be regarded as a fair average. There are two rates of duty on imported leaf tobacco depending on the amount of moisture present. The duty on leaf containing less than 10 p.c. of moisture is levied at a rate substantially higher than on leaf containing 10 p.c. or more of moisture. The manufacturer of the cheaper kinds of tobacco endeavours therefore to secure leaf containing moisture as little in excess of 10 p.c. as possible, and so to obtain a larger profit from the greater amount of water he can add in the process of manufacture. In cigarette, cigar, and other varieties of leaf requiring careful handling, a higher initial percentage of moisture is desirable, and these varieties of leaf sometimes contain as much as 20 p.c. of moisture.

The principal kinds of manufactured tobacco are cut, twist or roll, and cake tobacco; cigars, cigarettes, and snuff. Many kinds of leaf are blended for manufacturing cut tobacco, and in the commoner kinds a considerable quantity of

leaf other than American is employed. These 'substitutes' were adopted at the time of the civil war in the United States of North America, which caused a temporary shortage in the supplies of Virginia leaf tobacco. Many of these 'substitutes' have the distinct advantage of being able to retain a large quantity of moisture without appearing to be unduly moist. Other blends are made entirely from Empire-grown tobacco.

The first process in manufacturing tobacco is the 'liquoring' stage: the old crude method of employing a watering-pot has now been superseded by the use of steam appliances which ensure a more even distribution of the moisture. When 'strips' are not employed, the mid-rib of the leaf which absorbs more moisture than the lamina is then removed—this operation is called 'stripping.' A mechanically actuated knife is employed to cut the tobacco into shreds: 'shags' and such like tobaccos undergo the further process of 'panning,' which consists in thoroughly mixing up the cut tobacco on copper trays heated to a suitable temperature; the tobacco is then set aside to cool on racks. The moisture in the common kinds averages about 30 p.c., but the better kinds of smoking mixtures contain from 15 to 25 p.c. The distinctive flavours of these tobaccos are due either to the presence of Latakia, Perique, &c., in the blend of leaves used or to the addition of essential oils such as oils of cassia, geranium, cloves, bergamot, and winter-green. Acetic acid is employed as a preservative. For 'twist' tobacco the darker varieties of American leaf, such as Kentucky, Western, Clarksville, &c., are chiefly employed, but a small quantity of Empire-grown leaf is now used in this class of tobacco. 'Twist' tobacco is made either by hand or on a spinning-wheel: the damp strips or 'fillers' are formed into ropes, the thickness of which depends on the denomination of 'twist' intended to be manufactured, and these ropes are enclosed in a covering wrapper of leaf. The tobacco, at this stage, is known as 'brown twist,' for which a considerable demand exists, chiefly in the North of England. If the tobacco is intended for 'black twist' the rope of tobacco is made up into 'rolls,' consisting of several concentric layers superimposed one on the other. The rolls, after being enclosed in oiled cloths, and tightly bound up with rope, are then baked in steam-heated hydraulic presses until the tobacco assumes a rich black colour, and develops its full aroma; they are then removed to a cold press until cool and fully matured. In order to prevent the coils from sticking to one another in the rolls, olive oil is applied to the tobacco during the 'spinning' and 'rolling' or 'making up' processes, but the amount of oil used is regulated so as to ensure that the finished tobacco does not contain more than 4 p.c. of oil. Acetic acid and essential oils are also employed. Special names are given to different forms of 'twist,' e.g. the terms Ladies' twist, Aloa twist, Liverpool roll, Pigtail and Bogie, have reference to the thickness of the rope; Negrohead indicates a plaited variety; Nailrod is in the form of sticks, and Target is a thick twist coiled up in a single layer. 'Cake' tobacco is prepared either by pressing 'spun' tobacco or by rolling the damp strips under pressure

and then adding an outer covering of leaf. 'Flakes' and 'Cut Cavendish' are obtained by cutting these cakes.

The leaf employed for the manufacture of high-class cigars has to meet many requirements, and blends of different varieties are therefore employed. The component parts of a cigar are the 'filler,' the 'bunch wrapper,' and the 'outer wrapper.' The 'filler' consists of fragments or cuttings of leaf, or even cut tobacco. The 'bunch wrapper' is shaped like a balloon gore, and cut from a tobacco strip of fairly good quality. The outer wrapper is a long rectangular strip of leaf cut from a tough leaf with small veins, of a light and uniform colour and should not possess a pronounced flavour, as it comes in contact with the lips and tongue in smoking; the filler must, however, possess a good aroma, emit an agreeable odour on burning, and have good burning qualities. The finest leaf for cigars comes from Cuba, but Sumatra, North Borneo, Java, &c., supply a considerable quantity of the leaf used for cigar-making in this country. The leaves are moistened with water, opened out carefully, deprived of the midrib, smoothed out and sorted; the perfect leaves are cut in halves and are used as wrappers. The 'filler' is placed on the 'bunch wrapper,' near one end, and the bunch wrapper is then carefully wound round the filler. Over the 'bunch wrapper' the cigar-maker then winds spirally the 'outer wrapper,' commencing at the open end and finishing off at the pointed, or mouth, end. Uniformity in the commoner kinds is secured by the practice of pressing the cigars in moulds before applying the outer wrapper. The cigars are then gaged and cut to the proper length, sorted according to size and colour, dried and packed. Great dexterity is necessary in making cigars, especially in manipulating and keeping the cigars to shape, size, and weight, as well as in evenly packing. The moisture in the finished cigar is reduced to about 10 to 15 p.c. by storage in a drying-room.

The manufacture of cigarettes was introduced into this country by a Greek in the year 1860, and originally Turkish varieties of tobacco only were employed, but 'Virginian' blends are now made in very large quantities from American and other varieties of bright leaf. As the character and the aroma of a cigarette depend on the suitable blending of the various kinds of tobacco employed, this branch of the tobacco industry has become highly specialised. The tobacco used for cigarettes is comparatively dry, the moisture added is just sufficient to permit of the leaf being satisfactorily cut by the machines. The finer varieties of cigarettes are invariably made by hand, either by rolling up the tobacco in the paper, or by filling it into paper tubes closed at one end. In the latter method, charging cylinders slightly smaller in diameter are used, and the tobacco is transferred therefrom to the tubes by means of a funnel; the closed ends of the paper tubes are subsequently cut off. A great impetus has been given to the production of cigarettes by the employment of cigarette-making machines, which can easily turn out over 60,000 cigarettes per hour. Machines for arranging and packing the cigarettes in cartons are also employed, a single machine being able to deal with at least

380,000 cigarettes per day. The moisture in cigarettes varies according to the time they are stored in the drying-room, and usually ranges from 12 to 18 p.c.; if the tobacco is made too dry it is liable to be shaken out of the wrapper; on the other hand, if the tobacco is left too damp, the cigarette will not burn well. Mouthpieces are often fitted to cigarettes made from Turkish tobacco, on account of its superior burning quality. Cigarettes vary considerably in weight; an ounce may contain from 12 to 40 cigarettes, but 20 to 30 is about the average. Sweetening matter is not allowed to be used in making cigarettes, but the paper wrappers of the 'pectoral' kinds sometimes contain a small quantity of saccharin. Alcoholic solutions of essential oils may be added by manufacturers to the tobacco used in perfumed cigarettes.

Snuff is sold in two forms, dry and moist, the former is made from the stalk or midrib of the leaf, the latter contains a proportion of the lamina. The difference in the quality is dependent on the flavour, the pungency, and the scent. The dry varieties—the Welsh, Scotch, High Toast, and Irish kinds—are, as a rule, more finely ground than the moist varieties. The moisture ranges from about 20 p.c. in Scotch snuffs, to as little as 5 p.c. in Irish snuff. 'Rappees' include such well-known varieties as Latakia, Macuba, and Prince's mixture, and contain from 30 to 50 p.c. of moisture. The tobacco stalks used for snuff-making are cut into small pieces, moistened with alkaline water or sometimes with lime-water, and allowed to ferment, the fermentation period frequently lasting for several months. The material, in the case of Scotch snuff, is then ground to the required degree of fineness, dried down, flavoured, and sifted. The stalks for Irish and Welsh snuff, before being ground, are gently roasted, by which means the characteristic odour of these varieties is produced. For moist snuffs the material is ground wet in a special kind of mortar, and is then allowed to ferment until the required depth of colour is produced. Certain kinds of alkaline salts are mixed with the snuff-flour to increase its pungency, but, as already mentioned, the quantity and the kinds which may be employed are defined by statute. Essential oils, ground orris-root and ground Tonquin beans are used for flavouring purposes. Adulteration of snuff is now rarely practised, but such substances as the oxides of iron, red lead, lead chromates, &c., have been used as colouring materials, and chalk, magnesia, borax, sand, and excessive quantities of alkaline salts have been employed to increase the weight.

Prior to the passing of the Pure Tobacco Act of the year 1842, the adulteration of tobacco with sugar, treacle, honey, gum, &c., and such foreign vegetable matters as rhubarb, coltsfoot, &c., was very general; but in consequence of the heavy penalties imposed by that Act and the vigilance of the Revenue Authorities these practices have almost ceased. The enactments relating to the amounts of moisture and oil in tobacco are also strictly enforced. Such substances as malt combining, moss-litter, &c., are occasionally offered as substitutes for tobacco, but the offenders rarely escape detection and punishment. Manufactured tobacco frequently contains considerable quantities of sand, and

manufacturers are sometimes suspected of using it as an adulterant. The leaf, however, usually comes into their possession still retaining a proportion of the sand which was deposited upon it from the soil by the action of the wind and rain during growth. A portion of this sand only is detached from the leaf during the manufacturing operations, which accounts for the presence of sand in the finished article.

In the manufacture of tobacco, a considerable quantity of waste material is produced, siftings, sweepings, &c., and in addition the quantity of stalks obtained by stripping the midrib from the imported leaf is far in excess of that required for conversion into commercial snuff. Repayment of the duty, called 'drawback,' is made by the Crown Authorities on this refuse of tobacco when it is exported or deposited in an approved warehouse to be abandoned to the Crown, or in a bonded factory to be utilised in the manufacture of nicotine or the preparation of 'sheep-dip,' hop-powder, insecticides, &c. Denaturing materials are required to be added to the ground tobacco before it is allowed to be sold, in order to prevent such tobacco being used as a substitute for the duty-paid article. Anthracene oil, bone oil, ground moss-litter, and sulphur are some of the substances used for this purpose.

Statistics.—The amount of tobacco leaf imported into the United Kingdom and the consumption of manufactured tobacco have steadily increased. The imports in the year 1851 amounted to about 28,000,000 lbs. and the consumption was just over 1 lb. per head of the population; in the year 1925, the amount imported was over 152,000,000 lbs. and the consumption was slightly in excess of 3 lbs. per head of the population. The manufacture of tobacco is now one of the most important of the minor industries, and according to the returns made in connection with the Census of Production for the year 1907, the number of persons then employed in tobacco factories was 37,456. The net value of the raw material was £27,988,000 and, including 11,816,000 lbs. of manufactured tobacco exported, the output amounted to 108,292,000 lbs., representing a money value of £23,799,000. The weight of the different kinds was as follows: of cut and roll tobacco, 69,880,000 lbs.; of cigarettes, 29,904,000 lbs.; of cigars, 3,696,000 lbs.; of sweetened cavendish, 3,136,000 lbs.; and of snuff, 1,568,000 lbs. The degree of the popularity of the principal kinds of tobacco, as ascertained from these figures, is pipe tobacco 67·5 p.c., cigarettes 29·0 p.c., and cigars 3·5 p.c. respectively. Cigarettes have, however, materially gained in favour in recent years, and at the present time their proportion may be estimated at 80 p.c.

Tobacco occupies an important position as a source of revenue in the fiscal systems of most civilised countries. In the tariff of the United Kingdom the rate of duty has been more than doubled since the year 1914, and the net amount of duty paid into the Exchequer in the financial year 1924-25 was nearly five-two million pounds sterling.

D. A. G.

TOBACCO-SEED OIL. Tobacco seeds yield on pressing, or by extraction with carbon tetrachloride, about 20 to 25 p.c. of a greenish-yellow, mild, and odourless oil, η_{sp}/c 0·004 at 25° solidifying at -22° which contains some wax

exposed to the air. Acid value, 9.5; saponif. value, 196.4; and iodine value, 131.6.

According to Paris (Bot. tec. 1920, 17, 101), tobacco seed contains: water, 9.17 p.c.; crude protein, 21.87 p.c.; fat, 37.68 p.c.; amides and sugar, 6.05 p.c.; pentosans, 2.9 p.c.; cellulose, 7.15 p.c.; and ash, 3.84 p.c. The ash contains SO_2 , 1.97 p.c.; P_2O_5 , 22.12 p.c.; Na_2O , 3.48 p.c.; K_2O , 28.5 p.c.; CaO , 9.54 p.c.; MgO , 14.63 p.c.

A sample of oil from Kentucky seed had d_{20}^{20} 0.9408; temp. of solidification, 12° ; acid number, 4; saponif. number, 196; iodine number, 132.8; ether number, 192. The oil consisted of about 52.4 p.c. of olein, 22.1 p.c. of linolein, and 23.9 p.c. of palmitin. Nicotine is not present in the seed except when germinating. The dry, fat-free seed contained 6.5 p.c. of total nitrogen; 3.76 p.c. of protein nitrogen; 2.39 p.c. of nuclein nitrogen, and 0.35 p.c. of non-protein nitrogen. Arginine is present.

TODDALIA ACULEATA (Pers.). This Indian plant, belonging to the *Rutaceae*, is a rambling shrub found in the sub-tropical Himalayas, in the Khasia mountains, and throughout the Western Peninsula and Ceylon.

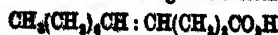
The root bark is or was used in Madras as a yellow dyestuff, and it is also highly spoken of by various writers as one of the most valuable Indian medical products, possessing tonic, stimulant, and antipyretic properties. It was introduced into European medicine in 1771, and at one time enjoyed some celebrity under the name of 'Lopez Root,' but it has long since fallen into disuse.

According to Brooks (Philippine Journal of Science, 1910, v. 442), the plant is common in the Philippines, but so far as is known is not used as a dye by the natives.

The colouring matter it contains is berberine (Perkin and Hummel, Chem. Soc. Trans. 67, 413).

A. G. P.

TÔHAKU OIL. An unsaturated acid $\text{C}_{11}\text{H}_{18}\text{O}_2$, light yellow oil, was isolated from Tôhaku oil obtained from *Lindera obtusiloba*, B.L., and purified through the methyl ester, b.p. 123° – 125°C ., its properties being as follows: iodine value 126.33, neutral value 282.26, m.p. 1.0° – 1.5°C ., sp.gr. at $15^\circ/4^\circ$ 0.9246, n_D^{20} 1.44922, n_D^{15} 1.45113, molecular refraction 57.71; 100 parts of water dissolve 0.027 part of the acid at 17°C . By Hazura's oxidation method, the oil yielded a hydroxy acid, $\text{C}_{11}\text{H}_{18}\text{O}_4(\text{OH})_2$, fine needles, m.p. 102°C ., which is easily soluble in hot water, alcohol, and ether, but sparingly soluble in cold water and ether. When the original acid was ozonised and decomposed with hot water, succinic and n -caprylic acids and n -caprylaldehyde were isolated. Y. Iwamoto therefore assigns the formula



and proposes the name *linderic acid* for the fatty acid (Y. Iwamoto, Kôgyô-Kwagaku Zasshi, J. Chem. Ind. Japan, 1923, 26, 708–716; cf. J. 1923, 258 A.; J. Soc. Chem. Ind. 1923, 42, 786 A.).

TOLAMINE. Syn. for Chloramine T (q.v.).

TOLUENE v. *Tolu*, art. **BALSAMS**.

TOLUIDINE. A method for the estimation of toluene. The sample is dissolved by heating with N/1 potassium dichromate and the toluene dihydrochloride precipitated by adding 10 times the

volume of saturated sodium chloride solution. The salt is allowed to crystallise for 20–30 mins., is filtered off and washed with saturated sodium chloride solution, dissolved in warm water, and the base liberated with slight excess of ammonia solution, methyl red being used as indicator and a measured volume of standard ammonia being run in. The precipitated toluidine is filtered off and washed with water and the excess of ammonia titrated with N/10 hydrochloric acid; 1 c.c. of N/10 ammonia solution equals 0.0106 gram of toluidine. Test analyses carried out on purified toluidine gave results varying between 99.52 p.c. and 99.96 p.c. Variations in the concentrations of sodium chloride and hydrochloric acid used are without appreciable effect on the result (S. Palkin, Ind. Eng. Chem. 1923, 15, 1045; J. Soc. Chem. Ind. 1923, 42, 1121 A.).

TOLIDENE (*Orthotolidene*) v. **DIPHENYL**.

TOLITE. A French term for trinitrotoluene. Used as an explosive.

TOLU v. **BALSAMS**.

TOLUENE, toluol or methylbenzene, C_6H_5 , or $\text{C}_6\text{H}_5\text{CH}_3$; first discovered by Pelletier and Walther (Ann. Chim. 1838 (2), 67, 278) among the by-products in the manufacture of illuminating gas from the resin of *Pinus maritima*, and named by them retinaphtha. Also obtained by distilling Tolu balsam (Deville, *ibid.* 1841 (3), 3, 168); from dragon's blood (Glenard and Boudault, Compt. rend. 1844, 19, 505); from coal tar (Manafield, Chem. Soc. Trans. 1847, 1, 244); from wood spirit and wood tar (Cahours, Compt. rend. 1850, 30, 320); from Rangoon tar (De la Rue and Müller, *cf.* Chem. Soc. Trans. 1861, 14, 54); from American petroleum (Young, *ibid.* 1898, 73, 906); from Borneo petroleum (Jones, Chem. Soc. Trans. 1907, 81, 1146f); and from other hydrocarbons (Rittmann, Eng. Pat. 9136 of 1915; J. Ind. Eng. Chem. 1915, 7, 945, 1014, 1019); in the products of distillation of a large number of substances (Ritthausen, J. pr. Chem. 1854, 61, 74; Bunte, J. Gasbeleucht, 1892, 35, 571; and others); and in a number of naturally occurring substances (Poni, Anal. Acad. romane, 23; and others). For sources of toluene, see also Rhéad (J. Soc. Chem. Ind. 1917, 36, 764).

It may also be prepared by the action of sodium on a mixture of bromobenzene and methyl iodide in ethereal solution, thus proving its constitution as methylbenzene (Fittig and Tollens, Ann. 1864, 131, 303); by the action of methyl chloride on benzene in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. 1884, (6) 1, 459; Sifton, Eng. Pat. 8886 and 9437 of 1915; Fr. Pat. 479297), and by other methods (Gardeur, Chem. Zentr. 1896, i. 438; Fromm and Aebart, Ber. 1903, 36, 534; Werner and Zilkina, *ibid.* 2116; Mai, *ibid.* 1902, 35, 162; and many others). It is also obtained in a yield of 12 p.c. by treating xylene with 2–4 p.c. of aluminium chloride at the boiling-point of xylene for 3 hours (F. Fischer and Niggemann, Ber. 1916, 49, 1475; Honkaha, U.S. Pat. 1334033, 1337317), and by cracking solvent naphtha under a variety of conditions (Egloff, J. Ind. Eng. Chem. 1918, 10, 8; Evans, U.S. Pat. 1336067; Synthetic Hydrocarbon Co., Fr. Pat. 479214; and others).

Commercial toluene is mainly obtained from coal tar by rectification of the fraction boiling

between 100°–120° (Coupler, *Dingl. poly. J.* 1866, 181, 386; Leuchart, *J. pr. Chem.* 1890, (2) 41, 301; cf. *J. Soc. Chem. Ind.* 1915, 34, 170, 416, 539, 1001; Butler and Popham, *J. Soc. Chem. Ind.* 1918, 37, 220 T).

Toluene may be purified by treatment with sulphuric acid (Friswell, *Chem. News*, 1893, 68, 27), and freed from thiotoluene by treatment with aluminium chloride (St. Denis Co., *Fr. Pat.* 240111 of 1894; D. R. P. 79505 of 1894), whilst analytically pure toluene is obtained by converting the less pure substance into the well crystalline potassium toluene *p*-sulphonate, which is subsequently hydrolysed (Miller, *Chem. Soc. Trans.* 1892, 61, 1025; see also Kelbe, *Ber.* 1886, 19, 93; Kraemer and Böttcher, *ibid.* 1887, 20, 601).

Properties.—Toluene is a colourless liquid, b.p. 111°/760 mm., 46·6°/92·0 mm., 38°/56·6 mm., 31·9°/42 mm., 23°/26·58 mm., 14·5°/14·56 mm. (Kahlbaum, *Siedetemp. u. Druck*, 95; cf. Neuback, *Zeitsch. physikal. Chem.* 1887, 1, 656; Young, *Chem. Soc. Trans.* 1898, 73, 906; Linebarger, *Amer. Chem. J.* 1896, 18, 437); m.p. –97° to –99° (Archibald and McIntosh, *J. Amer. Chem. Soc.* 1904, 26, 305; cf. Ladenburg and Krügel, *Ber.* 1900, 33, 638; Altschul and Schneider, *Zeitsch. physikal. Chem.* 1895, 16, 25); D_4^{20} 0·8812, D_{12}^{20} 0·87403 or 0·87417 (Orton and Jones, *Chem. Soc. Trans.* 1919, 115, 1067) D 0·8723, D_{25}^{25} 0·8649 or 0·85680 (Linebarger, *l.c.*); D_{50}^{50} 0·8490, D_{100}^{100} 0·8237 (Perkin, *Chem. Soc. Trans.* 1896, 69, 1191); $D_4^{13·1}$ 0·8708, D_{10}^{10} 0·77805 (Schiff, *Ann.* 1883, 220, 91); critical temperature 320·8° (Pawlewski, *Ber.* 1883, 16, 2634); critical pressure 41·6 atm. (Altschul, *Zeitsch. physikal. Chem.* 1893, 11, 590); magnetic rotatory power 12·16 at 13·1° (Perkin, *l.c.*; cf. Schönrock, *Zeitsch. physikal. Chem.* 1893, 11, 785); vapour pressure at low temperatures (Kahlbaum, *Zeitsch. physikal. Chem.* 1898, 26, 586, 616; Woringer, *ibid.* 1900, 34, 257); dielectric constant (Drude, *ibid.* 1897, 23, 309; Abegg, *Ann. Physik.* 60, 50; Landolt and Jahn, *Zeitsch. physikal. Chem.* 1892, 10, 299); refractive index (Landolt and Jahn, *l.c.*); molecular refraction 60·06 (Brühl, *Ber.* 1892, 25, 3075); capillarity constant at the b.p. $a^2 = 4·746$ (Schiff, *Ann.* 1884, 223, 104); molecular heat of combustion 933,762 Cal. (Stohmann, *J. pr. Chem.* 1887, (2), 35, 41; cf. Richards and Davis, *J. Amer. Chem. Soc.* 1917, 39, 341; 1920, 42, 1590). For the volatilisation of toluene in steam, see Barbaudy (*Compt. rend.* 1923, 176, 1616).

The nature of the products of oxidation of toluene is largely dependent upon the oxidising agent employed, thus, whilst chromic acid and dilute nitric acid yield mainly benzoic acid, potassium persulphate yields a mixture of dibenzyl, and benzaldehyde (Moritz and Wolfenstein, *Ber.* 1899, 32, 432), and manganese dioxide, acetic and sulphuric acids yield *o*- and *p*-tolylphenylmethane, benzaldehyde, benzyl alcohol, benzoic acid, complex hydrocarbons and carboxylic acids (Weiler, *Ber.* 1900, 33, 464).

On oxidation with manganese disulphate at 40°–50°, toluene yields benzaldehyde almost quantitatively, whilst at higher temperatures benzoic acid is formed (B. A. S. F., U.S. Pat. 796,494; D. R. P. 175,295 of 1900); for the

oxidation of toluene by means of lead peroxide, manganese peroxide, chromyl chloride, and persulphates, see Law and F. M. Perkin (*Chem. Soc. Trans.* 1907, 91, 260; 1908, 93, 1633), and for the preparation of benzaldehyde by oxidising toluene in presence of various catalysts, see Woog (*Compt. rend.* 1907, 145, 124) and Coquillion (*ibid.* 1873, 77, 444). Benzaldehyde and benzoic acid, together with other products, are also obtained by the electrolytic oxidation of toluene in presence of alcohol and dilute sulphuric acid (Renard, *Compt. rend.* 1891, 92, 965; Puls, *Chem. Zeit.* 1901, 25, 263; Merzbacher and Smith, *J. Amer. Chem. Soc.* 1900, 22, 723), the course of the reactions involved during the electrolytic oxidation is detailed by Fichter (*Zeit. elektrochem.* 1913, 19, 781).

100 grams of toluene containing 5 grams of anthraquinone yields, after exposure to sunlight and air for six weeks, 40 grams of benzoic acid, 10 grams of isohydrobenzoin and hydrobenzoin, 0·2 gram of benzaldehyde, and 0·1 gram of dibenzyl (Eckert, *Eng. Pat.* 182487, 1922).

When the vapour of toluene is passed through a red-hot tube, benzene, naphthalene, anthracene, phenanthrene, dibenzyl (Berthelot, *Bull. Soc. chim.* 1867, 7, 218; Graebe, *Ber.* 1874, 7, 48), styrene, diphenyl, &c. (Ferro, *Ber.* 1887, 20, 662) are formed; but when a mixture of the vapours of toluene and benzene is heated in this manner, a highly complex mixture of hydrocarbons is formed (Carnelley, *Chem. Soc. Trans.* 1880, 37, 702; cf. Barbier, *Ann. Chim.* 1876, [5] 7, 472). When electric sparks are passed through toluene, a gas containing acetylene (23–24 p.c.) and hydrogen (76–77 p.c.) is formed (Destrem, *Bull. Soc. chim.* 1884, 42, 267; *Compt. rend.* 1884, 99, 138), whilst distillation over red-hot lead oxide (PbO) yields stilbene, diphenyl, anthracene, phenanthrene, &c. (Lorenz, *Ber.* 1874, 7, 1098; Vincent, *Bull. Soc. chim.* 1890 (3), 4, 7; *Compt. rend.* 1889, 110, 907).

When air charged with toluene vapour is passed over finely divided platinum or manganese dioxide, the temperature rises until the metals become incandescent and the toluene is completely oxidised to carbon dioxide and water. In the presence of iron, nickel, or copper oxide, at temperatures between 150°–300°, it is converted into benzaldehyde, but with carbon at 370°, benzoic acid is formed (Woog, *Compt. rend.* 1907, 145, 124; cf. Coquillion, *ibid.* 1873, 77, 444).

When toluene is boiled in the presence of aluminium chloride, a complex mixture of hydrocarbons, including ethyltoluene, ditolyl (Friedel and Crafts, *Compt. rend.* 1885, 100, 692), benzene, *m*- and a little *p*-xylene (Anschütz, *Ann.* 1886, 235, 178; Anschütz and Immendorff, *Ber.* 1885, 18, 657) are formed; whilst with acetylene tetrabromide, methylene chloride or chloroform in the presence of aluminium chloride, 1 : 6- and 2 : 7-dimethylanthracene, m.p. 240° and 244·5° respectively, together with a little *p*-methylanthracene, di-*m*- and di-*p*-tolylmethane, benzene, *m*- and *p*-xylene, and other homologues are produced (Friedel and Crafts, *Ann. Chim.* 1887, (6) 11, 266; Lavanx, *Compt. rend.* 1904, 139, 976; 1905, 140, 44, 141, 204, 266; 1906, 143, 687; 1908, 144, 135, 345; 1911, 148, 1400). With ethylidene chloride and aluminium chloride, on the other hand, *p*-ethyltoluene

(a) *p*-ditolylethane and β -tetramethylanthracene hydride, $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3$, are said to be formed (Anschütz, Ann. 1886, 235, 313; Anschütz and Romig, Ber. 1885, 18, 662). When treated with sulphur dichloride in the presence of aluminium chloride, toluene yields ditolylene disulphide (cf. Jacobsen and Ney, Ber. 1889, 22, 904), whilst with sulphur monochloride the reaction is of a complicated nature (Bösesken and Koning, Rec. trav. chim. 1911, 30, 116). When pyrosulphuryl chloride reacts with toluene at 60° , it yields toluene *p*-sulphonic acid, toluene *p*-sulphonyl chloride, a mixture of dichlorotoluenes and 4-chloro-3 : 4'-ditolyl sulphone (m.p. 136°), which is also formed by the interaction of *o*-chlorotoluene and toluene *p*-sulphonyl chloride dissolved in light petroleum in presence of aluminium chloride at 55° . A vigorous reaction ensues when toluene is added to a mixture of pyrosulphuryl chloride and aluminium chloride at -5° to 0° with the formation of toluene *p*-sulphonic acid, *o*- and *p*-chlorotoluene, *p*:*p*-ditolylsulphone, and a substance, needles, m.p. 215° - 217° , containing chlorine but no sulphur (Steinkopf and Buchheim, Ber. 1921, 54, 2963). With isobutyl bromide and aluminium chloride, toluene yields tertiary butyltoluene, tertiary butylbenzene, ditertiary butylxylene, ditertiary butylbenzene, and ditertiary butyltoluene (Baur, Ber. 1894, 27, 1606; cf. Konowalow, J. Russ. Phys. Chem. Soc. 1898, 30, 1036; Verley, Bull. Soc. chim. 1898, (3) 19, 67). On boiling with ferric chloride a mixture of chlorotoluenes is formed, but no benzyl chloride (Thomas, Compt. rend. 1898, 126, 1213), and on heating with phosphonium iodide at 350° , a hydrocarbon, C_8H_{10} , is formed, whilst with concentrated hydriodic acid at 280° , toluene yields hexahydrotoluene, dimethylpentamethylene, and methylpentamethylene (Markownikoff and Karpowitsch, Ber. 1897, 30, 1216). On treating pure toluene with ozone, *o*-toluene, $\text{C}_8\text{H}_8\text{O}_3$, an amorphous explosive compound, which is decomposed by water into benzoic acid, formic acid, and carbon dioxide, is formed. By the prolonged interaction of nitrogen peroxide and toluene, *o*-nitrotoluene, dinitro-*o*-cresol, oxalic acid, benzoic acid, and a dihydroxybenzoic acid are produced (Leeds, Ber. 1881, 14, 482).

Nitrogen tetroxide at room temperature oxidises toluene to oxalic and benzoic acids, phenols, and benzaldehyde (Schaarschmidt and Smolla, Ber. 1924, 57, 32).

Nitrosyl chloride reacts readily with toluene in sunlight to give crystals of benzaldoxime hydrochloride (Lynn and Arkley, J. Amer. Chem. Soc. 1923, 45, 1045).

Like benzene and dimethylaniline, toluene reacts with tetramethyl-*d*-diaminodiphenylhydroxyanthranol, forming a colourless additive compound which yields highly coloured salts and reacts with one molecule of phenylhydrazine or hydroxylamine, eliminating two molecules of water and forming the compound



where $\text{X}=\text{OH}$ or $\text{C}_6\text{H}_4\text{NH}$ (Haller and Guyot, Compt. rend. 1903, 137, 606). Toluene reacts with ethyldiazosuccinate at 118° , forming ethyl 4-methylnorcaradiene carboxylate, b.p. 122° - $126^\circ/15$ mm. (Buchner and Feldmann, Ber. 1903, 36, 3509). It also condenses with benzaldehyde in presence of concentrated sulphuric acid forming di-*p*-tolylphenylmethane (Kliegl, Ber. 1905, 38, 84), and with diphenic anhydride forming fluorene derivatives (Pick, Monatsh. 1904, 25, 979).

Commercial toluene should give only a pale-brown coloration with concentrated sulphuric acid, but pure toluene should give no coloration with this reagent, and should not decolorise a $\text{N}/10$ solution of bromine. When shaken with nitric acid (sp.gr. 1.44), the acid should be coloured red, but should not become viscid or greenish. On distilling crude toluene at least 90 p.c. should boil below 120° ; and a 'pure toluene' of commerce should distil between 110° - 113° , and the greater part between 111° - 112° (Schultz, Chem. des. Steinkohlentheers). Unless coal-tar toluene has been purified by shaking with concentrated sulphuric acid, it always contains 2- and 3-methylthiophene (thiotoluene). For estimation of toluene in gases, see Davis, Davis and MacGregor (J. Ind. Eng. Chem. 1918, 10, 712). For the estimation of impurities in toluene, and the estimation of toluene in commercial mixtures, petroleum, &c., see Colman (J. Gas Lighting, 1915, 129, 196, 314); Wilson and Roberts (*ibid.* 1916, 134, 225); Harker (J. Roy. Soc. New South Wales, 1916, 50, 99); James (J. Soc. Chem. Ind. 1916, 35, 236); Edwards (*ibid.* 1916, 35, 587); Spielman and Jones (*ibid.* 1917, 36, 489); Thole (*ibid.* 1919, 38, 39 T); Colman and Yeoman (*ibid.* 1919, 38, 82 T); Lewis (*ibid.* 1920, 39, 50 T); Colman, (*ibid.* 1920, 39, 50 T); Northall-Laurie (Analyst, 1915, 40, 384); Evans (*ibid.* 1920, 45, 54); Egloff (Met. and Chem. Eng. 1917, 16, 259); Orton and Jones (Chem. Soc. Trans. 1919, 115, 1055); Lumsden (*ibid.* 1366); Tausz and Stube (Zeitsch. angew. Chem. 1919, 32, 175).

Toluene is employed in the manufacture of nitrotoluene, toluidine, benzyl chloride, benzal chloride, benzotrichloride, benzaldehyde, benzoic acid, and cinnamic acid. It is also used in the manufacture of dyestuffs, explosives, synthetic drugs and perfumes. Formerly toluene formed an essential ingredient of the benzene employed as the starting-point in the manufacture of magenta, but now it is usual to start with pure benzene and pure toluene.

HALOGEN DERIVATIVES OF TOLUENE.

In the chlorination or bromination of toluene, substitution may take place either in the nucleus or in the side chain. In contrast with the more qualitative nature of the observations relating to the process of chlorination, quantitative measurements, indicating the rôle played by the various factors in the side-chain or nuclear substitution, have been obtained in the case of the bromination of toluene. Temperature, catalysts, and the photo-chemical action of light are the conditions which play a prominent part in these reactions. A comprehensive account of the chlorination and bromination of toluene from

the point of view of 'halogen carriers' and the electrochemistry of light has been given by Bancroft (J. Phys. Chem. 1908, 12, 417). When chlorine or bromine acts upon toluene, side-chain substitution takes place in the sunlight at 0° and at higher temperatures (Schramm, Ber. 1884, 17, 2292; *ibid.* 1885, 18, 350, 606, 1272; *ibid.* 1886, 19, 212; Bull. Acad. Sci. Cracow, 1898, 61), in diffused daylight and in the dark, a mixture of *o*- and *p*-chloro- and bromo-derivatives is formed. According to Schramm, the most active rays are the yellow and green. Gaseous toluene and chlorine vapour on subjection to the action of ultra-violet rays yield benzyl chloride, benzal chloride, and benzotrichloride (Gibbs and Geiger, U.S. Pat. 1246739 of 1917).

Cannizzaro (Compt. rend. 1855, 41, 517) found that side-chain substitution also takes place in the dark at the boiling-point of toluene.

In the absence of a catalyst the chlorination of toluene at 100° yields benzyl chloride almost exclusively, but in the presence of lead chloride, however, the product is a mixture of *o*- and *p*-chlorotoluenes containing about 62 p.c. of the *o*-isomeride (Wahl, Normand and Vermeylen, Compt. rend. 1922, 174, 946; Book and Eggert, Zeitsch. Elektrochem. 1923, 29, 521).

According to Haussermann and Beck (Ber. 1892, 25, 2445) side-chain substitution is greatly facilitated in the case of nitrotoluene by the presence of sulphur, whence it appears that sulphur behaves differently from the usual 'halogen carriers.'

Selenium accelerates substitution by chlorine in the nucleus (Silberrad, Chem. Soc. Trans. 1925, 127, 2449).

On the other hand, nuclear substitution is effected in the presence of such 'carriers' as ferrio chloride, molybdenum pentachloride, antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple.

The work of Holleman, Polak, van der Laan and Euwens (Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 512; Rec. trav. chim. 1908, 27, 435), and of Bruner and co-workers (Zeitsch. physikal. Chem. 1902, 41, 513; Bull. Acad. Sci. Cracow, 1907, 691; 1909, 221, 265, 322; 1910, 516, 560; Zeitsch. Elektrochem. 1910, 16, 204) has shown that the relative proportion of bromine which enters the side-chain is not only increased by light, but in the dark it is increased by rise of temperature and by dilution of the reacting bromine, the influence of light being greater than that of heat in inducing substitution in the side-chain (Cohen, Dawson, Blockey and Woodmansey, Chem. Soc. Trans. 1910, 97, 1623; Cohen and Dutt, *ibid.* 1914, 105, 504; see also Cohen and Dakin, *ibid.* 1906, 89, 1455).

The influence of the nature of the medium on the distribution of bromine between the side-chain and the nucleus has also been investigated, and it has been found that the influence of such solvents as carbon disulphide, carbon tetrachloride, benzene, chloroform, acetic acid, benzonitrile, and nitrobenzene is not only observable in the dark, but also manifests itself in the process of photobromination. The effect of nitrobenzene, and, to a lesser extent, of acetic acid and benzonitrile, is greatly to diminish the

proportion of side-chain substitution, whilst in the case of dilution with carbon tetrachloride the distribution is the same as in the case of pure toluene. The most noteworthy contribution is the work of Cohen, Dawson, Blockey and Woodmansey (*l.c.*), who showed that at the boiling-point of toluene moist chlorine in the dark produces nuclear substitution to the extent of nearly 90 p.c., whereas, in the light, dry chlorine increases side-chain substitution, yielding on the average about 94 p.c. of benzyl chloride. It thus appears to be established that side-chain substitution is favoured by light, rise of temperature and the absence of moisture, and that the effect of moisture is opposed to that of light.

Various hypotheses have been proposed to account for these phenomena. Bruner supposes that side-chain substitution is due to molecular halogen, whilst nuclear substitution is effected by atomic or ionic bromine, resulting from the dissociation of the bromine molecules. According to this hypothesis, the action of 'carriers,' such as iodine, consists in forming compounds with bromine, which undergo dissociation with the production of bromine atoms or ions in much greater concentration than that which is obtained in the case of pure solutions of bromine; hydrogen perbromide is supposed to be a dissociating compound of this nature.

Bruner's theory that nuclear substitution is due to ionic bromine is shared by Bancroft (*l.c.*), who further assumes that nuclear substitution only occurs when negative bromine ions are present in excess of the corresponding positive ions, a condition which would be attained by the combination of molecular bromine with the positive bromine ions, thus: $\text{Br}_2 = \text{Br}^+ + \text{Br}^-$; $\text{Br}_2 + \text{Br}^+ \rightarrow \text{Br}_2^+ \cdot \text{Br}^+$. On the other hand, Bancroft maintains that side-chain substitution is effected under conditions which tend to produce a preponderance of positive bromine ions.

Holleman (*l.c.*), however, assumes that side-chain substitution is due to molecular bromine and that nuclear substitution is induced by a perbromide, HBr_2 .

According to Cohen (*l.c.*), the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears, on the whole, to be the more acceptable, for the facts are difficult to reconcile with the ionic theory of nuclear substitution, and it must be confessed that nothing definite is known about the mechanism of the process. An explanation of these and similar phenomena on the basis of the electronic theory of valency has been put forward by Fry (The Electronic Conception of Valency, and the Theory of Benzene, by H. S. Fry, Longmans, Green and Co., 1921).

Fichter and Glantzstein (Ber. 1916, 49, 2473) have observed that at least three atoms of chlorine are introduced into the benzene nucleus before the methyl group is attacked when toluene is electrochemically chlorinated in the dark. This is taken as evidence in support of Bruner's hypothesis that atomic chlorine attacks the ring and molecular chlorine the aliphatic side-chain, and the fact that the electrochemical chlorination is an almost impossible process in the aliphatic series confirms this.

FLUORO DERIVATIVES OF TOLUENE.

o-Difluoro-toluene $C_6H_4OHF_2$. By treating *o*-difluoro-*o*-chlorotoluene with sodium amalgam in alcoholic solution. Liquid, b.p. 133.5°. Decomposed by warm concentrated sulphuric acid or water at 200°, yielding hydrogen fluoride and benzaldehyde (Swarts, Bull. Acad. roy. Belg. 1900, 414).

o-Trifluoro-toluene.—Together with *o*-difluorochlorotoluene and *o*-dichlorofluorotoluene by treating benzonitrichloride with antimony fluoride. Colourless liquid, b.p. 103.5°, D_{20}^{25} 1.19632, n_D^{20} 1.41707. Very resistant to the action of water, alkalis, arylamines, phenol and copper (Swarts, Bull. Acad. roy. Belg. 1920, 389, 390).

p-Fluoro-toluene.—By heating *p*-fluorotoluene sulphonic acid (prepared from *p*-toluidine *m*-sulphonic acid) with concentrated hydrochloric acid (Paterno and Oliveri, Gazz. chim. ital. 1883, 13, 535); by treating *p*-toluenediazopiperidine (obtained by treating a cold aqueous solution of *p*-toluenediazonium chloride with piperidine) with concentrated hydrofluoric acid (Wallach, Ann. 1886, 235, 261; cf. Holleman, Rec. trav. chim. 1906 (2), 25, 330); by warming an aqueous solution of *p*-toluenediazonium chloride with hydrofluoric acid (Valentiner and Schwarz, Eng. Pat. 9827 of 1897; U.S. Pat. 656229; Fr. Pat. 266155; D. R. P. 96153 of 1896).

Liquid, with odour of bitter almonds, b.p. 116°–117°, sp.gr. 0.992 at 25° (Wallach). Oxidised by chromic acid mixture at 160° to *p*-fluorobenzoic acid. On nitration it yields a very small proportion of two fluoronitrotoluenes, m.p. 27°, b.p. 138°–139°/83 mm., and b.p. 134°–135°/83 mm., respectively, the chief product being 3-nitro-*p*-cresol (Slotthouwer, Chem. Weekblad, 1914, 11, 856).

CHLORO DERIVATIVES.

As previously mentioned chlorotoluenes are usually prepared by means of chlorine in the presence of a carrier, but there are other methods of producing these compounds, thus the electrolytic chlorination of toluene has been studied by Cohen, Dawson and Crossland (Chem. Soc. Trans. 1905, 87, 1034); Brunner and co-workers, Bull. Acad. Sci. Cracow, 1907, 691; 1909, 221, 265, 322; Fichter and Glantzstein (Ber. 1916, 49, 2473). Datta and Fernandes (J. Amer. Chem. Soc. 1914, 36, 1007) found that toluene could be chlorinated by means of a mixture of nitric and hydrochloric acids, whilst advantage is often taken of the ease with which derivatives of toluene, such as the sulphonic acids, are chlorinated and subsequently hydrolysed (B. A. S. F., D. R. P. 294638 of 1914; Ges. für Chem. Ind. in Basel, D. R. P. 133000 of 1901; Green and Herbert, Eng. Pat. 170056 of 1920). Amino-derivatives of toluene are readily chlorinated in the nucleus by means of sodium chlorate and acetic and hydrochloric acids (Reverdin and Priepetz, Ber. 1900, 33, 2503), and this reaction together with the Sandmeyer reaction readily leads to the production of higher chlorinated toluenes. The use of bleaching powder as a chlorinating agent in the case of amino-derivatives—a reaction employed by Claus and Schilling (Ann. 1897, 374, 396), and studied by Ostrowsky and Orton (Chem. Soc.

Trans. 1900, 77, 790, &c.)—is often of advantage for the preparation of chloro-derivatives of toluene, for by this method better yields are sometimes obtained than by the ordinary methods.

Toluene on chlorination in the presence of the aluminium-mercury couple yields 65 *p*-*o*-chloro-toluene and 35 *p*-*c*-chloro-toluene (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1111). For the rapid analysis of chlorinated toluenes, see Lubs and Clark (J. Amer. Chem. Soc. 1918, 40, 1449).

Prior to the exhaustive examination of the products of the nuclear chlorination of toluene by Cohen and his collaborators, the work carried out by various observers on the formation of dichlorotoluenes was both conflicting and unsatisfactory. Beilstein and Geitner (Ann. 1866, 139, 331), Beilstein and Kuhlberg (*ibid.* 1869, 150, 313; 152, 234) in their first papers described only one monochlorotoluene. Hübner and Majert (Ber. 1873, 6, 790) found two chloro-derivatives, and identified them as *o*- and *p*-compounds. Aronheim and Dietrich (Ber. 1875, 8, 1401), using molybdenum pentachloride, gave proof of the existence of two dichloro-derivatives, by conversion into the barium salts of the dichlorobenzoic acids, thus agreeing substantially with Beilstein and Kuhlberg. R. Schultz (Ann. 1877, 187, 260) repeated the work of the previous investigators, and by the fractional crystallisation of the barium salts of the chlorobenzoic acids, obtained on oxidation of the crude product of chlorination, gave evidence of the existence of three dichlorotoluenes. A more thorough investigation by Seelig (Ann. 1887, 237, 129) of the action of chlorine on toluene in the presence of ferric chloride or molybdenum chloride, showed the presence of a 2:4- and 2:3-dichloro-derivative, with no mention of either the 3:4- or 2:6-isomerides. According to Seelig the 2:3- and 2:4-dichlorotoluenes may be separated by means of their calcium sulphates, and the 2:3-dichlorotoluene gives a dinitro-compound, m.p. 121°, and the 2:4-dichloro-toluene a dinitro-derivative, m.p. 101°–102°. Wynne (Chem. Soc. Trans. 1892, 61, 1051) regards the evidence in support of the 2:3-formula as inconclusive, and considers the 2:5-formula more probable. Armstrong (*ibid.* 1892, 61, 1035), after a study of the bromination of toluene carried out by Miller (*ibid.* 1892, 61, 1023), also favours the 2:5-formula. Miller (*l.c.*) states that by brominating *o*-bromotoluene, 3:5-dibromotoluene is formed as the chief product and 2:4-dibromotoluene as the subsidiary product, whilst from *p*-bromotoluene he obtained 3:4-dibromotoluene as the chief, and the 2:4-isomeride as the subsidiary product. Contrary evidence, however, is afforded by the work of Willgerodt and Salmann (J. pr. Chem. 1889, (2) 39, 465), who showed that by brominating *o*-chlorotoluene the 2:4- and 3:6-compounds are formed, whilst by chlorinating *p*-bromotoluene, the 2:4- and 3:4-derivatives are produced, no 2:5-derivative being observed. Claus and Stavenhagen (Ann. 1892, 293, 234) have found that by chlorinating *o*-chlorotoluene two dichlorotoluenes are formed, which, on oxidation, give 2:4- and 3:6-dichlorobenzoic acids, from which it would appear that 2:3-dichlorotoluene is one of the direct products

of chlorination. The combined results of all these observers afford evidence of the existence of four dichlorotoluenes formed by chlorinating toluene in the presence of molybdenum or ferric chloride, viz. 2:3-, 2:4-, 3:4-, 2:6-, with the possibility of a fifth, 2:5-dichlorotoluene. The cause of these conflicting results is the impossibility of separating the liquid dichloro-derivatives into the constituents by fractional distillation as their boiling-points lie too close together, and the isolation of solid derivatives is a matter of difficulty. Cohen and Dakin (Chem. Soc. Trans. 1901, 79, 1111), by using the aluminium-mercury couple as the 'carrier,' established the presence of 2:3-, 2:4-, 2:6-, 3:4-, and the probable existence of 2:5-dichlorotoluene, but could find no trace of the 3:5-isomeride. *o*-Chlorotoluene on chlorination yields 2:3-, 2:6-, 2:4-, and probably the 2:5-dichlorotoluene, whilst *m*-chlorotoluene yields 3:4- and 2:5-dichlorotoluene, and *p*-chlorotoluene yields the 2:4- and 3:4-isomerides. With regard to the trichlorotoluenes, though some of the various isomerides have been obtained by the direct chlorination of toluene in the presence of various 'carriers,' it is preferable to obtain them by chlorinating the dichlorotoluenes. Thus, 2:4:5- and 2:3:4-trichlorotoluene have been obtained by Limpricht (Ann. 1866, 139, 326), Aronheim and Dietrich (Ber. 1875, 8, 1401), and Seelig (Ann. 1887, 237, 231), by chlorinating toluene and *o*- or *p*-chlorotoluene in presence of iodine, molybdenum pentachloride, or ferric chloride, whilst the former is also obtained, together with 2:3:4-trichlorotoluene and probably a small amount of the 2:4:6-isomeride, by chlorinating 2:4-dichlorotoluene in presence of the aluminium-mercury couple, and, together with 2:3:6-trichlorotoluene, by chlorinating 2:5-dichlorotoluene in a similar manner (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1340, 1342). 2:3:4-Trichlorotoluene is accompanied by a tetrachlorotoluene when 2:3-dichlorotoluene is chlorinated in presence of the couple (Cohen and Dakin, *ibid.* 1339). 3:4-Dichlorotoluene, on the other hand, yields 2:4:5-trichlorotoluene almost exclusively in a similar manner, whilst 2:3:5-trichlorotoluene and 2:3:6-trichlorotoluene are obtained almost exclusively from 3:5- and 2:6-dichlorotoluene, respectively.

By chlorinating toluene Limpricht (Ann. 1886, 139, 327) obtained a tetrachlorotoluene, m.p. 96°, b.p. 276.5°, whilst Beilstein and Kuhlberg (Ann. 1869, 150, 286), repeating Limpricht's work which they carried out in the first stage with iodine and subsequently with antimony pentachloride, obtained a product, fine needles, m.p. 91°-92°, b.p. 271°. Pieper (Ann. 1867, 142, 305) prepared a liquid tetrachlorotoluene (b.p. 280°-290°) by heating the additive compound, $C_7H_4Cl_4$, with alcoholic potash at 110°. This product is impure or more probably a totally different compound, and the substance prepared by Beilstein and Kuhlberg would be either 2:3:4:6- or 2:3:5:6-tetrachlorotoluene, m.p. 91°-92° and 93°-94° respectively, or a mixture of the two, since both compounds are formed on chlorination (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1279). 2:3:4:6-Tetrachlorotoluene is also produced by the further chlorination of 2:4:6-trichlorotoluene in presence of the aluminium-mercury

couple, whilst 2:3:5:6-tetrachlorotoluene is produced by the chlorination of 2:3:6- and 2:3:5-trichlorotoluene under similar conditions. On the other hand, there is no evidence of the production of 2:3:4:5-tetrachlorotoluene by the further chlorination of 2:4:5-trichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1279; 1906, 89, 1453). Beilstein and Kuhlberg (Ann. 1869, 150, 298) by chlorinating toluene initially in the presence of iodine and finally with phosphorus pentachloride obtained pentachlorotoluene.

Benzyl chloride, ω -chlorotoluene, $C_7H_7CH_2Cl$; by passing hydrogen chloride into benzyl alcohol (Cannizzaro, Ann. 1853, 88, 130; 1855, 96, 246; Deville, Ann. Chim. 1841, [3] 3, 178); by the action of chlorine on boiling toluene (Cannizzaro, Ann. Chim. 1855, [3] 45, 468; Beilstein and Geitner, Ann. 1866, 139, 337; Wahl, Normand and Vermeylen, Compt. rend. 1922, 174, 946); by the action of chlorine on toluene in sunlight (Schramm, Ber. 1885, 18, 608); from equimolecular proportions of methylene chlorhydrin and benzene in carbon disulphide solution in presence of zinc dust or zinc chloride and hydrochloric acid (Grasse-Cristaldi and Maselli, Gazz. chim. ital. 1898, 28, 498); from benzylamine and nitrosyl chloride in ethereal solution at -15° to -20° (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431); in small quantities together with other products by the action of *aqua regia* on benzylamine (Solonina, *l.c.* 822).

Benzyl chloride is manufactured by passing chlorine into toluene contained in acid-proof earthenware vessels and heated to boiling by means of a lead steam-spiral. The operation is interrupted when the toluene shows the theoretical increase in weight (37.5 p.c.). The vapours are condensed in a reflux worm, and the escaping hydrogen chloride passed into water. The product is shaken with dilute alkali and then rectified, by which means it is freed from unchanged toluene and higher chlorinated products. The addition of a small quantity of phosphorus trichloride and the action of sunlight increases the velocity of chlorination. Very good yields are also said to be obtained by allowing sulphuryl chloride to act on an excess of toluene in the dark at a temperature a little below 130° (Wohl, D. R. P. 139552 of 1901). Further, a mixture of toluene and bleaching powder is treated with sulphur dioxide, and the resulting benzyl chloride separated by distillation (Conant, U.S. Pat. 1233986 of 1917; J. Soc. Chem. Ind. 1917, 36, 1002).

M.p. -48° (Haase, Ber. 1893, 26, 1053), or -43.2° (Schneider, Zeitsch. physikal. Chem. 1897, 22, 233); b.p. 175°-176.2°/760.3 mm. (Schiff, Ann. 1883, 220, 90; *c.f.* Ber. 1889, 19, 563); b.p. 63°/8-16 mm.; 73.9°/17 mm.; 78.2°/22-14 mm.; 81.8°/26-74 mm.; 89.9°/40 mm.; 98.8°/63 mm.; 106.2°/92 mm.; 176°/760 mm. (Kahlbaum, Siedetemp. u. Druck, 84); 64°-64.2°/12 mm. (Anschütz and Burns, Ber. 1887, 20, 1300); D_4^{25} 1.1135; D_{15}^{25} 1.1040; D_{20}^{25} 1.0967 (Pierkin, Chem. Soc. Trans. 1896, 69, 1243); D_4^{175} 0.94335 (Schiff, *l.c.*); absorption spectrum (Spring, Rec. trav. chim. 1897, 16, 1); magnetic rotatory power 14.01 at 15.2° (Pierkin, *l.c.*); dielectric

constant (Jahn and Möller, *Zeitsch. physikal. Chem.* 1894, 13, 387).

Insoluble in water, but by heating with water to 100°-110°, or by boiling with water under a reflux for 24 hours, it is converted into benzyl alcohol (Vandevelde, *Bull. Acad. roy. Belg.* 1897, [3] 34, 894; Niederist, *Ann.* 1879, 196, 353); the same transformation is still more readily effected by boiling benzyl chloride with the calculated quantity of potassium carbonate dissolved in about 8 to 10 parts of water (Meunier, *Bull. Soc. chim.* 1882, [2] 38, 159; Busch and Weiss, *Ber.* 1900, 33, 2702). When boiled with hydrazine hydrate in aqueous alcoholic solution, it yields α -dibenzyl-hydrazine (Busch and Weiss, *l.c.*), dibenzyl and stilbene (Rothenburg, *Ber.* 1893, 26, 867). On oxidation it yields first benzaldehyde and then benzoic acid, and on heating with water at 200° and distilling the product, anthracene and benzyl-toluene, amongst other substances, are formed (Dorp, *Ber.* 1872, 5, 1070; Zincke, *Ber.* 1874, 7, 276; Limpricht, *Ann.* 1866, 139, 309). When treated with aluminium chloride in carbon disulphide solution, an insoluble hydrocarbon ($C_{11}H_{10}$) is obtained (Friedel and Crafts, *Bull. Soc. chim.* 1885, 43, 53). Aluminium chloride or zinc dust acts upon a mixture of benzyl chloride and benzene yielding diphenylmethane and a product which on distillation yields anthracene and toluene (Zincke, *Ann.* 1871, 159, 374; Friedel and Crafts, *Ann. Chim.* 1884, (6) 1, 478; cf. Perkin and Hodgkinson, *Chem. Soc. Trans.* 1880, 37, 726; Hirst and Cohen, *ibid.* 1895, 67, 827; Radziwanowski, *Ber.* 1894, 27, 3236; 1895, 28, 1136). With a large amount of benzene in presence of aluminium chloride, anthracene is the main product (Schramm, *Ber.* 1893, 26, 1706). On boiling with zinc dust a vigorous reaction occurs with evolution of hydrogen chloride, and the product, on distillation, yields toluene, anthracene, phenyl-tolyl-methane and a substance $C_{11}H_{10}$ (?) (Prost, *Bull. Soc. chim.* 1886, [2] 46, 248). Phenyl acetate and benzyl chloride in the presence of aluminium chloride yield acetic anhydride, toluene, anthracene and an oil, b.p. 310°-320° (Perkin and Hodgkinson, *l.c.*). By heating benzyl chloride with aromatic hydrocarbons and zinc dust, the benzyl group enters the hydrocarbon nucleus, thus with benzene, benzylbenzene is formed, and with toluene, *p*-benzyltoluene, a little *o*-benzyltoluene, anthracene, and a hydrocarbon $C_{11}H_{10}$ are formed (Zincke, *Ann.* 1872, 161, 93; *Ber.* 1873, 6, 137). When heated with sodium or copper, benzyl chloride is converted into dibenzyl (Cannizzaro and Rossi, *Ann.* 1862, 121, 250; Fittig and Stelling, *Ann.* 1866, 137, 258; Comey, *Ber.* 1890, 23, 1115; Onufrowicz, *Ber.* 1884, 17, 838). When benzyl chloride is boiled with an aqueous solution of lead nitrate benzaldehyde is obtained. The latter is also formed, together with benzoic acid and anthracene, by heating benzyl chloride with potassium nitrite and a little water at 150° (Brunner, *Ber.* 1876, 9, 1745). Fusing nitric acid yields nitrobenzyl chloride, whilst alcoholic ammonia yields a mixture of benzylamine, dibenzylamine and tribenzylamine (Cannizzaro, *Ann.* 1865, 134, 128; *ibid.* Suppl. 4, 24, 80; Dhoms, *Compt. rend.* 1901, 133, 636). When treated with chromyl chloride in carbon disulphide solution benzyl chloride yields a brown pre-

cipitate, $C_6H_5CH_2Cl \cdot CrO_2Cl_2$, which is converted slowly by moist air into benzaldehyde. The compound when heated to 170° loses hydrogen chloride, forming a compound, $C_6H_5CHCl \cdot CrO_2Cl_2$, which also yields benzaldehyde with moist air (Etard, *Ann. Chim.* 1881, [5] 22, 235). With aniline, benzyl chloride forms benzylaniline, and with methylaniline it gives the hydrochloride of benzylmethylaniline, from which the free base, b.p. 305°-306°, may be obtained by treatment with sodium hydroxide. The corresponding ethyl compound, b.p. 286°/710 mm., $D_{18}^{25} 1.034$, is obtained in a similar manner. Both these substances and their sulphonic acids are used as intermediates in the preparation of dyes. When treated with a metallic salicylate at 130°-140° benzyl chloride yields *benzyl salicylate*, an odourless, colourless liquid, b.p. 208°/26 mm., which is said to be useful for external application in medicine (*Eng. Pat.* 25735 of 1899). When subjected to an electric current, hydrochloric acid is evolved and stilbene is formed (Loeb, *Zeitsch. Elektrochem.* 1903, 9, 903).

Benzyl chloride is used in the preparation of benzaldehyde and benzoic acid, and also for introducing the benzyl group into basic colouring matters, prior to sulphonation, in the preparation of acid colouring matters.

Commercial benzyl chloride generally contains moisture, benzal chloride and benzo-trichloride, chlorotoluenes, and even unchanged toluene. It should show the correct boiling-point and specific gravity. In order to determine the chlorine present in the side-chain, a weighed quantity of the substance is boiled for some minutes with a hot saturated alcoholic solution of silver nitrate under a reflux; the silver chloride, which will represent only the chlorine from the side-chain, is then collected and weighed (Schulze, *Ber.* 1884, 17, 1675). Benzotrichloride may be detected by the green colouring matter (Malachite Green) which is formed when the substance is heated with dimethylaniline and zinc chloride (Döbner).

m-Chlorobenzyl chloride; by chlorinating *m*-chlorotoluene at its boiling-point until the increase in weight amounts to about one-half of that required by theory. B.p. 213°-214°/740 mm. (Kenner and Witham, *Chem. Soc. Trans.* 1921, 119, 1460).

p-Chlorobenzyl chloride; by chlorinating benzyl chloride in presence of iodine, or more conveniently, by chlorinating *p*-chlorotoluene at its boiling-point (Beilstein, Kuhlberg and Neuhoof, *Ann.* 1868, 146, 320; Jackson and Field, *Amer. Chem. J.* 1880-1, 2, 85; *P. Amer. A.* 14, 54; *Ber.* 1878, 11, 904); by chlorinating toluene first in the cold and finally at the boiling-point (Walther and Wetzlich, *J. pr. Chem.* 1900, [2] 61, 187; cf. van Raalte, *Rec. trav. chim.* 1899, 18, 387). Needles or prisms, m.p. 29°, b.p. 213°-214° (Jackson and Field; cf. Beilstein, Geitner and Kuhlberg, *Zeit. f. Chem.* 1866, 2, 66, 307, 653; Beilstein, Kuhlberg and Neuhoof, *Ann.* 1868, 147, 339). On boiling with water it yields *p*-chlorobenzyl alcohol (Jackson and Field), whilst with lead nitrate it yields *p*-chlorobenzaldehyde (Beilstein and Kuhlberg, *Ann.* 1866, 146, 320; 1868, 147, 352), and with oxidising agents *p*-chlorobenzoic acid. By the action of potassium cyanide on a boiling alcoholic solution at 120°-130°, it yields *p*-chlorobenzyl-acetonitrile (Neuhoof, *l.c.*), and on treatment with

potassium iodide, *p*-chlorobenzyl iodide, needles, m.p. 64°.

Dichlorobenzyl chloride, b.p. 241°; by chlorinating benzyl chloride in presence of iodine (Beilstein and Kuhlberg).

Trichlorobenzyl chloride; by chlorinating hot trichlorotoluene. Oil, b.p. 273°, D₂₀²⁰ 1.547 (Beilstein and Kuhlberg, Ann. 1869, 150, 286).

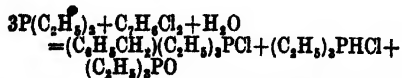
Tetrachlorobenzyl chloride; by chlorinating tetrachlorotoluene at high temperatures. Oil, p.b. 290°, D₂₀²⁰ 1.634 (Beilstein and Kuhlberg, Ann. 1869, 15 0, 298). Further chlorination gives hexachlorobenzene and carbon tetrachloride.

Pentachlorobenzyl chloride; by chlorinating benzyl chloride in presence of antimony pentachloride; also by chlorinating boiling pentachlorotoluene (Beilstein and Kuhlberg; cf. Deville, Ann. 1841, 44, 304).

Benzylidene chloride, *benzal chloride*, *ω*-dichlorotoluene, C₆H₄CHCl₂; by the action of phosphorus pentachloride (Cahours, Ann. Chim. 1848, (3) 23, 329; Ann. 1849, 70, 39; Suppl. 2, 253, 306), succinyl chloride (Rembold, Ann. 1866, 138, 189), or phosgene (Kempf, Zeit. f. Chem. 1871, 7, 79), on benzaldehyde; by chlorinating toluene at the boiling-point (Beilstein, Ann. 1860, 116, 336; Beilstein and Kuhlberg, Ann. 1868, 146, 322; Lauth and Grimaux, Bull. Soc. chim. 1860, 2, 347; cf. Limpricht, Ann. 1866, 139, 318); in nearly theoretical yield from toluene with 2 mols. of phosphorus pentachloride at 170°–200° (Colson and Gautier, Ann. Chim. 1887, (6) 11, 21). It is manufactured by chlorinating boiling toluene in direct sunlight.

Colourless, powerfully refractive liquid, b.p. 212°–214° (Hübner and Bente, Ber. 1873, 6, 804), or 203.5°/756.2 mm. (Schiff, Ber. 1886, 19, 563), m.p. –16.1° (Zeitsch. physikal. Chem. 1897, 22, 234; cf. Altschul, *ibid.* 1895, 16, 24); D₂₀²⁰ 1.2699; D₄²⁰ 1.2122; D₄²⁰ 1.1877; D₂₀²⁰ 1.0407 (Schiff, l.c.), D₄²⁰ 1.2557.

Water at 140°–160°, or sulphuric acid at 50° (Oppenheim, Ber. 1869, 2, 213), alkalis and silver oxalate (Golowskinsky, Ann. 1859, 111, 252), convert benzylidene chloride into benzaldehyde. When treated with sodium it yields stilbene, and with copper powder at 100° stilbene dichloride, C₆H₄·CHCl·CHCl·C₆H₄, and the corresponding tetrachloride are produced (Onufrowicz, Ber. 1884, 17, 833). Ammonia yields hydrobenzamide (C₆H₄)₂N₂ (cf. Böttinger, Ber. 1878, 11, 840). The reaction with triethylphosphine in presence of alcohol at 120°–130° proceeds thus:



whilst phosphonium iodide yields tribenzylphosphine (Hofmann, Ann. Suppl. 1, 323).

When treated with anhydrous alkali acetates for 10–20 hours at 180°–200° cinnamic acid is formed (B. A. S. F., Eng. Pat. 3330 of 1880; Fr. Pat. 138275; D. R. P. 17467 of 1880, and 18222 of 1881). For the behaviour of benzylidene chloride with acid esters or alcohols in presence of metals or metallic salts, see E. Jacobsen, Eng. Pat. 2878 of 1880; Fr. Pat. 137419; D. R. P. 11494 of 1879, and 13127 of 1880.

It forms *p*-nitro-benzylidene chloride

(Hübner and Bente, Ber. 1873, 6, 803; cf. Beilstein, Ann. 1868, 146, 333); red-hot soda lime forms benzene (Limpricht, Bull. Soc. chim. 1866, (2) 6, 467); and zinc ethyl diluted with benzene forms C₁₁H₁₀, diethylphenylmethane, and C₁₂H₁₀ (Dafert, Monatsb. 1884, 4, 618).

Benzylidene chloride is employed in the manufacture of benzaldehyde, benzoic acid and cinnamic acid. The commercial product is always impure. It may be tested by its boiling-point, and by determining the percentage of chlorine.

o-Chlorobenzylidene chloride; from salicylaldehyde and phosphorus pentachloride (Henry, Ber. 1869, 2, 135); by passing a current of chlorine through a mixture of dry *o*-chlorotoluene and phosphorus pentachloride at 150°–180° in bright daylight (Erdmann, Ann. 1893, 272, 151; Vanino, Präparative Chemie, 1923, vol. ii. p. 410); by passing chlorine over *o*-toluenesulphonyl chloride at 150°–200° (Gilliard, Monnet and Cartier, Eng. Pat. 29717 of 1896; U.S. Pat. 606470; Fr. Pat. 268607; D. R. P. 98433 of 1896); by chlorinating benzylidene chloride in presence of iodine (Beilstein and Kuhlberg, l.c.). Oil, b.p. 227°–230° [H], or 228.5° (Gill, Ber. 1893, 26, 650); D₂₀²⁰ 1.4 [H], D₄²⁰ 1.399 [G]. It is decomposed by water at 170°, yielding *o*-chlorobenzaldehyde and hydrogen chloride, and with chromic acid yielding *o*-chlorobenzoic acid, whilst with silver in methyl alcoholic solution it yields *o*; *o*-dichloro-stilbene dichloride, and on distillation with dry oxalic acid *o*-chloro-benzaldehyde is formed (Anschütz, Ann. 1884, 226, 19).

p-Chlorobenzylidene chloride; by chlorinating benzylidene chloride in presence of iodine (Beilstein and Kuhlberg, l.c.); together with *p*-chlorobenzotrichloride by passing chlorine over toluene *o*-sulphonyl chloride (Gilliard, Monnet and Cartier, l.c.). Hübner and Bente (Ber. 1873, 6, 804) obtained a chlorobenzylidene chloride, b.p. 255°–260°, which on oxidation yielded impure *p*-chlorobenzoic acid. *p*-Chlorobenzylidene chloride is a liquid, b.p. 234°.

(β) 2:4-Dichlorobenzylidene chloride; by passing chlorine into 2:4-dichlorotoluene heated at 230°. Liquid, b.p. about 260°. On treatment with sulphuric acid it yields the corresponding dichlorobenzaldehyde (Seelig, Ann. 1887, 237, 167).

2:5-Dichlorobenzylidene chloride; by careful addition of chlorosulphonic acid to a chloroform solution of 2:5-dichlorobenzaldehyde. Cubic crystals, m.p. 42° (Gnehm and Schuele, Ann. 1898, 299, 358).

3:4-Dichlorobenzylidene chloride; by chlorinating boiling 3:4-dichlorotoluene. Oil, b.p. 257°, D₂₀²⁰ 1.518 (Beilstein and Kuhlberg). When heated with water at 220°, 3:4-dichlorobenzaldehyde is formed.

2:3:4-Trichlorobenzylidene chloride; by chlorinating 2:3:4-trichlorotoluene near the boiling-point. It melts at 84°, boils at 275°–285°, and yields 2:3:4-trichlorobenzaldehyde with fuming sulphuric acid (Seelig).

2:4:5-Trichlorobenzylidene chloride; by chlorinating 2:4:5-trichlorotoluene at the boiling-point. Liquid, solidifying to crystalline needles at 0°. It boils at 280°–281°, and has D₂₀²⁰ 1.607. Decomposed by water at 250°, or by sulphuric acid, yielding hydrochloric acid and

2:4:5-trichlorobenzaldehyde (Beilstein and Kuhlberg, Ann. 1869, 156, 298).

Tetrachlorobenzylidene chloride; by chlorinating boiling tetrachlorotoluene. Liquid, b.p. 305°-306°, D_{20}^{20} 1.704. With water at 280° it yields tetrachlorobenzaldehyde (Beilstein and Kuhlberg; cf. Cassella & Co., Eng. Pat. 16317 of 1914).

Pentachlorobenzylidene chloride; by chlorinating benzyldene chloride in presence of iodine and subsequently in presence of antimony pentachloride. Long flat plates, m.p. 109°, b.p. 334° (Beilstein and Kuhlberg), m.p. 119.5° (Zincke, Ber. 1893, 26, 318). It is not affected by water at 300°.

Benzotrichloride, *phenyl-chloroform*; from benzoyl chloride and phosphorus pentachloride (Schischkoff and Rösing, Compt. rend. 1858, 46, 367; Limpricht, Ann. 1865, 134, 55; 1865, 135, 80; Bull. Soc. chim. 1886, (2) 6, 468; Wöhler and Liebig, Ann. 1832, 3, 265); by exhaustive chlorination of heated toluene (Limpricht, Ann. 1865, 135, 80; 1866, 139, 323); by chlorinating toluene (Naquet, Compt. rend. 1862, 55, 407; 1863, 56, 482), or benzyldene chloride (Cahours, *ibid.* 1863, 56, 703); manufactured by chlorinating boiling toluene in direct sunlight until the weight of the product no longer increases. Colourless, powerfully refractive liquid, m.p. -22.5° (Haase, Ber. 1893, 26, 1053) or -21.2° (Schneider, Zeitsch. physikal. Chem. 1897, 22, 234); setting-point -17° (Altschul, *ibid.* 1895, 16, 24); b.p. 213°-214° (Beilstein and Kuhlberg); D_{15}^{15} 1.380 [L]. With water at 150° or with water in presence of iron or iron salts at 90°-95° (Schultze, D. R. P. 82927 of 1894) it yields benzoic and hydrochloric acids; with alcohol, ethyl benzoate and hydrochloric acid; with sodium ethoxide, ethyl orthobenzoate $C_6H_5C(OC_2H_5)_2$; with ammonia, benzoic acid, benzamide and benzonitrile; with aniline, benzenyldiphenylamine; with dimethylaniline and zinc chloride, Malachite Green; with methyldiphenylamine or diamylaniline, similar green colouring matters; with aniline hydrochloride, nitrobenzene and iron filings at 180° for 3-4 hours, diamino-triphenylcarbinol $(NH_2C_6H_4)_3C-OH(C_6H_5)$ (Doebner, Ber. 1882, 15, 232); with phenol, dihydroxytriphenylcarbinol (Doebner, Ann. 1883, 217, 226); with copper powder, toluene tetrachloride $C_6H_5Cl_4$, α - and β -toluene di-chloride $C_6H_4Cl_2$ (Hanhart, Ber. 1882, 15, 899; cf. Onufrowicz, Ber. 1884, 17, 825); with zinc ethyl in presence of benzene, diethylphenylmethane $C_6H_5CH(C_2H_5)_2$ (Lippmann and Loughine, Zeitsch. f. Chem. 1867, (2) 3, 674); with fuming nitric acid, *m*-nitro-benzoic acid (Beilstein and Kuhlberg, Ann. 1868, 146, 333). By treating benzotrichloride with chlorine in sunlight, the compound $C_{11}Cl_{10}$, m.p. 152°-153°, is obtained, which on treatment with zinc and sulphuric acid yields the compound $C_{11}HCl_{10}$, m.p. 102° (Smith, Jahresbericht, 1877, 420; Ber. 1880, 13, 33). For the behaviour of benzotrichloride with metals, metallic chlorides and other salts, see E. Jacobsen (Eng. Pat. 2878 of 1890; Fr. Pat. 137419; D. R. PP. 11494 of 1879; and 13127 of 1890); and for its use in the preparation of rhodamine dyes, see B. A. S. F. (D. R. P. 34018 of 1899).

Commercial benzotrichloride is tested by

examining its boiling-point. It generally contains compounds chlorinated in the nucleus.

o-Chlorobenzotrichloride; from salicylaldehyde and phosphorus pentachloride (Kolbe and Lautemann, Ann. 1860, 115, 195), m.p. 30°, b.p. 260°, D_{15}^{15} 1.51 (in liquid state). With water at 150° it yields hydrochloric acid and *o*-chlorobenzoic acid, and with copper powder in presence of benzene it yields α - and β -*o*-dichlorotoluene dichloride (Fox, Ber. 1893, 26, 653).

m-Chlorobenzotrichloride; from *m*-sulphobenzoic acid and phosphorus pentachloride (Carius and Kämmerer, Ann. 1864, 131, 158); from *m*-hydroxy-benzoic acid and 3 mols. of phosphorus pentachloride at 180° (Anschütz and Moore, Ann. 1887, 239, 342). Liquid, b.p. 247°-250° (A. and M.).

p-Chlorobenzotrichloride; by chlorinating benzotrichloride in presence of iodine (Beilstein and Kuhlberg, *l.c.*); by heating *p*-oxybenzide

$C_6H_5\begin{matrix} O \\ \diagup \\ CO \end{matrix}$ with phosphorus pentachloride at

290°-300° (Klepl, J. pr. Chem. 1883, (2) 28, 204); in small quantities by heating 1 mol. of *p*-hydroxybenzoic acid with 3 mols. of phosphorus pentachloride at 180° (Anschütz and Moore, *l.c.* 347); in small quantities, together with benzotrichloride, from benzoyl chloride and phosphorus pentachloride in a similar manner (Limpricht, Ann. 1865, 134, 57; 1866, 139, 326); from toluene *p*-sulphonyl chloride by the action of chlorine at 150°-200° (Gilliard, Monnet and Cartier, D. R. P. 98433 of 1896). Liquid, b.p. 245° or 255°, D_{15}^{15} 1.495 (Limpricht). With water at 200° or warm concentrated sulphuric acid it is decomposed, yielding *p*-chlorobenzoic acid.

Dichlorobenzotrichloride; by chlorinating boiling dichlorotoluene. Liquid, b.p. 273°, D_{15}^{15} 1.587 (Beilstein and Kuhlberg, Ann. 1869, 150, 298). From the work of Aronheim and Dietrich (Ber. 1875, 8, 1401), as well as that of Schultz (Ann. 1877, 187, 260), it appears that by the chlorination of dichlorotoluene three isomerides are formed, since crude dichlorotoluene is itself a mixture of 3 isomerides.

2:4:5-Trichlorobenzotrichloride; by passing chlorine into boiling trichlorotoluene. Very fine needles, m.p. 82°, b.p. 307°-308°. Decomposed by water at 250°, yielding 2:4:5-trichlorobenzoic acid (Beilstein and Kuhlberg, Ann. 1869, 156, 305).

Tetrachlorobenzotrichloride; by chlorinating boiling tetrachlorotoluene. Needles, m.p. 104°, b.p. 316°. Decomposed by prolonged action of water at 270° into tetrachlorobenzoic acid (Beilstein and Kuhlberg, *l.c.*, 306).

Dichlorotoluene hexachloride $Cl_6C_6H_2Cl_2CH_3$; by treating toluene with an excess of chlorine and allowing the mixture to stand (Pieper, Ann. 1867, 142, 304). Large prisms, m.p. 150°, partially decomposed by water at 200°. When treated with alcoholic potash at 100° it is said to yield a *tetrachlorotoluene*, b.p. 290°-290° (but this is either impure or possibly a totally different substance), and dichlorobenzoic acid.

o-Difluoro-*o*-chlorotoluene $C_6H_3ClF_2$; together with trifluorotoluene from benzotrichloride and antimony fluoride. Colourless liquid of strongly irritant odour, b.p. 142°-173° mm., D_{15}^{15} 1.3645. With water it yields

acid; and with sodium amalgam, ω -difluorotoluene; with fuming nitric acid and phosphoric oxide below 0° it yields a *nitro-derivative*, colourless liquid, b.p. 230° , D_{15}^{20} 1.4638, and some *m*-nitrobenzoic acid (Swarts, Bull. Acad. roy. Belg. 1900, 414).

ω -Dichloro- ω -fluorotoluene; by the action of antimony fluoride on benzotrichloride at low temperatures. Colourless liquid of piercing odour, b.p. 178° – 180° , D_{15}^{20} 1.3138, n_D^{20} 1.5180; *nitro-derivative*, colourless liquid, b.p. 260° (Swarts, l.c.). Fluorine derivatives of toluene have been described by Holleman (Rec. trav. chim. 1906, (2) 25, 330).

o-Chlorotoluene; by chlorinating toluene in presence of iodine (Hübner and Majert, Ber. 1873, 6, 790), or better, in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 152); in a yield of 65 p.c. by chlorination in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1119); from *o*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, Ann. 1870, 156, 79; Erdmann, *ibid.* 1893, 272, 145; Sandmeyer, Ber. 1884, 17, 2651; Gasiorowski and Wayss, Ber. 1885, 18, 1939; Vanino, Präparative Chemie, 1923, vol. ii. p. 406; Wynne, Chem. Soc. Trans. 1892, 61, 1072); by chlorination of toluene *p*-sulphonic acid, or its chloride or amide in sulphuric acid solution, followed by the removal of the sulphonic group by heating in a current of steam (B. A. S. F., D. R. P. 294638 of 1914); by hydrolysis of *o*-chlorotoluene *p*-sulphonic acid by boiling with 80 p.c. sulphuric acid (Ges. für Chem. Ind. in Basel, D. R. P. 133000 of 1901); readily by hydrolysis of 6-chlorotoluene *o*-sulphonic acid (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920). M.p. -34° (Haase, Ber. 1893, 26, 1053); b.p. 159.5° /759.5 mm., n_D^{20} 1.4977 (Wibaut, Rec. trav. chim. 1913, (2) 32, 244); D_{15}^{20} 1.0973, D_{15}^{25} 1.0877, D_{25}^{25} 1.0801 (Perkin, Chem. Soc. Trans. 1896, 69, 1243), D_{20}^{20} 1.08073 (Seubert, Ber. 1889, 22, 2520). For specific gravity and boiling-point under diminished pressure, see Feitler (Zeitsch. physikal. Chem. 1889, 4, 73); molecular refractive power and dispersion coefficient (Seubert, l.c.); magnetic rotatory power at 15.4° , 13.72 (Perkin, l.c.).

On treatment with chromyl chloride and subsequent treatment of the product with water, *o*-chlorotoluene yields *o*-chlorobenzaldehyde (Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 804); the latter product is also obtained in a yield of 66 p.c. by the gradual addition of cerium oxide to a suspension of *o*-chlorotoluene in 60–65 p.c. sulphuric acid at 50° , the temperature being raised gradually to 90° (M. L. B., D. R. P. 174238 of 1903). It is reduced by hydriodic acid and phosphorus to toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 41, 322), whilst on oxidation with potassium permanganate it yields *o*-chlorobenzoic acid, m.p. 134° – 135° (Wroblewski, Zeit. f. Chem. 1869, (2) 5, 460; Cohen and Dakin, l.c. 1120). *o*-Chlorotoluene exists in two modifications (von Ostrowskij, Zeitsch. physikal. Chem. 1906, 57, 341).

m-Chlorotoluene; from *m*-toluidine or 3-chloro-*p*-toluidine (Wroblewski, Ann. 1873, 168, 199; Vanino, Präparative Chemie, 1923, vol. ii. p. 406); the diazo-reaction; from 5-chloro-*o*-

toluidine and 3-chloro-*p*-toluidine by treating the corresponding hydrazines with copper sulphate solution (Wynne, Chem. Soc. Trans. 1892, 61, 1047, 1059); from the dibromide of dihydro-*m*-chlorotoluene by boiling with quinoline (Klages and Knoevenagel, Ber. 1894, 27, 3022). M.p. -47.8° ; b.p. 162.2° /756.52 mm.; $D_{162.2}^{20}$ 0.92723 (Haase, Ber. 1893, 26, 1053); D_{20}^{20} 1.07218 (Seubert, Ber. 1889, 22, 2520); molecular refractive power and dispersion coefficient (Seubert, l.c.); specific gravity and boiling point under diminished pressure (Feitler, Zeitsch. physikal. Chem. 1889, 4, 76). On nitration it yields a mixture of *o*- and *p*-nitrochlorotoluenes (Reverdin and Crépiaux, Ber. 1900, 33, 2505). On heating with dilute nitric acid in a sealed tube at 130° – 140° it yields 3-chlorobenzoic acid, needles, m.p. 152° (Wynne, l.c.).

p-Chlorotoluene; by chlorinating toluene in presence of iodine (Beilstein and Geitner, Ann. 1866, 139, 334; Bull. Soc. chim. 1869, (2) 1, 251), or molybdenum pentachloride (Aronheim and Dietrich, Ber. 1875, 8, 1402), in a yield of 35 p.c. by using the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1119); from *p*-toluidine by the diazo-reaction (Gasiorowski and Wayss, Ber. 1885, 18, 1939; Hübner and Majert, Ber. 1873, 6, 794; Sandmeyer, Ber. 1884, 17, 2651; Vanino, l.c.); by hydrolysis of *p*-chlorotoluene *o*-sulphonic acid (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920). M.p. 7.4° (Seubert); b.p. 162.3° /756.4 mm.; D_{15}^{20}

1.0847, D_{15}^{25} 1.0749, D_{25}^{25} 1.0672 (Perkin, Chem. Soc. Trans. 1896, 69, 1243), D_{20}^{20} 1.06974 (Seubert, Ber. 1889, 22, 2519), $D_{162.3}^{20}$ 0.92360 (cf. Feitler, Zeitsch. physikal. Chem. 1889, 4, 78); magnetic rotatory power at 15.2° , 13.25 (Perkin, l.c.). It is oxidised by chromic acid mixture or by potassium permanganate (Cohen and Dakin, l.c. 1120) to *p*-chlorobenzoic acid, m.p. 236° ; and when treated with hydriodic acid and phosphorus it is converted into toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322).

(a) 2:3-Dichlorotoluene; by chlorination of *o*-chlorotoluene in presence of the aluminium-mercury couple; from 2-chloro-3-toluidine by the diazo-reaction (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1128); *o*-chlorotoluene sulphonic acid (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151); by chlorination of toluene or *o*-chlorotoluene in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 157, 168); from crude dichlorotoluene by treatment with fuming sulphuric acid at high temperatures, then neutralising the product with lime, the calcium sulphonate of 2:3-dichlorotoluene being less soluble than that of the accompanying 2:4-dichlorotoluene. The calcium salt is then converted into the sodium salt, and the sulphonic group removed by steam distillation at 180° in presence of sulphuric acid (Seelig). • Doubt has been cast upon the orientation of Seelig's product by Wynne (Chem. Soc. Trans. 1892, 61, 1051) and by Armstrong (*ibid.* 1892, 61, 1035).

Liquid, b.p. 204° – 206° /755 mm. (Cohen and Dakin, l.c. 1128) or 207° – 208° /760 mm. (Wynne and Greeves, l.c.). On oxidation with nitric acid in a sealed tube at 140° for some hours it yields

2:3-dichlorobenzoic acid, m.p. 163° (Cohen and Dakin, l.c.), or 164° (Wynne and Greeves, l.c.), or 166° (Seelig, l.c.). It yields a *nitro-derivative*, m.p. 50.5°-51.5°; a *dinitro-derivative*, m.p. 71°-72°; a *sulphonamide*, m.p. 221°-222° (Cohen and Dakin, l.c.); a *sulphonyl chloride*, needles, m.p. 45° (Wynne and Greeves, l.c.). Wynne and Greeves state that 2:3-dichlorotoluene on sulphonation yields two isomeric sulphonic acids, the one whose amide and chloride are described above being accompanied by 2:3-dichlorotoluene 5-sulphonic acid (*chloride*, prisms, m.p. 85°, *amide*, m.p. 183°), but this was not confirmed by Cohen and Dakin.

(β) 2:4-Dichlorotoluene; by chlorination of toluene or *p*-chlorotoluene (Seelig, Ann. 1887, 237, 162), in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1116); from 2:4-tolylene-diamine (Erdmann, Ber. 1891, 24, 2769; Vanino, l.c.) or *o*-chloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 314); by treating 2:4-dibromo-*o*-toluenediazonium chloride with hydrogen chloride in alcoholic solution (Hantzsch, Ber. 1897, 30, 2334); from 2:4-dinitro-*o*-toluidine; from *o*-chlorotoluenesulphonic acid (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151). M.p. 28.5° (Hantzsch, l.c.), b.p. 194°/735 mm. (Lellmann and Klotz); b.p. 199°-200°/760 mm. (Wynne and Greeves, l.c.), D₂₀²⁰ 1.24597 (L. and K.). It yields a *mononitro-compound*, m.p. 54°-55°, and a *dinitro-compound*, prisms, m.p. 103°-104° (Cohen and Dakin, l.c. 1129) on nitration; 2:4-dichlorotoluene 5-sulphonic acid (*chloride*, m.p. 71°, *amide* m.p. 177°) on sulphonation (Wynne and Greeves, l.c.); and 2:4-dichlorobenzoic acid, m.p. 159°-160°, b.p. 198°-200°, on oxidation (Cohen and Dakin, l.c.).

2:5-Dichlorotoluene; from 5-chloro-*o*-toluidine by the diazo-reaction (Lellmann and Klotz, Ann. 1885, 231, 318; Wynne, Chem. Soc. Trans. 1892, 61, 1049); by chlorination of *o*- and *m*-chlorotoluene in presence of the aluminium-mercury couple (Cohen and Dakin, l.c.); by chlorination of aceto-*o*-toluidide followed by hydrolysis and replacement of the amino-group by chlorine (Lellmann and Klotz, l.c.); by the action of sodium hypochlorite on aceto-*o*-toluidide followed by conversion of the nitrogen chloride into 5-chloroaceto-*o*-toluidide, hydrolysis and replacement of the amino-group by chlorine (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790; Cohen and Dakin, l.c. 1130); by hydrolysis of 2:5-dichlorotoluene *p*-sulphonic acid which is prepared by chlorinating toluene *p*-sulphonic acid or its soluble salts (B. D. C. Green and Gibbens, Eng. Pat. 189025 of 1920; cf. Wynne, l.c.). Liquid, b.p. 200°/770 mm. (Wynne, l.c.), 194°/745 mm. (Lellmann and Klotz), 198°-199°/760 mm., which solidifies in a freezing mixture to crystals, m.p. 5° (Cohen and Dakin, l.c.).

On nitration it yields a *mononitro-derivative*, m.p. 50°-51°, and a *dinitro-derivative*, m.p. 100°-101°, and on oxidation with dilute nitric acid at 150° for 10 hours it yields 2:5-dichlorobenzoic acid, m.p. 182° (Wynne, l.c.; Cohen and Dakin, l.c.).

2:6-Dichlorotoluene; by chlorination of *o*-chlorotoluene in presence of the aluminium-mercury couple (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1117); from 6-nitro-*o*-toluidine

or 6-nitro-*p*-toluidine (Cohen and Dakin, *ibid.* 1131); readily by distilling an aqueous solution of the sodium salt of 2:6-dichlorotoluene *p*-sulphonic acid with superheated steam at 250° (Davies, Chem. Soc. Trans. 1920, 119, 873). Liquid, b.p. 197°-199°/757 mm. (Davies), yielding on nitration a *mononitro-derivative*, m.p. 53°, and a *dinitro-derivative*, m.p. 121°-122° (Cohen and Dakin, *ibid.* 1132; Davies, l.c.); and, on oxidation with dilute nitric acid in a sealed tube, 2:6-dichlorobenzoic acid, colourless needles, m.p. 139°-140° (Cohen and Dakin, l.c.; Wynne and Greeves, l.c.; cf. Claus and Stavenhagen, Ann. 1892, 289, 224.)

3:4-Dichlorotoluene; from 3-chloro-*p*-cresol and phosphorus pentachloride (Schall and Dralle, Ber. 1884, 17, 2535); by chlorination of toluene, *o*- and *m*-chlorotoluene (Beilstein and Geitner, Ann. 1866, 139, 341; Beilstein and Kuhlberg, Ann. 1869, 150, 313; Aronheim and Dietrich, Ber. 1875, 8, 1401; Neuhoof, Zeit. f. Chem. 1886 (2) 2, 653; Schultz, Ann. 1877, 187, 263; Cohen and Dakin, l.c.); from 3-nitro-*p*-toluidine (Cohen and Dakin); from 3-chloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 312; Wynne, Chem. Soc. Trans. 1892, 61, 1060; Vanino, l.c.); by hydrolysis of 3:4-dichlorotoluene sulphonic acid (Wynne, *ibid.* 1069). Liquid, b.p. 205.5°-206.5°/763.6 mm. (Wynne), 200.5°/741 mm. (L. and K.); D₂₀²⁰ 1.2512 (L. and K.). On nitration it yields 3:4-dichloro-6-nitrotoluene, m.p. 63°-64°, and 3:4-dichloro-2:6-dinitrotoluene, m.p. 91.5°-92.5° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1133; 1902, 81, 1349); and, on oxidation with dilute nitric acid in a sealed tube, 3:4-dichlorobenzoic acid, m.p. 202° (Wynne; Cohen and Dakin).

3:5-Dichlorotoluene (cf. Hantzsch, Ber. 1897, 30, 2334); from 3:5-dichloro-*p*-toluidine (Lellmann and Klotz, Ann. 1885, 231, 323); from 3:5-dichloro-*o*-toluidine (Wynne and Greeves, Chem. Soc. Trans. 1892, 61, 1060); from 3:5-dichloroaceto-*o*-toluidide (prepared according to the method of Chattaway and Orton, *ibid.* 1896, 69, 850) by hydrolysis with hydrochloric acid in a sealed tube for 8 hours at 150°, followed by elimination of the amino-group (Cohen and Dakin, *ibid.* 1133). M.p. 26°, b.p. 195°/729 mm. (L. and K.), or 201°-202°/atm. (Wynne and Greeves), sublimes at the ordinary temperature. Yields a *nitro-derivative*, needles, m.p. 61°-62°, and a *dinitro-derivative*, needles, m.p. 99°-100°, and on oxidation with dilute nitric acid at 150° it yields 3:5-dichlorobenzoic acid, long needles, m.p. 182°-183° (Cohen and Dakin).

(β) 2:3:4-Trichlorotoluene, together with 2:4:5-trichlorotoluene, by chlorinating either *o*- or *p*-chlorotoluene in presence of ferric chloride or molybdenum pentachloride (Seelig, Ann. 1887, 237, 36, 133; cf. Prentiss, Ann. 1897, 296, 180); together with a tetrachlorotoluene, by chlorinating 2:3-dichlorotoluene in presence of the aluminium-mercury couple; together with 2:4:5-trichlorotoluene and probably a small amount of 2:4:6-trichlorotoluene by chlorinating 2:4-dichlorotoluene in a similar manner; from 4-nitro-2:3-dichlorotoluene by reduction and diazotisation (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1333, 1339). Volatile in steam.

Forms a *mononitro-derivative*, white needles, m.p. 60°–61°, a 5:6-*dinitro-derivative*, m.p. 140°–141°, and a *sulphonic acid* which is decomposed by superheated steam at 210°, whilst on oxidation with dilute nitric acid in a sealed tube at 150° it yields 2:3:4-trichlorobenzoic acid, m.p. 186°–187° (Cohen and Dakin; Seelig, *l.c.*, gives m.p. 129°).

2:3:5-*Trichlorotoluene*; almost exclusively by chlorination of 3:5-dichlorotoluene in presence of the aluminium-mercury couple; from 3:5-dichloro-*o*-toluidine (prepared by hydrolysis of the acetyl-derivative obtained by the action of bleaching powder on aceto-*o*-toluidide according to the method of Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 791) by the diazo-reaction, and from 2:5-dichloro-*m*-toluidine. Long needles, m.p. 45°–46°, b.p. 229°–231°/757 mm. Yields a *nitro-derivative*, felted needles, m.p. 58°–59°, a *dinitro-derivative*, flat needles, m.p. 149°–150°, and with 20 p.c. nitric acid in a sealed tube at 140°, it yields 2:3:5-trichlorobenzoic acid, m.p. 162° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

2:3:6-*Trichlorotoluene*; almost exclusively by chlorination of 2:6-dichlorotoluene; together with 2:4:5-trichlorotoluene by chlorination of 2:5-dichlorotoluene in presence of the aluminium-mercury couple; from 2:6-dichloro-*m*-toluidine by the diazo-reaction. On nitration it yields a *mononitro-derivative*, long needles, m.p. 57°–58°, and 2:3:6-trichloro-4:5-*dinitrotoluene*, prisms, m.p. 140°–142°, and on oxidation, 2:3:6-trichlorobenzoic acid, flaky crystals, m.p. 163°–164° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1331, 1343). The chlorination of toluene *p*-sulphonic acid or its soluble salts results in the formation of 2:5-dichloro- and 2:3:6-trichlorotoluene *p*-sulphonic acid. The latter is readily separated on account of the much greater insolubility of its sodium salt, and on hydrolysis a good yield of 2:3:6-trichlorotoluene is claimed (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920).

(a) 2:4:5-*Trichlorotoluene*, together with 2:3:4-trichlorotoluene by chlorinating toluene in presence of iodine (Limpricht, Ann. 1866, 139, 326), 4–1 p.c. of molybdenum pentachloride (Aronheim and Dietrich, Ber. 1875, 8, 1401) or ferric chloride (Seelig, Ann. 1887, 237, 131), the crude product being shaken with two parts* of fuming sulphuric acid for a minute at 60° (whereby only the 2:3:4-isomeride is sulphonated) and precipitated with water and steam distilled; together with 2:3:4-trichlorotoluene and probably a small amount of 2:4:6-trichlorotoluene by chlorinating 2:4-dichlorotoluene in presence of the aluminium-mercury couple; together with 2:3:6-trichlorotoluene by chlorinating 2:5-dichlorotoluene in a similar manner, and as sole product by chlorinating 3:4-dichlorotoluene in a similar manner; from 4:6-dichloro-*m*-toluidine and 4:5-dichloro-*o*-toluidine (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1332, 1343); from 2:5-dichloro-*p*-toluidine and 5-chloro-2:4-tolylenediamine by the diazo-reaction (Morgan and Drew, *ibid.* 1920, 117, 789; 1900, 77, 1200). Long white needles volatile with steam, m.p. 81°–82° (Cohen and Dakin), b.p. 229°–230°/716 mm. On nitration it yields a *mononitro-derivative*, m.p. 91°–92°, 2:4:5-trichloro-3:6-*dinitrotoluene*,

m.p. 226°–227°, and on oxidation 2:4:5-trichlorobenzoic acid, white silky needles, m.p. 182°–184° (Cohen and Dakin; Seelig; Jannasch, Ann. 1887, 142, 301).

2:4:6-*Trichlorotoluene*; see 2:3:4- and 2:4:5-trichlorotoluenes; by chlorinating aceto-*m*-toluidide in glacial acetic acid—hydrochloric acid solution by means of sodium chlorate at 15°–25°, followed by hydrolysis and elimination of the amino-group (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1335); from 6-chloro-2:4-tolylenediamine by the Sandmeyer reaction (Morgan and Drew, *ibid.* 1920, 117, 788). Long white needles, m.p. 33°–34°, yielding on nitration the 3-*nitro-derivative*, m.p. 54° (indefinite), the 3:5-*dinitro-derivative*, m.p. 178°–180°, and on oxidation 2:4:6-trichlorobenzoic acid, m.p. 160°–161° (Cohen and Dakin, *l.c.*).

3:4:5-*Trichlorotoluene*; by hydrolysis of potassium 3:4:5-trichlorotoluene sulphonate (Wynne, Chem. Soc. Trans. 1892, 61, 1070); from 3:5-dichloro-*p*-toluidine or 4:5-dichloro-*m*-toluidine (Cohen and Dakin, *ibid.* 1902, 81, 1336); as a derivative of the products of the action of sulphuryl chloride on aceto-*p*-toluidide (Wynne, *ibid.* 1892, 62, 1042). M.p. 44°–45°–45°–5°, volatile with steam (Cohen and Dakin). On oxidation with dilute nitric acid it yields the corresponding trichlorobenzoic acid (Wynne; Cohen and Dakin).

2:3:4:5-*Tetrachlorotoluene*; from 2:4:5- or 3:4:5-trichlorotoluene by nitration, reduction and replacement of the amino-group by chlorine. There is no evidence of the formation of this substance by the further chlorination of 2:4:5-trichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1900, 89, 1453); the product, m.p. 86°–88°, previously stated (*ibid.* 1904, 85, 1280) to be 2:3:4:5-tetrachlorotoluene is probably a mixture of tetrachlorotoluene and trichloronitrotoluene (m.p. 81°). 2:3:4:5-Tetrachlorotoluene melts at 97°–98° and forms a *nitro-derivative*, m.p. 159° (Cohen and Dakin, *ibid.* 1906, 89, 1483).

2:3:4:6-*Tetrachlorotoluene*; from 2:4:6-trichloro-aceto-*m*-toluidide by hydrolysis and replacement of the amino-group by chlorine; by further chlorination of 2:4:6-trichlorotoluene in presence of the aluminium-mercury couple. Shining needles, m.p. 91°–92°. 5-*Nitro-derivative*, m.p. 131°–134° (not pure), and on further nitration a compound, highly refractive plates, m.p. 153°, is formed (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1280, 1284).

2:3:5:6-*Tetrachlorotoluene*; from 2:3:6-trichlorotoluene by nitration, reduction and replacement of the amino-group by chlorine; by chlorination of 2:3:5- and 2:3:6-trichlorotoluenes in presence of the aluminium-mercury couple. White opaque felted needles, m.p. 93°–94°; 4-*nitro-derivative*, small hexagonal plates, m.p. 150°–152° (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1281). The tetrachloro-derivatives obtained by Limpricht (Ann. 1866, 189, 327), Beilstein and Kahlberg (Ann. 1869, 150, 286), and Pieper (Ann. 1867, 143, 305) are impure. A tetrachlorotoluene has been obtained in 90 p.c. yield, together with less highly halogenated derivatives and traces of pentachlorotoluene, by passing dry chlorine over a mixture of dry toluene and anhydrous iron chloride with stirring; the maximum tempera-

ture being 50°, whilst, if the temperature be kept at 12°–15°, trichlorotoluene is formed (Cassella & Co., Eng. Pat. 16317 of 1914).

Pentachlorotoluene; by chlorinating toluene initially in presence of iodine and finally in presence of phosphorus pentachloride. Long hair-like needles, m.p. 218°, b.p. 301° (Beilstein and Kuhlberg, Ann. 1869, 150, 298).

Bromo derivatives.—A quantitative examination of the influence of light, temperature and bromine 'carriers' on the action of bromine on an excess of toluene has been carried out by Holleman and van der Laan (Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 512), van der Laan (Chem. Weekblad, 1906, 3, 15), Holleman, Polack, van der Laan and Euwes (Rec. trav. chim. 1908, (2) 27, 435); cf. Andrich and le Blanc (Zeitsch. Wiss. Photochem. 1916, 15, 148) and Swensson (*ibid.* 1921, 20, 206). The investigations of van der Laan have left the question undecided whether *m*-bromotoluene is formed by the bromination of toluene in addition to *o*- and *p*-bromotoluene and benzyl bromide. Holleman (Rec. trav. chim. 1914 (2), 33, 183) concludes, on the evidence of the index of refraction and of the first and second points of solidification of the products of bromination, that *m*-bromotoluene is not produced when bromine acts on a large excess of toluene. Cohen and Dutt (Chem. Soc. Trans. 1914, 105, 504), however, arrive at a contrary conclusion when using the aluminium-mercury couple, although Holleman regards the experimental proof of the presence of *m*-bromotoluene as not sufficiently definite. A further proof of the contention of Cohen and Dutt is given in Chem. Soc. Proc. 1914, 30, 271.

In addition to the ordinary methods for brominating toluene, a mixture of nitric and hydrobromic acids may be used, but it is preferable to use a mixture of bromine and nitric acid (Datta and Chatterjee, J. Amer. Chem. Soc. 1916, 38, 2545).

***o*-Bromotoluene** on further bromination in presence of the aluminium-mercury couple yields mainly 2:5-dibromotoluene with smaller quantities of 2:4-dibromotoluene; *m*-bromotoluene similarly yields 2:5-dibromotoluene together with 3:4-dibromotoluene, a little 1:4:5-tribromotoluene and a trace of 3:4-dibromotoluene; whilst *p*-bromotoluene yields 3:4-dibromotoluene as the main product together with 3:4-dibromotoluene (Cohen and Dutt, *loc. cit.*) and 2:4:5-tribromotoluene (Miller, *ibid.* 1892, 61, 1023).

2:3-Dibromotoluene on similar treatment yields 2:3:6-tribromotoluene as the main product, together with a little of the 2:3:5-isomeride, whilst the presence of 2:3:4-tribromotoluene is doubtful; 2:4-dibromotoluene yields a mixture of 2:4:5- and 2:4:6-bromotoluenes; 2:5-dibromotoluene yields mainly 2:4:5-tribromotoluene together with 2:3:6-isomeride; whilst 3:4-dibromotoluene yields mainly 2:4:5-tribromotoluene, together with a very small amount of 3:4:5-tribromotoluene, and 3:5-dibromotoluene yields 2:5-tribromotoluene (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 501). The bromination of chlorotoluenes in presence of the aluminium-mercury couple yields mainly 3-chloro-5-bromotoluene, together with smaller quantities of

2-chloro-4-bromotoluene; of *m*-chlorotoluene, 3-chloro-6-bromotoluene and smaller quantities of 3-chloro-4-bromotoluene; of *p*-chlorotoluene, mainly 4-chloro-2-bromotoluene together with 4-chloro-3-bromotoluene. The chlorination of *o*-bromotoluene under similar conditions yields mainly 4-chloro-2-bromotoluene together with 6-chloro-2-bromotoluene; of *m*-bromotoluene, mainly 6-chloro-3-bromotoluene together with 4-chloro-3-bromotoluene; and of *p*-bromotoluene, 2-chloro-4-bromotoluene as main product together with 3-chloro-4-bromotoluene (Cohen and Smithells, *ibid.* 1914, 105, 1910).

Benzyl bromide; by saturating benzyl alcohol with hydrogen bromide (Kekulé, Ann. 1866, 137, 190); by the action of bromine on toluene at the boiling-point (Beilstein, Ann. 1867, 143, 369; Jackson and Field, Amer. Chem. J. 1880–1, 2, 11), in sunlight (Schramm, Ber. 1885, 18, 608; cf. Grimaux and Lauth, Bull. Soc. chim. 1867 (2), 7, 108). From benzyl chloride and arsenic tribromide (Brix, Ann. 1884, 225, 163). Liquid, b.p. 198°–199°; D_{20}^{25} 1.4380.

The vapour has lachrymatory properties.

The zinc-copper couple reacts energetically with benzyl bromide yielding two isomeric benzylenes (C_6H_5)₂ with evolution of hydrogen bromide, whilst if the reaction be carried out in ethereal solution no hydrogen bromide is evolved, and toluene and dibenzyl are formed when the reaction product is treated with water. Similar products are obtained in presence of ethyl alcohol or water (Gladstone and Tribe, Chem. Soc. Trans. 1885, 47, 448).

***o*-Bromobenzyl bromide**; together with the *p*-compound by brominating crude toluene, most of the *p*-compound being removed by pressing the cooled product, the remainder being distilled with steam when the *o*-compound distils first; in a pure condition by brominating *o*-bromotoluene. Crystallises at 0° in very pungent rhombic plates, volatile with steam, m.p. 30°, and on treatment with sodium in ethereal solution it yields phenanthrene, anthracene, dibenzyl and other products (Jackson and others, Amer. Chem. J. 1879, 1, 93; 1880–1, 2, 315; Ber. 1876, 9, 932; 1879, 12, 1965; 1880, 13, 1218).

***m*-Bromobenzyl bromide**; by brominating heated *m*-bromotoluene. Pungent plates or needles, m.p. 41°, slightly volatile with steam, but very volatile with ether vapour; like *o*-bromobenzyl bromide, it is unattacked by chromic acid (Jackson, Ber. 1876, 9, 931; Amer. Chem. J. 1879, 1, 93).

***p*-Bromobenzyl bromide**; by passing bromine vapour into boiling *p*-bromotoluene; by brominating benzyl bromide (Jackson, *loc. cit.*); by brominating *p*-bromotoluene in the cold and in presence of sunlight (Schramm, Ber. 1884, 17, 2922; 1885, 18, 350). Very pungent needles or large rhombic prisms, m.p. 61°, volatile with steam. When boiled with alcoholic potash it yields *p*-bromobenzyl alcohol and ethyl *p*-bromobenzoate (Elbe, J. pr. Chem. 1886, (2) 34, 341), and with zinc dust *p*-*p*-dibromodibenzyl (Errera, Gazz. chim. ital. 1898, 18, 237; cf. Fittig and Stelling, Ann. 1866, 137, 366).

Benzylidene bromide; from benzaldehyde and phosphorus pentabromide (Michelson and Lippmann, Bull. Soc. chim. 1905, (3) 2, 351; Carls-

and Quedenfeldt, J. pr. Chem. 1898, (2) 58, 389). Liquid, b.p. $156^{\circ}/23$ mm., $D_{20}^{25} = 1.51$, $n_D = 1.541$. It is decomposed by cold water forming hydrogen bromide and benzaldehyde, whilst with alcohol it yields ethyl bromide and a liquid, b.p. $50^{\circ}/15$ mm. ($C_6H_5 \cdot CHBrOC_2H_5$?), which on treatment with water yields hydrogen bromide and benzaldehyde (Curtius and Quedenfeldt). With sodium at 180° it yields toluene and dibenzyl (Michaelson and Lippmann).

p-Bromobenzyl chloride; by heating *p*-bromobenzyl alcohol with fuming hydrochloric acid at 150° for 3-4 hours. Glistening needles, m.p. 38° - 39° (Errera, Gazz. chim. ital. 1888, 18, 239).

o-Bromotoluene; together with *p*-bromotoluene by brominating cold toluene in the dark, in daylight or in presence of iodine (Longuinine, Ber. 1871, 4, 514; Dmochowsky, Ber. 1872, 5, 333; Schramm, Ber. 1885, 18, 607; Glinzer and Fittig, Ann. 1865, 133, 47; 1865, 136, 301; Kekulé, Ann. 1866, 137, 192; Cannizzaro, Ann. 1867, 141, 198; Beilstein, Ann. 1867, 143, 369; Fittig, Ann. 1868, 147, 39; Hübner and Post, Ann. 1873, 169, 1; Hübner and Jannasch, Ann. 1873, 170, 117; Hübner and Wallach, Ann. 1870, 154, 293; Zeit. f. Chem. 1869, (2) 5, 22, 138, 499; Rosenstiehl and Nikiforoff, *ibid.* 1869, (2) 5, 635; Hübner and Retschy, *ibid.* 1871, (2) 7, 618; Lauth and Grimaux, Bull. Soc. chim. 1866, (2) 5, 347; 1867, (2) 7, 108; Miller, Chem. Soc. Trans. 1892, 61, 1025).

The product is shaken with dilute sodium hydroxide to remove bromine, steam distilled and fractionated. The crude mixture of *o*- and *p*-bromotoluenes is then subjected to the alternate action of a good freezing mixture and weakly fuming sulphuric acid, when an approximate separation is effected (Miller); another method of separation is given by Reyman (Bull. Soc. chim. 1876, (2) 26, 533). A better method of preparing *o*-bromotoluene is to add bromine to a concentrated solution of pure potassium toluene *p*-sulphonate and to heat at 60° - 70° . The mixture is then steam distilled, when the *o*-bromosulphonate crystallises from the residual solution on cooling. On hydrolysing the latter, pure *o*-bromotoluene is obtained (Miller). It may also be prepared from *o*-toluidine by the Sandmeyer reaction (Wroblewsky, Ann. 1873, 168, 171) and together with naphthalene by the action of α -bromonaphthalene on toluene in the presence of aluminium chloride (Roux, Bull. Soc. chim. 1886, (2) 45, 520). M.p. -25.9° ; b.p. $180.33^{\circ}/753.91$ mm. (Haase, Ber. 1893, 26, 1053; cf. Feitler, Zeitsch. physikal. Chem. 1889, 4, 73); $D_{20}^{25} = 1.4437$, $D_{15}^{25} = 1.4309$ or 1.431 , $D_{25}^{25} = 1.4222$ (Perkin, Chem. Soc. Trans. 1896, 69, 1243; Miller, *ibid.* 1892, 61, 1025; Kelbe, Ber. 1886, 19, 93), $D_{20}^{20} = 1.4222$ (Seubert, Ber. 1889, 22, 2520), $D_{18}^{20} = 1.21861$ (Haase, l.c.); molecular refractive power and dispersion coefficient (Seubert, l.c.); magnetic rotatory power at 16.7° 15.67 (Perkin, l.c.).

On treatment with dilute nitric acid (Zincke, Ber. 1874, 7, 1502) or by prolonged heating with potassium ferrocyanide (Noyes, Amer. Chem. J. 1885, 7, 145) it is oxidised to *o*-bromobenzoic acid; and with chromyl chloride in carbon disulphide solution, followed by decomposition of the product with water, it yields *o*-bromobenzaldehyde and *o*-bromobenzylidene chloride

(Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 804). When brominated in presence of iodine (Miller, *ibid.* 1892, 61, 1032) or the aluminium-mercury couple (Cohen and Dutt, *ibid.* 1914, 105, 501) it yields 2:5-dibromotoluene and a small quantity of 2:4-dibromotoluene, and on reduction with hydriodic acid and phosphorus at 250° it yields toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322). The zinc-copper couple has no action (Gladstone and Tribe, Chem. Soc. Trans. 1885, 47, 448). For its conversion into *o*-ditolyl, see Fittig (Ann. 1866, 139, 178) and Carnelley (Jahresbericht, 1877, 384), and for the two modifications of *o*-bromotoluene, see Ostromisslensky (Zeitsch. physikal. Chem. 1906, 57, 341).

For its conversion into *o*-cresol, see Bodroux (Compt. rend. 1903, 136, 158; Bull. Soc. chim. 1904, (3) 31, 34).

m-Bromotoluene; from *m*-toluidine by the diazo-reaction and from *m*-bromo-*p*-toluidine by the elimination of the amino-group (Wroblewsky, Zeit. f. Chem. 1871, (2) 7, 609; Ann. 1873, 168, 155; cf. Grete, *ibid.* 1875, 177, 231; Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 950); from *m*-bromo-*p*-toluidine by nitration, elimination of the amino-group, reduction and replacement of the amino-group by bromine (Wroblewsky, Ann. 1878, 192, 206). M.p. -39.8° ; b.p. $183.67^{\circ}/759.46$ mm.; $D_{20}^{25} = 1.20082$ (Haase, Ber. 1893, 26, 1053; Feitler, Zeitsch. physikal. Chem. 1889, 4, 73); $D_{20}^{25} = 1.40988$, $D_{20}^{20} = 1.4009$ (Wroblewsky) (Seubert, Ber. 1889, 22, 2520). Optical behaviour (Seubert) Oxidised by chromic acid to *m*-bromobenzoic acid. When sodium acts on a mixture of *m*-bromotoluene and bromobenzene in ethereal solution at 40° - 50° for 5 hours, a mixture of diphenyl, *m*-ditolyl and *m*-phenyltoluene is formed (Perrier, Compt. rend. 1891, 114, 484; Bull. Soc. chim. 1892, (3) 7, 182). On bromination in presence of the aluminium-mercury couple, *m*-bromotoluene yields 2:5-dibromotoluene, 3:4-dibromotoluene, a little 2:4:5-tribromotoluene and a trace of 3:5-dibromotoluene (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 506), whilst on chlorination under similar conditions it yields mainly 4-chloro-2-bromotoluene together with 6-chloro-2-bromotoluene (Cohen and Smithells, *ibid.* 1914, 105, 1910).

p-Bromotoluene; together with *o*-bromotoluene by brominating cold toluene (see under *o*-bromotoluene and Hübner and Post, Ann. 1873, 169, 1; Miller, Chem. Soc. Trans. 1892, 61, 1025; Michaelis and Genzken, Ann. 1887, 242, 165); together with *o*-bromotoluene *p*-sulphonic acid by brominating potassium toluene *p*-sulphonate (Miller). The products of the latter reaction are steam distilled, and the oily, volatile product, consisting of *p*-bromotoluene, a dibromotoluene and *p*-bromobenzyl bromide, is fractionally distilled. The fraction boiling at about 185° solidifies on cooling and consists of *p*-bromotoluene, which is readily obtained pure by redistillation and crystallisation (Miller).

Rhombic crystals (Hübner and Post) or colourless plates (Miller); m.p. 28.5° ; b.p. 185.2° (Hübner and Post) or $183.67^{\circ}/759.46$ mm. (Feitler); $D_{20}^{25} = 1.3959$, $D_{20}^{25} = 1.3856$, $D_{20}^{20} = 1.3837$ (Perkin, Chem. Soc. Trans. 1894, 68,

1243), *Diss.* 1-13306 (Hübner and Post; cf. Fittler, *Diss.* 1-133977 (Seubert, Ber. 1889, 22, 2519; cf. Kekulé, Ann. 1866, 137, 182); magnetic rotatory power at 39° 15-06 (Perkin); optical behaviour (Seubert).

On bromination in presence of the aluminium-mercury couple (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 509) or iodine (Miller, *ibid.* 1892, 61, 1304), it yields 2:4- and a little 3:4-dibromotoluene, and on treatment with chromyl chloride in carbon disulphide, followed by decomposition of the product with water, it yields *p*-bromobenzaldehyde (Etard, Ann. Chim. 1881, (5) 22, 241), whilst on reduction with hydriodic acid at 250° it is converted into toluene (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 322). Sodium reacts with a mixture of *p*-bromotoluene and bromobenzene to form *p*-phenyltoluene (Carnelley, Chem. Soc. Trans. 1876, 29, 16; 1880, 37, 706). With sodium it yields 4:4-ditolyl, dibenzyl, 3:4-ditolyl and 4-tolylphenylmethane, etc. (Zincke, Ber. 1871, 4, 396; Longuinine, Ber. 1871, 4, 514; Weiler, Ber. 1899, 32, 1056). The zinc-copper couple has no reaction (Gladstone and Tribe), whilst chromic acid yields *p*-bromobenzoic acid. When chlorinated hot *p*-bromotoluene yields *p*-bromobenzyl chloride (Bäseken, Rec. trav. chim. 1904, 23, 98). It condenses with benzophenone in the presence of sodium to yield *p*-tolylidiphenylmethane (Acree, Amer. Chem. J. 1903, 29, 588).

The magnesium derivative of *p*-bromotoluene on treatment with oxygen yields *p*-cresol (Bodroux, Compt. rend. 1903, 136, 158; Bull. Soc. chim. 1904, (3) 31, 34), whilst it condenses with ethyl-*o*-formate to yield *p*-tolualdehyde (Bodroux, Bull. Soc. chim. 1904, (3) 31, 586; Compt. rend. 1904, 138, 92, 700), with dimethyl sulphate to form *p*-xylene (Werner and Zilkens, Ber. 1903, 36, 2116; Houben, *ibid.* 3083), and with carbonyl sulphide to form *p*-thiotoluic acid and a little tritolyl-carbinol. A similar reaction takes place with the magnesium derivative of *o*-bromotoluene (Weigert, *ibid.* 1007).

2:3-Dibromotoluene; from 5:6-dibromo-*m*-toluidine by elimination of the amino-group (Neville and Winther, Ber. 1890, 13, 962; 1881, 14, 417; Chem. Soc. Trans. 1880, 37, 429). According to Fittig (Ann., 1868, 147, 39) a *p*-bromotoluene, long needles, m.p. 107°-108°, is obtained by brominating cold toluene without the addition of iodine. The constitution of this product is questioned by Neville and Winther, and Miller (Chem. Soc. Trans. 1892, 61, 1031) regards it as being probably impure 2:4:5-tribromotoluene.

2:3-Dibromotoluene melts at 27.4°-27.8° (N. and W.) or 30°-31° (Wynne, Chem. Soc. Trans. 1892, 61, 1040). On oxidation with dilute nitric acid at 130°, 2:3-dibromobenzoic acid, m.p. 146°-148°, is formed, whilst on bromination in carbon tetrachloride solution in presence of the aluminium-mercury couple it yields mainly 2:3:6-tribromotoluene together with a little of the 2:3:5-tribromoisomeride, whilst the presence of the 2:3:4-tribromo-isomeride is doubtful (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 516).

2:4-Dibromotoluene; from *p*-bromo-*o*-toluidine and 3:5-dibromo-*m*-toluidine by the

diazo-reaction (Neville and Winther, *l.c.*); together with a greater proportion of 2:5-dibromotoluene by bromination of *o*-bromotoluene, or together with 3:4-dibromotoluene and 2:4:5-tribromotoluene by brominating *p*-bromotoluene (Miller, Chem. Soc. Trans. 1892, 61, 1023).

Liquid, which does not solidify at -20°, b.p. 152°-158°/80 mm. (Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 50). On oxidation with dilute nitric acid it yields 2:4-dibromobenzoic acid, tables, m.p. 168°-170° (N. and W.), whilst on bromination a mixture of 2:4:5- and 2:4:6-tribromotoluene is formed (Cohen and Dutt, *l.c.*).

2:5-Dibromotoluene; by brominating toluene (Wroblewsky, Zeit. f. Chem. 1870, (2) 6, 239) or *m*-bromotoluene (Wroblewsky, Ann. 1873, 168, 681); from 6-bromo-*m*-toluidine or 5-bromo-*o*-toluidine by the diazo-reaction (Neville and Winther, *l.c.*); as the main product, together with 2:4-dibromotoluene, by brominating *o*-bromotoluene (Miller, Chem. Soc. Trans. 1892, 61, 1031; cf. Cohen and Dutt, *ibid.* 1914, 105, 506).

Liquid, which does not solidify at -20°, b.p. 236°, *D*₁₅²⁰ 1.8127 (Wroblewsky). On prolonged boiling with dilute nitric acid it yields 2:5-dibromobenzoic acid, and on bromination in carbon tetrachloride solution in presence of the aluminium-mercury couple, it yields mainly 2:4:5-tribromotoluene together with the 2:3:6-isomeride (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 518).

2:6-Dibromotoluene; from 2:6-dibromo-*m*-toluidine, 2:6-dibromo-*p*-toluidine (Neville and Winther, *l.c.*; Wroblewsky, *l.c.*), and 6-bromo-*o*-toluidine (Blanksma, Chem. Weekblad. 1912, 9, 968) by the diazo-reaction.

Colourless crystals, m.p. 2° (Blanksma), b.p. 246°, *D*₁₅²⁰ 1.812 (Wroblewsky; cf. Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 51). On bromination it yields 2:3:6-tribromotoluene (Cohen and Dutt, *l.c.*).

3:4-Dibromotoluene; from 3-bromo-*p*-toluidine (Neville and Winther, *l.c.*; Wroblewsky); the product obtained by Jannasch (Ann. 1875, 176, 286) by brominating toluene is stated to be a mixture of isomerides by Miller (Chem. Soc. Trans. 1892, 61, 1605); together with other products by brominating *p*-bromotoluene (Miller, *l.c.*). Liquid, b.p. 160°-165°/65 mm. (Cohen and Zortman, Chem. Soc. Trans. 1906, 89, 52), b.p. 238°-239°, *D*₁₅²⁰ 1.812 (Wroblewsky). On oxidation with dilute nitric acid or chromic acid, 3:4-dibromobenzoic acid, m.p. 232°-233° (cf. Burghardt, Ber. 1875, 8, 559), is obtained. On further bromination 2:4:5-tribromotoluene, together with a very small quantity of 3:4:5-tribromotoluene, is formed (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 519).

3:5-Dibromotoluene; from 3:5-dibromo-*p*-toluidine or 3:5-dibromo-*o*-toluidine (Wroblewsky, *l.c.*; Neville and Winther). Long needles, m.p. 39°, b.p. 246° (Neville and Winther). On oxidation with chromic acid it yields 3:5-dibromobenzoic acid, m.p. 208°-209°, whilst on further bromination 2:3:5-tribromotoluene is formed (Cohen and Dutt, *l.c.*).

Dibromotoluene, m.p. 108°. The existence of this substance, said to be formed by the bromination of toluene (Fittig, Ann. 1866, 147, 39) is questioned by Neville and Winther.

2:3:4-Tribromotoluene; from 4:5:6-tribromotoluene by the

bromo-*m*-toluidine (Nevile and Winther, *l.c.*); by bromination of 4:5-dibromoaceto-*m*-toluidine, followed by hydrolysis with dilute sulphuric acid and elimination of the amino-group. It melts at 45°-46° and when heated for 6 hours in a sealed tube at 150°-160° with dilute nitric acid it yields 2:3:4-tribromobenzoic acid (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 511).

2:3:5-Tribromotoluene; from 3:5-dibromo-*o*-toluidine (N. and W.) or 5:6-dibromo-*m*-toluidine (Cohen and Dutt, *l.c.*) by the diazo-reaction. Long flat needles, m.p. 52°-53°. On oxidation with dilute nitric acid at 135°-140° for 6 hours it yields 2:3:5-tribromobenzoic acid, m.p. 193°-194°.

2:3:6-Tribromotoluene; from 2:5:6-tribromo-*m*-toluidine (N. and W.), 2:5:6-tribromo-*p*-toluidine, and 5:6-dibromo-*o*-toluidine (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 514). Flat needles, m.p. 58°-59° (N. and W.). The corresponding tribromobenzoic acid could not be obtained by direct oxidation with dilute nitric acid in a sealed tube (Cohen and Dutt, *l.c.*).

2:4:5-Tribromotoluene; from 4:6-dibromo-*m*-toluidine and 4:5-dibromo-*o*-toluidine (Nevile and Winther, *l.c.*; Cohen and Dutt, *l.c.*); from 5-bromo-2:4-toluylenediamine (Morgan and Clayton, *Chem. Soc. Trans.* 1905, 87, 951); by nitration of 3:4-dibromotoluene followed by reduction (Nevile and Winther, *Ber.* 1881, 14, 417); by brominating *p*-bromotoluene (Miller, *Chem. Soc. Trans.* 1892, 61, 1033).

Colourless needles, m.p. 112°-113°. On oxidation with dilute nitric acid in a sealed tube it yields 2:4:5-tribromobenzoic acid, m.p. 195°-196° (Cohen and Dutt, *l.c.*). According to Plankuch (*J. pr. Chem.* 1873, (2) 6, 108) a tribromotoluene, small needles, m.p. 150°, is obtained by heating the potassium salt of tribromophenol with potassium acetate.

2:4:6-Tribromotoluene; from 2:4:6-tribromo-*m*-toluidine by the diazo-reaction (Nevile and Winther, *Ber.* 1880, 13, 975; 1881, 14, 417; *Chem. Soc. Trans.* 1880, 37, 446); by brominating *m*-toluidine followed by the elimination of the amino-group (Cohen and Dutt, *l.c.*). M.p. 66° (N. and W.), b.p. 290° (Wroblewsky, *Ann.* 1873, 168, 194). On oxidation it yields 2:4:6-tribromobenzoic acid, m.p. 186°-187° (Cohen and Dutt).

3:4:5-Tribromotoluene; from 3:5-dibromo-*p*-toluidine by the diazo-reaction. M.p. 88°-89° (Nevile and Winther, *l.c.*; Cohen and Dutt, *l.c.*). On oxidation it yields 3:4:5-tribromobenzoic acid, m.p. 235° (Cohen and Dutt).

(v)-2:3:4:5-Tetrabromotoluene; from 4:5:6-tribromo-*m*-toluidine by the diazo-reaction. Needles, m.p. 111°-111.5° (Nevile and Winther).

(a)-2:3:4:6-Tetrabromotoluene; from 2:4:6-tribromo-*m*-toluidine and tetrabromo-*m*-toluidine (m.p. 224°) by the diazo-reaction. M.p. 106.8°-108° (Nevile and Winther).

(s)-2:3:5:6-Tetrabromotoluene; from 2:5:6-tribromo-*m*-toluidine by the diazo-reaction. Fine needles, m.p. 116°-117° (Nevile and Winther).

Pentabromotoluene; by careful addition of toluene to pure bromine at 0° in presence of

aluminium bromide (Gustavson, *J. Russ. Phys. Chem. Soc.* 1877, 9, 286; *Bull. Soc. chim.* 1877, (2) 28, 347; *Ber.* 1877, 10, 971); from tetrabromo-*m*-toluidine (m.p. 223°-224°) (Nevile and Winther, *Ber.* 1880, 13, 976; *Chem. Soc. Trans.* 1880, 37, 450); from cycloheptane (Markownikoff, *J. Russ. Chem. Phys. Soc.* 1893, 25, 544) or methylcyclohexane (Kursanoff, *Ber.* 1899, 32, 2973) by the action of bromine in presence of aluminium bromide; from ethyl- and propyl-cymene by means of bromine in presence of aluminium (Klages and Sommer, *Ber.* 1906, 39, 2306; Klages, *Ber.* 1907, 40, 2360).

Long needles which sublime, m.p. 282°-283° (Kursanoff) or 279°-280° (Zelinsky and Generosow, *Ber.* 1896, 29, 732; cf. Jäger, *Z. Kristall.* 1903, 38, 89). It is reduced to toluene by phosphorus and hydriodic acid at 302° (Klages and Liecke, *J. pr. Chem.* 1900, (2) 61, 322).

2-Chloro-3-bromotoluene, m.p. 18°, on oxidation yields 2-chloro-3-bromobenzoic acid, m.p. 165°, and on nitration yields a mononitro-derivative, m.p. 44°-45°, and a dinitro-derivative, m.p. 89°-93° (Cohen and Smithells, *Chem. Soc. Trans.* 1914, 105, 1908).

2-Chloro-4-bromotoluene; from 2-nitro-*p*-toluidine (Cohen and Raper, *Chem. Soc. Trans.* 1904, 85, 1266); together with 3-chloro-4-bromotoluene by chlorinating *p*-bromotoluene (Cohen and Smithells, *l.c.* 1910; cf. Willgerodt and Salzmann, *J. pr. Chem.* 1889, (2) 39, 465). Liquid, b.p. 100°-110°/10 mm., which on oxidation yields 2-chloro-4-bromobenzoic acid, m.p. 166°-167° (Cohen and Raper). Its nitro-derivative melts at 65°-66° and its dinitro-derivative at 110°-111° (Cohen and Smithells).

2-Chloro-5-bromotoluene; from 5-nitro-*o*-toluidine. Liquid, b.p. 127°-129°/45 mm. It yields 2-chloro-5-bromobenzoic acid on oxidation (Cohen and Raper), and on nitration a mononitro-derivative, m.p. 68°-69°, and a dinitro-derivative, m.p. 109°-110° (Cohen and Smithells).

2-Chloro-6-bromotoluene; from 2:6-dinitrotoluene. Liquid, b.p. 118°-120°/40 mm. which yields 2-chloro-6-bromobenzoic acid, m.p. 143°-144°, on oxidation (Cohen and Raper, *l.c.*; Willgerodt and Salzmann) and a mononitro-derivative, m.p. 50°-52°, and a dinitro-derivative, m.p. 143°-144°, on nitration (Cohen and Smithells).

3-Chloro-2-bromotoluene; from 3-nitro-*o*-toluidine (Cohen and Raper, *Chem. Soc. Trans.* 1904, 85, 1266). It melts at 4°-5° (Cohen and Smithells, *ibid.* 1914, 105, 1908) and boils at 103°-105°/25 mm. On oxidation it yields 3-chloro-2-bromobenzoic acid, m.p. 143°-144° (Cohen and Raper), and on nitration a mono- and a dinitro-derivative, m.p. 58°-59.5° and 81° respectively (Cohen and Smithells).

3-Chloro-4-bromotoluene; from *m*-chloro-*p*-toluidine by the diazo-reaction (Cohen and Raper, *l.c.*); by chlorinating *p*-bromotoluene (Willgerodt and Salzmann, *l.c.*). Liquid, b.p. 125°-130°, which on oxidation yields 3-chloro-4-bromobenzoic acid, m.p. 218° (Cohen and Raper), and on nitration yields a mono- and a dinitro-derivative, melting at 72° and 101°-102° respectively (Cohen and Smithells, *l.c.*).

3-Chloro-5-bromotoluene; from aceto-*p*-toluidide by successive bromination and chlorination with hydrochloric acid and sodium chlorate in acetic acid, followed by hydrolysis to 3-chloro-

5-bromo-*p*-toluidine and elimination of the amino-group; by chlorination of aceto-*p*-toluidide and hydrolysis to 3-chloro-*p*-toluidine followed by bromination and elimination of the amino-group. Crystals, m.p. 26°-27°. Its 6-nitro-derivative, colourless needles, melts at 71° and its 2:6(?)-dinitro-derivative at 144°. On oxidation it yields 3-chloro-5-bromobenzoic acid, m.p. 189°-190° (Cohen and Raper; Cohen and Smithells; Cohen and Murray, Chem. Soc. Trans. 1915, 107, 847).

4-Chloro-2-bromotoluene; by chlorinating *o*-bromotoluene or by brominating *p*-chlorotoluene; from 2-nitro-*p*-toluidine. Liquid, b.p. 112°-114°/12 mm. On oxidation it yields 4-chloro-2-bromobenzoic acid, m.p. 154°-155° (Cohen and Raper, Chem. Soc. Trans. 1904, 85, 1267; cf. Willgerodt and Salzmann, J. pr. Chem. 1889, (2) 39, 465, and Cohen and Dakin, Chem. Soc. Trans. 1899, 75, 895), and on nitration a mononitro- and a dinitro-derivative, melting at 64°-65° and 124°-5° respectively, are formed (Cohen and Smithells, Chem. Soc. Trans. 1914, 105, 1908).

4-Chloro-3-bromotoluene; from *m*-nitro-*p*-toluidine. Liquid, b.p. 120°-125°/28 mm. It yields 4-chloro-3-bromobenzoic acid, m.p. 214°, on oxidation (Cohen and Raper, l.c.), and a mononitro-derivative, m.p. 87°-5°, and a dinitro-derivative, m.p. 127°, on nitration (Cohen and Smithells).

4-Chloro-dibromotoluene; by brominating bromo-*p*-chlorotoluene in presence of the aluminium mercury couple. M.p. 94° (Cohen and Dakin, Chem. Soc. Trans. 1899, 75, 893).

5-Chloro-2-bromotoluene; from 5-chloro-*o*-toluidine. Liquid, b.p. 98°-100°/25 mm. The nitro-derivative melts at 66°-67°, the dinitro-derivative at 117°, and oxidation yields 5-chloro-2-bromobenzoic acid, m.p. 153° (Cohen and Raper; Cohen and Smithells).

The following compounds have been obtained by Willgerodt and Salzmann (J. pr. Chem. 1889, (2) 39, 482): *o*-chloro-dibromotoluene, needles, m.p. 100°, b.p. 275°-280°, by brominating *o*-chlorotoluene; dichloro-*p*-bromotoluene, glistening needles, m.p. 87°, b.p. 240°-245°; trichloro-*p*-bromotoluene, needles, m.p. 55°-60°, b.p. 265°-275°; and tetrachloro-*p*-bromotoluene, needles, m.p. 213°, by chlorinating *p*-bromotoluene.

3:4:6(?) - Trichloro-5-bromotoluene, m.p. 98°-100°, is obtained from 3:4-dichloro-5-bromotoluene by nitration, reduction and replacement of the amino-group by chlorine. Its nitro-derivative melts at 171°-173° (Cohen and Dakin, Chem. Soc. Trans. 1906, 89, 1453).

2(?) : 3:4 - Trichloro-5-bromotoluene, m.p. 92°-94°, is formed by chlorinating 3:4-dichloro-5-bromotoluene. Its nitro-derivative melts at 175°-176° (Cohen and Dakin, l.c.).

2-Chloro-3:4:5:6-tetrabromotoluene melts at 258°-259° (Mouneyrat and Pouret, Compt. rend. 1899, 129, 807).

o-Iodotoluene; from *o*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, Ann. 1871, 158, 347; Kekulé, Ber. 1874, 7, 1007; Mabery and Robinson, Amer. Chem. J. 1882, 4, 101); together with *p*-iodotoluene by heating a solution of toluene in light petroleum with powdered sulphur iodide and an excess of dilute nitric acid (D 134) for several hours at 100°

(Edinger and Goldberg, Ber. 1900, 33, 2875). Oil, b.p. 204° (B. and K.) or 211° (Kekulé), D₂₀⁴ 1.697 (B. and K.).

When oxidised with dilute nitric acid it yields *o*-iodobenzoic acid, m.p. 157°. With chromyl chloride and treatment of the product with water, it yields *o*-iodo-*o*-dichlorotoluene and a little *o*-iodobenzaldehyde (Stuart and Elliot, Chem. Soc. Trans. 1888, 53, 805). When heated with sulphuric acid it yields di- and tri-iodotoluene, together with iodotoluene sulphonic acid (Neumann, Ann. 1887, 241, 62; Ber. 1887, 20, 581), whilst on nitration mainly 5-nitro-2-iodotoluene is formed (Reverdin, Ber. 1897, 30, 3000). On treatment with chlorine in chloroform solution *o*-iodotoluene yields a dichloride, crystals, decomposing about 91° (Willgerodt, Ber. 1893, 26, 360).

m-Iodotoluene; from *m*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, l.c.). Liquid, b.p. 204°, D₂₀⁴ 1.698.

p-Iodotoluene; from *p*-toluidine by the diazo-reaction (Körner, Zeitsch. f. Chem. 1868, (2) 4, 327; Bull. Acad. roy. Belg. 1867, 157); together with *o*-iodotoluene by the iodination of toluene according to the method of Edinger and Goldberg (above). Plates which sublime, m.p. 35°, b.p. 211°-5°. *p*-Iodotoluene is stated to be formed also by the action of iodine on mercury ditolyl, the melting-point being given as 20° (Dreher and Otto, Ann. 1870, 154, 171).

When chlorinated, two forms of the iodo-dichloride are obtained, the α -form separates from chloroform in needles, decomposing at 85°, and the β -form in irregular rhombic crystals, exploding at 110°-118° (Willgerodt, Ber. 1893, 26, 357). With nitric acid (D 151) at the ordinary temperature it yields *p*-nitrotoluene, *p*-iodo-*o*-nitrotoluene, and a di-iodo-nitrotoluene (Reverdin, Ber. 1897, 30, 3001), and on heating with sulphuric acid di- and tri-iodotoluene and iodotoluene sulphonic acid are formed (Neumann, Ann. 1887, 241, 58; Ber. 1887, 20, 581). On oxidation it yields *p*-iodobenzoic acid.

2:3-Di-iodotoluene; from 2-iodo-*m*-toluidine by the diazo-reaction. Colourless plates, m.p. 31°-32° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:4-Di-iodotoluene; by heating 1 part of *o*- or *p*-iodotoluene with 1 part of sulphuric acid (D 185) at 170°. Oil, b.p. 295°-296°. With dilute nitric acid at 200° it yields 2:4-di-iodobenzoic acid (Neumann, Ann. 1887, 241, 51; Ber. 1887, 20, 581).

2:5-Di-iodotoluene; from 5-iodo-*o*-toluidine by the diazo-reaction. Long colourless plates, m.p. 30°-31° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 498).

2:6-Di-iodotoluene; from 2-iodo-6-amino-toluene by the diazo-reaction. Almost colourless needles, m.p. 40°-42° (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1827).

3:5-Di-iodotoluene; from 3:5-di-iodo-*p*-toluidine by the diazo-reaction. Yellow needles, m.p. 44°-45°-5° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:3:4-Tri-iodo-toluene; from 4:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. It melts at 92° (Wheeler, Brantlecht, Hoffman and Scholes, Amer. Chem. J. 1910, 44, 126, 493).

2:3:5-*Tri-iodotoluene*; from 2:5- or 5:6-di-iodo-*m*-toluidine by the diazo-reaction. Pale orange plates, m.p. 72°-73° (Wheeler, etc.).

2:3:6-*Tri-iodotoluene*; m.p. 80.5°, is obtained from 2:6-di-iodo-*m*-toluidine or 3:6-di-iodo-*o*-toluidine by the diazo-reaction (Wheeler, etc.).

2:4:5-*Tri-iodotoluene*; from 4:5-di-iodo-*o*-toluidine, 2:5-di-iodo-*p*-toluidine, and 4:6-di-iodo-*m*-toluidine (Wheeler, etc.); or by heating equal parts of *o*- or *p*-iodotoluene with sulphuric acid (D 1.85) at 170° (Neumann, Ann. 1887, 241, 55). Long brown needles, m.p. 119°-120°, b.p. above 300°.

2:4:6-*Tri-iodotoluene*; from 2:4:6-tri-iodo-*m*-toluidine by the diazo-reaction. Colourless needles, m.p. 105° (Wheeler, etc.).

3:4:5-*Tri-iodotoluene*; from 3:5-di-iodo-*p*-toluidine by the diazo-reaction. Long silky needles, m.p. 122°-123° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2:3:4:5-*Tetraiodotoluene*; from 4:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. Straw-coloured needles, m.p. 284°-285° (Wheeler, etc.).

2:3:4:6-*Tetraiodotoluene*; from 2:4:6-tri-iodo-*m*-toluidine by the diazo-reaction. Long needles, m.p. 170° (Wheeler, etc.).

2:3:5:6-*Tetraiodotoluene*; from 2:5:6-tri-iodo-*m*-toluidine by the diazo-reaction. Colourless needles, m.p. 125° (Wheeler, etc.).

Penta-iodotoluene; from 2:4:5:6-tetraiodo-*m*-toluidine by the diazo-reaction. Small dull yellow needles, m.p. 340° (decomp.) (Wheeler, etc.).

Chloro-o-iodotoluene; from chlorinated *o*-toluidine. B.p. 240°, D₄²⁰ 1.702 (Beilstein and Kuhlberg, Ann. 1870, 156, 82).

o-*Chloriodotoluene* does not solidify at -14°, b.p. 242°, D₁₇¹⁷ 1.716 (Wroblewsky, Ann. 1873, 168, 210).

β-*Chloriodotoluene* solidifies at 10°, b.p. 240°, D_{16.5}^{16.5} 1.770 (Wroblewsky).

2-*Chloro-6-iodotoluene*; from 2-chloro-6-aminotoluene by the diazo-reaction. Colourless liquid, b.p. 132°-133°/25 mm., D₂₀²⁰ 1.844 (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627).

5-*Chloro-4-iodo-3-nitrotoluene*; from 5-chloro-3-nitro-*p*-toluidine. Colourless plates, m.p. 92° (Kenner and Judd, *ibid.* 1920, 117, 776).

m-*Bromo-o-iodotoluene*; by treating *m*-bromo-*o*-diazo-toluene with hydriodic acid (Wroblewsky). Colourless liquid, b.p. 260°, D₁₆¹⁶ 2.139.

2-*Bromo-6-iodotoluene*; from 2-bromo-6-aminotoluene by the diazo-reaction. Colourless liquid, b.p. 135°-140°/15 mm., D₂₀²⁰ 2.044 (Cohen and Miller).

3-*Bromo-4-iodotoluene*; from *m*-bromo-*p*-toluidine by the diazo-reaction. Oil, b.p. 265°, D₁₆¹⁶ 2.044. It yields a *mononitro-derivative*, m.p. 116° (Wroblewsky).

3-*Bromo-2-iodotoluene*; from 6-iodo-*m*-toluidine by the diazo-reaction. B.p. 262°-265°, n_D^{20} 1.6484 (Holleman, Rec. trav. chim. 1912, 31, 267).

The constitution of the product obtained by Hirtz (Ber. 1896, 29, 1406) by brominating *o*-iodotoluene as 4-(1)-*bromo-2-iodotoluene* is doubtful, as the reaction-product is of a very complicated nature (Holleman, *l.c.*).

3:5-*Dibromo-2-iodotoluene*; from 3:5-di-bromo-*o*-toluidine by the diazo-reaction. Needles, m.p. 68°, b.p. 314° (with slight decomp.).

On chlorinating in chloroform solution it yields a *dichloride*, yellow cubic crystals, m.p. 95° (decomp.) (McCrae, Chem. Soc. Trans. 1898, 73, 891).

3:5-*Dibromo-4-iodotoluene*; from 3:5-di-bromo-*p*-toluidine by replacement of the amino-group by iodine (Wroblewsky, Ann. 1873, 168, 190); from 3-bromo-5-nitro-*p*-toluidine by replacement of the amino-group by iodine and of the nitro-group by bromine (Wroblewsky, Ann. 1878, 192, 209). Long needles, m.p. 86°, b.p. 270°. Its *mononitro-derivative* melts at 69°.

3:5-*Dibromo-2:4-di-iodotoluene*; from nitrated bromiodotoluene by replacing the nitro-group by iodine. Prisms, volatile with steam, m.p. 68°. Its *mononitro-derivative* melts at 129° (Wroblewsky, Ann. 1878, 192, 212).

o-*Iodosotoluene*; from *o*-iodotoluene dichloride and dilute sodium hydroxide solution (Willgerodt, Ber. 1893, 26, 361) or water and pyridine (Ortoleva, Gazz. chim. ital. 1900, 30, ii. 5). Almost colourless crystals, m.p. 178° (decomp.), *acetate* m.p. 130°-132° (Ortoleva). 3:5-*Dibromo-2-iodosotoluene*, is obtained from the corresponding dichloride by treatment with soda solution. Yellow amorphous mass decomposing at about 87°. Its *acetate* forms needles, m.p. 66.5° (McCrae, *l.c.*).

m-*Iodosotoluene*; from *m*-iodotoluene dichloride (yellow needles, decomposing at 104°) by the action of water on a solution in pyridine (Ortoleva), or by the action of sodium hydroxide (Willgerodt and Umbach, Ann. 1903, 327, 269). Yellowish-white amorphous powder exploding at 206°-207° (Willgerodt and Umbach) or decomposing at 180°-185° (Ortoleva). The *acetate*, colourless needles, melts at 148°-149° (Ortoleva; Willgerodt and Umbach), the *difluoride*, small colourless needles, melts at 180°, decomposing at 188°, on rapid heating (Weinland and Stille, Ann. 1903, 328, 132).

p-*Iodosotoluene*; by treating *p*-iodotoluene dichloride with dilute sodium hydroxide solution, followed by purification of the crude product with chloroform (Willgerodt, Ber. 1893, 26, 359); or in a manner analogous to that of the *o*-isomeride (Ortoleva, *l.c.*). It decomposes at 175°-178°, and on boiling with water yields a mixture of *p*-iodotoluene and *p*-iodoxytoluene (Willgerodt). On adding hydrofluoric acid slowly to a solution of *p*-iodosotoluene in acetic acid, *p*-toluene-iodo-fluoride, small yellow needles, m.p. 112°, decomposing at 116°, is formed (Weinland and Stille, *l.c.*).

o-*Iodoxytoluene*; by boiling *o*-iodosotoluene with water in presence of air (Willgerodt, Ber. 1893, 26, 361); by oxidising *o*-iodotoluene with Caro's acid (Bamberger and Hill, Ber. 1900, 33, 535). Crystalline mass, exploding at 210°, which when treated with hydrofluoric acid yields *o*-toluene-iodosulfonate, leafy aggregates of granules, commencing to melt at 120° and decomposing at 170°-190° (Weinland and Stille, Ber. 1901, 34, 2631).

m-*Iodoxytoluene*; by treating an intimate mixture of *m*-tolyl iododichloride and a concentrated solution of bleaching powder with a little hydrochloric acid (Willgerodt and Umbach); by oxidising a pyridine solution of *m*-iodotoluene

with chlorine (Ortoleva, Gazz. chim. ital. 1900, 30, ii. 1). White needles, exploding at 220° (Ortoleva, l.c.; cf. Bamberger and Hill). On warming with aqueous hydrogen peroxide it yields *m*-iodotoluene.

p-**Iodotoluene**; in a similar manner to the *o*- and *m*-isomerides. Silky leaflets, exploding at 228° (Willgerodt, Ber. 1896, 29, 1573; Bamberger and Hill, Ber. 1900, 33, 525; Ortoleva, Gazz. chim. ital. 1900, 30, ii. 8). It forms an *iodosulfonate*, lustrous needles, decomposing at 206° (Weinland and Stille, l.c.).

NITROSO- AND NITRO-DERIVATIVES.

2-Nitrosotoluene; by oxidation of *o*-tolylhydroxylamine (Bamberger, Ber. 1895, 28, 249); by the action of nitrogen trioxide or peroxide on a cold chloroform solution of mercury-*o*-ditolyl (Kunz, Ber. 1898, 31, 1530). White needles, melting at 72°–72.5° to a green liquid, extremely volatile with steam. On treatment with cold concentrated sulphuric acid it yields 4-nitroso-2'-3-ditolylhydroxylamine, glistening yellow needles (+H₂O), decomposing about 130°; the anhydrous product melts at 110°–115° (Bamberger, Büsdorf and Sand, Ber. 1898, 31, 1517). 3-Nitro-2-nitrosotoluene, pale yellow leaflets, m.p. 126°–127° (decomp.), is obtained by oxidising 3-nitro-*o*-toluidine with Caro's acid, and is transformed by nitric acid into 2:3-dinitrotoluene (Meisenheimer and Hesse, Ber. 1919, 52, 1161). Its 5-nitro-derivative, almost colourless crystals, m.p. 143°–144°, is formed by the action of Caro's acid on the corresponding amine, and together with dinitroazoxytoluene by treating 2:5-dinitrotoluene with hydroxylamine followed by acidification. It is readily oxidised to 2:5-dinitrotoluene. When the reduction of 2:5-dinitrotoluene by means of hydroxylamine is effected in highly concentrated solution *potassium nitrotoluene-iso-diazotate* is precipitated in yellow needles, decomposing at 202° (Meisenheimer and Hesse, l.c.). Its 6-nitro-derivative, obtained by oxidising an aqueous alcoholic solution of 6-nitro-*o*-tolylhydroxylamine with ferric chloride in presence of sodium acetate, forms colourless needles, melting at 117° to a green liquid (Brand and Zöller, Ber. 1907, 40, 3324).

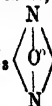
3-Nitrosotoluene is prepared in a similar manner to the *o*-derivative. Small needles, readily volatile with steam, m.p. 53°–53.5° (Bamberger, l.c.). Its 2-nitro-derivative forms yellow leaflets, m.p. 92°–93°, and its 4-nitro-derivative, yellow leaflets, m.p. 141° (Meisenheimer and Hesse, l.c.); its 6-nitro-derivative, m.p. 113°, is obtained by oxidising 6-nitro-*m*-toluidine by means of Caro's acid (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 859).

4-Nitrosotoluene; by oxidation of *p*-tolylhydroxylamine (Bamberger, l.c.; Bamberger and Brady, Ber. 1900, 33, 274); by oxidation of *p*-toluidine by means of potassium permanganate in sulphuric acid solution in presence of formaldehyde (Bamberger and Tschirner, Ber. 1898, 31, 1524); together with other products by the action of nitrogen trioxide or peroxide on a cold chloroform solution of mercury-*p*-ditolyl (Kunz, Ber. 1898, 31, 1528). White needles, extremely volatile with steam, m.p. 49.5°. For the action of hydrogen chloride and hydrogen bromide, see Bamberger, Büsdorf and Szalayki (Ber. 1899,


32, 216). Its 2-nitro-derivative, colourless needles, m.p. 87°, is formed by oxidising 2-nitro-*p*-tolylhydroxylamine (Brand and Zöller); its 3-nitro-derivative is obtained by oxidising *m*-nitro-*p*-toluidine by means of Caro's acid (Bamberger and Hübner, Ber. 1903, 36, 3803), or together with 4-nitro-3-nitroso-toluene and other products by the action of hydroxylamine on 3:4-dinitrotoluene, followed by acidification (Meisenheimer and Hesse), and forms greenish-yellow needles, m.p. 145°–145.5°.

As a result of the work of Green and Rowe (Chem. Soc. Trans. 1912, 101, 2452; 1913, 103, 897), Forster and Fierz (*ibid.* 1907, 91, 1842), and Forster and Barker (*ibid.* 1913, 103, 1918), the compounds originally regarded as '*o*-dinitroso' compounds are shown to be actually *iso*-oxadiazole oxides, furoxans or furazan oxides, and whereas the above constitution has been proved to be correct for the '*o*-dinitroso' compounds, it appears probable that only the '*p*-dinitroso' compounds have the constitution of '*quinone-dioxime peroxides*,' ascribed by Forster and Fierz to the whole class.

Tolu-2:3-iso-oxadiazole oxide, toluofurozan,

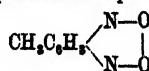
tolufurazon oxide, CH₃C₆H₄  O; from 3-

nitro-2-diazo-toluene-imide by the action of heat. Leaflets, m.p. 60° (Zincke, J. pr. Chem. 1896, [2] 53, 340; Zincke and Schwarz, Ann. 1899, 307, 28). The corresponding *diazime* melts at 140° (decomp.) and the *iso-oxadiazole* or

furazan, CH₃C₆H₄  O, at 44° (Zincke, and

Schwarz). The 4(?)*-nitro-derivative* forms brown crystals, m.p. 162°; the 5-nitro-derivative, yellow plates, m.p. 70°; the 4:6(?)*-dinitro-derivative*, yellow needles, m.p. 122°–123° (Zincke and Drost, Ann. 1900, 313, 299).

Tolu-2:5-quinonedioximeperoxide



by oxidation of 2:5-toluquinonedioxime with alkaline potassium ferricyanide (Nietzki and Guitermann, Ber. 1888, 21, 432; Mehne, *ibid.* 21, 734). Yellow crystals, volatile with steam, m.p. 133° (N. and G.) or 144° with slight detonation (M.). Oxidation with nitric acid yields 2:5-dinitrotoluene, whilst treatment with hydroxylamine regenerates the dioxime. Its 4-chloro-derivative is a lemon-yellow powder, m.p. 163°–165° (Kehrmann, Silva and Keleti, Ber. 1915, 48, 2029).

Tolu-3:4-iso-oxadiazole oxide, m.p. 96°–97°, is formed by heating the corresponding nitro-diazoimide (Zincke, J. pr. Chem. 1896, [2] 53, 340), or by the oxidation of *m*-nitro-*p*-toluidine or *p*-nitro-*m*-toluidine with alkaline sodium hypochlorite (Green and Rowe). The corresponding *diazime*, yellowish-brown needles, melts at 127°–128°, and the *iso-oxadiazole* or *furazan*, long white needles, melts at 37° (Zincke and Schwarz, Ann. 1899, 307, 28); the latter compound is also formed by the oxidation of *m*-nitrosoaceto-*p*-toluidide with alkaline sodium hypochlorite (Green and Rowe, Chem. Soc.

Trans. 1917, 111, 612). The 2 (or 6)-nitro-derivative, obtained by nitrating the furoxan or the imide of *o*-nitro-*p*-toluidine and heating the product of the latter reaction in a brine-bath, forms pale yellow needles, m.p. 164° (decomp.). This nitro-compound, on nitration in presence of sulphuric acid, yields the 2:6-dinitro-derivative, silky yellow needles, m.p. 133° (decomp.). Its 5(?)-nitro-derivative forms yellowish-leaflets, m.p. 145° (Zincke and Drost, Ann. 1900, 313, 299).

NITRO DERIVATIVES.

When toluene is nitrated with nitric acid (D 1.475), the quantity of *o*-, *m*-, or *p*-mononitro-derivative obtained depends on the temperature, solvent, and other factors (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1908, 11, 248; Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; Bruner and Vorbrodt, Anzeiger Akad. Wiss. Cracow, 1909, 221; cf. Kohn, Monatsh. 1910, 31, 745; Fischer, Zeitsch. Elektrochem. 1910, 16, 161; Bell and Spry, J. Ind. Eng. Chem. 1921, 13, 60; Friswell, J. Soc. Chem. Ind. 1908, 27, 258; van der Arend, Verslagen. K. Akad. Wetensch. Amsterdam, 1908, 208; Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 275; Holdermann, Ber. 1906, 39, 1256). When the nitration is carried out at -30°, 0°, 30°, and 60° with nitric acid (D 1.475) the product contains 41.7 p.c., 40.9 p.c., 39.9 p.c., and 38.5 p.c. respectively, of *p*-nitrotoluene, 55.6 p.c., 56 p.c., 56.9 p.c., and 57.5 p.c. respectively, of *o*-nitrotoluene, and 2.7 p.c., 3.1 p.c., 3.2 p.c., and 4.0 p.c. respectively, of *m*-nitrotoluene (Holleman), thus showing that the percentage of *p*-nitrotoluene decreases with rise of temperature, whilst that of the *o*- and *m*-nitrotoluenes increases, the last being always present only in small quantity. When a mixture of pure nitric acid and acetic anhydride is added to toluene at 30° a violent reaction sets in and the product contains 57.7 p.c. *o*-, 4.4 p.c. *m*-, and 37.3 p.c. *p*-nitrotoluene (Holleman, Vermeulen and De Mooy).

Toluene is readily nitrated in the cold with nitric acid of specific gravity not less than 1.5. In the manufacture of nitrotoluene 1 part of toluene is poured into 1½ parts of nitric acid (D 1.5), the temperature not exceeding 15°. By this means the *o*-derivative is readily formed and is isolated by fractionating the oil which is formed when the nitration mixture, after standing for 10 hours, is poured into water. Commercial nitrotoluene usually contains about 60 p.c. *ortho*-, 2 p.c. *meta*-, and 38 p.c. *para*-nitrotoluene; this mixture has a specific gravity of 1.167, and distils between 220°-240°.

o- and *p*-Nitrotoluene may be separated by treating the crude nitrotoluene with sulphonating agents, whereby the *o*-derivative is sulphonated, and the *p*-isomeride remains unchanged (Lange, Eng. Pat. 1407 of 1890), or by fractional reduction by means of sulphides or hydrosulphides, particularly with Le Blanc soda residues (Clayton Aniline Co., Fr. Pat. 255957; D. R. P. 92991 of 1896). *o*-Nitrotoluene may also be separated from its isomerides by heating with salts of arsenious acid, and the *o*-nitrotoluene, which is unaltered by this treatment, is isolated by treatment with acid, steam distillation, &c. (Loesner, D. R. P. 78002 of 1894; J. pr. Chem.

1894, [2] 50, 567). *o*- and *p*-Nitrotoluenes may also be separated by fractional distillation at a pressure of 20 mm. (Molinari, Atti Congr. Nar. Chim. Ind., 1924, 402; Chem. Soc. Abstr. 1925, 128, i. 380).

For the estimation of nitrotoluenes by means of stannous chloride and titanous chloride, see Colver and Prideaux (J. Soc. Chem. Ind. 1917, 36, 480, 856) and Knecht (*ibid.* 1917, 36, 494).

o-Nitrotoluene; by nitration of toluene (Glenard and Boudault, Compt. rend. 1844, 19, 505; Hofmann and Muspratt, Ann. 1845, 53, 221; Kekulé, Zeit. f. Chem. 1867 [2] 3, 225; Rosenstiehl, Ann. Chem. 1872, [4] 27, 433); by elimination of the amino-group from 2-nitro-*p*-toluidine and nitrated *m*-toluidine (Bellstein and Kuhlberg, Ann. 1870, 155, 1; 1871, 188, 348). When freshly distilled *o*-nitrotoluene is cooled rapidly to -20°, it solidifies sometimes to the labile α -modification, m.p. -10.56°, and sometimes to the stable β -form, m.p. -4.14°. The latter may also be prepared by cooling the liquid to -50° or -60°, when the α -form separates first, but changes rapidly into the β -form. Superheating of the vapours during distillation also favours the formation of the latter modification (Ostromisslensky, Zeitsch. physikal. Chem. 1907, 57, 341; cf. Walker and Spencer, Chem. Soc. Trans. 1904, 85, 1109). According to Knoevenagel (Ber. 1907, 40, 508) the α -form melts at -9.4° and the β -form at -3.6° (cf. Streng, Ber. 1891, 24, 1987, and Schneider, Zeitsch. physikal. Chem. 1896, 19, 157). It is possible to purify *o*-nitrotoluene by cooling the crude product to temperatures between -4° and -10°, and removing the liquid portion by means of the centrifuge when about half has crystallised (M. L. B., D. R. P. 158219 of 1903; Fr. Pat. 350200 of 1904).

Pure *o*-nitrotoluene is a clear liquid, solidifying at -10.56° (see above), b.p. 218° (Spreng, Ber. 1891, 24, 1987) or 225.7° (corr.) (Perkin, Chem. Soc. Trans. 1896, 69, 1250) or 220.4°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 624); D_4^{20} 1.1742, D_{15}^{25} 1.1643, D_{28}^{28} 1.1572 (Perkin), D_{15}^{25} 1.168 (Spreng). Refractive index, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218); absorption spectrum, Spreng (Rec. trav. chim. 1897, 16, 1); magnetic rotatory power, Perkin (*l.c.*); dielectric constant, Turner (Zeitsch. physikal. Chem. 1901, 35, 421); n_D^{20} 1.5462, n_D^{25} 1.5271 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1).

When oxidised with nitric acid or chromic acid in the cold it yields *o*-nitro-benzaldehyde (Lauth, Bull. Soc. chim. 1904, (3) 31, 133), whilst treatment with potassium permanganate or long boiling with alkaline potassium ferricyanide yields *o*-nitrobenzoic acid. The extent to which manganese dioxide and sulphuric acid oxidise *o*-nitrotoluene depends upon the concentration of the acid. When heated in an autoclave with 2 parts of finely powdered manganese dioxide and 10 parts of sulphuric acid (D 1.26-1.38) at 140°-165° for 2-3 hours at a pressure not exceeding 10 atmospheres, the product is chiefly *o*-nitrobenzaldehyde, whilst with sulphuric acid (D 1.43-1.71) at 135°-145° *o*-nitrobenzoic acid is the main product (B. A. S. F., D. R. P. 179589 of 1899).

The former product is also formed when the oxidation is effected by means of cerium chloride

and sulphuric acid (60-65 p.c.) at 80°-85° (M. L. B., D. R. P. 174238 of 1903). When oxidised electrolytically *o*-nitrotoluene yields chiefly *o*-nitrobenzyl alcohol (Pierron, Bull. Soc. chim. 1901, [3] 25, 852; Fichter and Bonhöte, Helv. Chim. Acta. 1920, 3, 395). When treated with bromine at 170° *o*-nitrotoluene is converted into 3 : 4-dibromo-2-(or 6)-aminobenzoic acid (Wachendorff, Ann. 1877, 185, 281; Greiff, Ber. 1880, 13, 288), but with bromine in the presence of iron 4-bromo-2-nitrotoluene is formed (Glud, Ber. 1915, 48, 432). It forms a compound with chromyl chloride which on treatment with water regenerates *o*-nitrotoluene and yields a little *o*-nitrobenzaldehyde (Richter, Ber. 1886, 19, 1062). On chlorination it yields *o*-nitrobenzyl chloride, *o*-chlorotoluene, and *o*-chlorobenzyl chloride and other products (Kalle & Co., Eng. Pat. 11260 of 1897; D. R. P. 110010 of 1898).

On long keeping in contact with alcoholic or aqueous potassium hydroxide, anthranilic acid, together with the corresponding azo- and azoxybenzoic acids are formed (Preuss and Binz, Zeit. für angew. Chem. 1900, 14, 385; B. A. S. F., Eng. Pat. 18319 of 1899; Fr. Pat. 292468; D. R. P. 114839 of 1899). With nitrous esters and sodium ethoxide it yields *o*-nitrobenzaldehyde (M. L. B., D. R. P. 107095 of 1898; Fr. Pat. 290643 of 1899). When reduced by heating with iron or zinc and sodium hydroxide at 100°, it yields *o*-azxytoluene, but when acid is added to the product, toluene-*o*-azobenzoic acid is produced. The sulphonation product of *o*-nitrotoluene differs from that of *p*-nitrotoluene in giving no red colour when boiled with alkalis (Reverdin and de la Harpe, Bull. Soc. chim. 1888, [2] 50, 44).

m-Nitrotoluene; in small quantity by nitration of toluene (cf. Holleman and co-workers under *o*-nitrotoluene; Monnet, Reverdin and Nölting, Ber. 1879, 12, 443; Nölting and Witt, Ber. 1885, 18, 1337); from nitrated *o*- or *p*-toluidine (Beilstein and Kuhlberg, Ann. 1878, 158, 335; Vanino, Präparative Chemie, 1923, vol. ii. p. 451); or from 3-nitro-*p*-toluidine (Bachka, Ber. 1889, 22, 829) by the diazo-reaction. M.p. 16°, b.p. 230°-231° (cf. Neuback, Zeitsch. physikal. Chem. 1887, 1, 658), D₄²⁰ 1.168, n_D²⁰ 1.5470, n_D²⁵ 1.5275 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). It is oxidised readily to *m*-nitrobenzoic acid by chromic acid mixture and slowly by alkaline potassium ferricyanide. When oxidised electrolytically it yields chiefly *m*-nitrobenzaldehyde (Pierron, Bull. Soc. chim. 1901, [3] 25, 852) and, in sulphuric acid solution, 5-amino-*o*-cresol (Gattermann, Ber. 1894, 27, 1890). With bromine at 140° it yields *m*-nitrobenzyl bromide and *m*-nitrobenzylidene bromide (Wachendorff, Ann. 1877, 185, 266; Ber. 1876, 9, 1345). Stannous chloride and aqueous hydrochloric acid reduce it to pure *m*-toluidine, while zinc dust and aqueous hydrochloric acid yield chloro-*m*-toluidine also. *m*-Nitrotoluene is readily reduced by the method of Elbs and Kopp (Zeitsch. Elektrochem. 1898, 5, 106), forming *m*-azotoluene in a yield of 91 p.c.; further reduction gives *m*-hydrazotoluene (Rohde, *ibid.* 1899, 5, 232). When *m*-nitrotoluene is nitrated with nitric and sulphuric acids at 50°, 3 : 4-dinitrotoluene, together with smaller amounts at 2 : 3- and 3 : 6-dinitrotoluenes, are formed, the separation of the three isomers being effected

by fractionation in *vacuo* and freezing the distillate (Holleman and Sirks, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 280; Sirks, Rec. trav. chim. 1907, 27, 208; cf. Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 276).

p-Nitrotoluene (see also under *o*-nitrotoluene); by nitration of toluene (Rosenstiehl, Zeitsch. f. Chem. 1869, (2) 5, 190; cf. Jaworsky, *ibid.* 1865, 223); 1 part of toluene is poured into 3-4 parts of nitric acid (D 1.5) and heated to 30°. The yellow oil produced consists chiefly of *p*-nitrotoluene, which crystallises on cooling the fraction boiling above 225°.

Large thick rhombic crystals, m.p. 51.6°-51.9° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 60), 51.4° (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; cf. van der Arend, *ibid.* 1909, 28, 409), or 54° (Schiff, Ann. 1884, 223, 261; Gazz. chim. ital. 1884, 14, 181). The increase in melting-point with increase of pressure has been studied by Pusfin (Chem. Soc. Trans. 1924, 125, 2628). B.p. 237.7°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 624); D₅₅²⁵ 1.1392, D₆₅²⁵ 1.1858 (Perkin, Chem. Soc. Trans. 1896, 69, 1239); magnetic rotatory power at 54.3° 10.17 (Perkin); n_D²¹ 1.5554, n_D^{22.5} 1.5346 (Holleman, Vermeulen and de Mooy). It is much less volatile with steam than the *o*-nitro-derivative. Chlorine in presence of aluminium chloride or iodine yields *p*-nitrobenzyl chloride and *p*-nitrobenzoic acid (Zimmermann and Müller, Ber. 1885, 18, 990). By the electrolysis of *p*-nitrotoluene in 5-10 parts of sulphuric acid, amino-nitro-*o*-benzyltoluene is obtained (Gattermann, Ber. 1893, 26, 1852; cf. Gattermann and Koppert, *ibid.* 2811). When heated with bromine at 140°, it yields *p*-nitrobenzyl bromide and *p*-nitrobenzylidene bromide (Wachendorff, Ann. 1877, 185, 268). It is oxidised by alkaline potassium ferricyanide to *p*-nitrobenzoic acid (Noyes, Ber. 1883, 16, 52), whilst electrolytic oxidation in acetic-sulphuric acid yields *p*-nitrobenzyl alcohol (Elbs, Zeitsch. Elektrochem. 1896, 2, 522), *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid (Fichter and Bonhöte, Helv. Chim. Acta. 1920, 3, 395). It is reduced by iron and dilute hydrochloric acid to *p*-toluidine, whilst zinc dust and dilute hydrochloric acid yield a chlorinated toluidine. Reduction in alkaline solution yields *p*-azotoluene, and in presence of formaldehyde and hydrochloric acid *p*-dimethyl-toluidine and dimethylene-di-toluidine are produced (Löb, Zeitsch. Elektrochem. 1898, 4, 428). It condenses with ethyl oxalate in presence of sodium ethoxide yielding *p*-nitrophenylpyruvic acid (Reissert, Ber. 1897, 30, 1047).

Zinc dust and sodium hydroxide yield azotoluene, m.p. 144°, two azoxy-compounds, m.p. 75° and 70° respectively, and a hydrazo-compound, m.p. 126° (Janowski and Reimann, Ber. 1889, 22, 40). For the action of sodium and caustic alkalis on *p*-nitrotoluene, see Bender and Schultz (Ber. 1886, 19, 3234), Schmidt (*ibid.* 1890, 32, 2911), Klinger (*ibid.* 1893, 16, 941), Fischer and Hepp (*ibid.* 1893, 26, 2332), Green and collaborators (*ibid.* 1897, 30, 3097; 31, 1628; Chem. Soc. Trans. 1904, 35, 1424, 1425; *ibid.* 1907, 31, 2076; *ibid.* 1908, 32, 1273). On heating with a solution of sodium in toluene

in sulphuric acid it is converted into *p*-aminobenzaldehyde (Geigy & Co., D. R. P. 86874 of 1895). When treated with amyl nitrite in presence of sodium ethoxide the oxime of *p*-nitrobenzaldehyde is formed (Angeli and Angelico, Atti R. Accad. Lincei. 1900, [5] 8, ii. 32; Gazz. chim. ital. 1900, 31, i, 27; cf. M. L. B., Fr. Pat. 290643 of 1899; D. R. P. 107095 of 1898). For estimation of *p*-nitrotoluene, see Reverdin and de la Harpe (Zeit. f. analyt. Chem. 1890, 29, 215), and for volumetric estimation of *p*-nitrotoluene in crude nitrotoluene, see Glasmann (Ber. 1903, 36, 4260; J. Russ. Phys. Chem. Soc. 1904, 36, 312).

Normal- ω -nitrotoluene, phenylnitromethane, $C_6H_5CH_2(NO_2)$; together with phthalic anhydride by decomposing a dilute aqueous solution of the disodium derivative of nitrobenzylidene-phthalide with 12 mols. of very dilute acetic acid; by boiling hydroxynitrobenzylidiphenylmaleide with water (Cohn, Ber. 1891, 24, 3867); from toluene and nitric acid (D. 1:12) by heating for 48 hours at 100° in a sealed tube (Konowalow, Ber. 1895, 28, 1861; J. Russ. Phys. Chem. Soc. 1899, 31, 254); from benzyl chloride (Holleman, Rec. trav. chim. 1894, 13, 405) or benzyl iodide (Hantzsch and Schultze, Ber. 1896, 29, 700) and silver nitrite, or preferably mercurous nitrite (Neogi and Adhicary, Zeitsch. anorg. Chem. 1911, 40, 270); together with other products by the interaction of *iso*-nitromethane and diazobenzene in alkaline solution (Bamberger, Schmidt and Levinstein, Ber. 1900, 33, 2053); together with phthalic anhydride by dissolving nitroxylidene-phthalide in sodium hydroxide and saturating the solution with oxalic acid (Goldberg, Ber. 1900, 33, 2818), and by other methods (van Raalte, Rec. trav. chim. 1899, 18, 383).

Liquid, which does not solidify in a freezing mixture, b.p. 225°-227°, decomposing into water, nitric oxide and benzaldehyde, or b.p. 158°-160°/35 mm. with slight decomposition (Holleman); D_4^{20} 1.1756, D_4^{20} 1.1598; molecular refractive power 36.61, n_D^{20} 1.53230.

On treatment with zinc dust and dilute sulphuric acid it yields benzylamine. With fuming hydrochloric acid at 150° it is decomposed into hydroxylamine and benzoic acid (Gabriel and Koppe, Ber. 1886, 19, 1145). With alkalis it is converted into the salt of *iso*-phenylnitromethane, from which phenylnitromethane is obtained by treatment with carbon dioxide, or *iso*-phenylnitromethane by treatment with cold dilute hydrochloric acid. It is unaffected by phenyl *iso*-cyanate (Hantzsch and Schultze, Ber. 1896, 29, 2254). Its *o*-, *m*-, and *p*-nitro-derivatives melt at 72°, 94°, and 90° respectively (Holleman, Rec. trav. chim. 1896, 15, 356, 365; *ibid.* 1895, 14, 123; Hantzsch and Veit, Ber. 1899, 32, 621).

Phenyl- ω -nitromethane, $C_6H_5CH_2NOH$; by the action of dilute hydrochloric acid on the potassium salt of phenylnitromethane (Hantzsch and Schultze, Ber. 1896, 29, 700); together with other products by oxidising benzaldoxime with Caro's acid (Bamberger, Ber. 1900, 33, 1781). It crystallises from a mixture of absolute ether and ligroin and melts at 84° when heated quickly (Hantzsch, Ber. 1896, 29, 2251). It is readily soluble in soda solution, and in contrast

to the indifferent phenylnitromethane, when treated with ammonia in presence of water-free solvents it yields the ammonium salt. It also readily reacts with phenyl *iso*-cyanate and phosphorus pentachloride (Hantzsch and Veit, Ber. 1899, 32, 620). On warming with ether or alcohol, or on keeping with hydrochloric acid, it is converted into the normal phenylnitromethane. On reduction with sodium amalgam or zinc dust in alkaline solution it yields benzaldoxime. When the sodium salt is treated with acetyl chloride acetylbenzhydroxamic acid is formed (van Raalte, *ibid.* 1899, 18, 383). When treated with benzoyl chloride, dibenzhydroxamic acid, m.p. 161°, is produced, and with *p*-nitrobenzoyl chloride it yields bis-*p*-nitrobenzoylbenzhydroxamic acid and *p*-nitrobenzoylbenzhydroxamic acid (Holleman, Rec. trav. chim. 1896, 15, 356, 365), whilst its sodium salt on treatment in aqueous solution with hydrochloric acid yields benzhydroxamic acid (Bamberger and Rust, Ber. 1902, 35, 45).

ω -Dinitrotoluene, phenyldinitromethane, large white prisms, m.p. 79° (Ponizio, Gazz. chim. ital. 1901, 31, 133; 1908, 38, 417; Ponizio and Charrier, Atti R. Accad. Sci. Torino, 1908, 43, 475).

DINITROTOLUENES.

Commercial dinitrotoluene is chiefly a mixture of the α -, β -, and γ -dinitrotoluenes, and forms a cake of yellow crystals, m.p. 66°-68°, b.p. about 300° (partial decomp.). The 2:4-dinitro-compound is present in the greatest proportion in the dinitrotoluene used in the explosive industry.

2:3-Dinitrotoluene; by heating 2:3-dinitro-*p*-toluic acid with 5 p.c. hydrochloric acid for 6 hours at 265° (Rozanski, Ber. 1889, 22, 2681); from 3-nitro-*o*-toluidine by replacing the amino-group by a nitro-group (Grell, Ber. 1895, 28, 2565). It is best obtained by nitrating aceto-*o*-toluidide with nitric acid in presence of acetic acid and treating the mixture of 3- and 5-nitro-aceto-*o*-toluidides with hydrochloric acid, the separation of the isomeric amines being accomplished by diluting the acid solution largely with water when the very feebly basic 3-nitro-*o*-toluidine is precipitated. The latter is converted into 3-nitro-2-nitrosotoluene, which is then transformed into 2:3-dinitrotoluene (Meisenheimer and Hesse, Ber. 1919, 52, 1161); also from 5:6-dinitro-*m*-toluidine by the diazo-reaction (Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 531). M.p. 61° (M. and H.) or 63° (Rozanski).

(a) 2:4-Dinitrotoluene; by nitration of toluene (Deville, Ann. 1842, 44, 307; Cahours, Compt. rend. 1847, 24, 555; Noelling and Witt, Ber. 1885, 18, 1336; Beilstein and Kuhlberg, Ann. 1870, 153, 13; Limpriecht, Ber. 1885, 18, 1402), and of *o*- and *p*-nitrotoluene; by boiling 2:4-toluylenediamine with sodium peroxide solution (O. Fischer and Trout, Ber. 1893, 26, 3085); from dinitrotoluidine by elimination of the amino-group (Staedel, Ann. 1898, 259, 220). Long monoclinic needles, m.p. 70.5° (Deville), or 69.21°-69.57° (Mills, Phil. Mag. 1882, [5] 14, 27), or 69.9°-70.2° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 160). When treated for a long time with fuming nitric acid it yields 2:4-dinitrobenzoic acid. Partial reduction with ammonium sulphide in the cold yields 2-nitro-*p*-toluidine, whilst

at higher temperatures 4-nitro-*o*-toluidine is also formed (Graeff, Ann. 1885, 229, 343; Limpricht, Ber. 1885, 18, 1400). Alcoholic stannous chloride, on the other hand, yields 4-nitro-*o*-toluidine (Anschütz and Heussler, Ber. 1886, 19, 2161). When reduced completely it yields *m*-toluylenediamine (Baeyer, Ber. 1874, 7, 1638). On electrolytic oxidation it yields 2:4-dinitrobenzoic acid (Sachs and Kempf, Ber. 1902, 35, 2704). It does not react with chromium oxychloride (Richter, Ber. 1886, 19, 1062). It condenses with benzaldehyde in presence of piperidine to form stilbene derivatives (Thiele and Escalas, Ber. 1901, 34, 2842); with dimethylaminobenzaldehyde to form 2':4'-dinitro-4-dimethylaminostilbene (Sachs and Steinert, Ber. 1904, 37, 1733); with nitrosodimethylaniline in presence of sodium carbonate to form 2:4-dinitrobenzaldehyde-*p*-dimethylaminoanil (Sachs and Kempf, *ibid.* 1902, 35, 1224).

(*B*) 2:5-Dinitrotoluene; from 5-nitro-*o*-toluidine by the diazo-reaction (Grell, Ber. 1895, 28, 2565); by the action of nitrogen peroxide on toluquinonediaxime in ethereal solution (Oliveri and Tortorel, Gazz. chim. ital. 1900, 30, i, 534); by treating '*p*-dinitrosotoluene' with cold fuming nitric acid (Nietzki and Guitermann, Ber. 1888, 21, 433); readily from 5-nitro-2-nitrosotoluene by oxidation with nitric acid (Meisenheimer and Hesse, Ber. 1919, 52, 1161); by heating 2:5-dinitro-*p*-toluic acid with 3 parts of 5 p.c. hydrochloric acid for 6 hours at 250° (Rozanski, Ber. 1889, 22, 2679). It appears to occur also among the products of the nitration of toluene (Limpricht, Ber. 1885, 18, 1402).

Needles or large wedge-shaped crystals, m.p. 50°-51° (Meisenheimer and Hesse), 52°-5° (Rozanski) or 48° (Nietzki and Guitermann). It is reduced by alcoholic ammonium sulphide to 6-nitro-*m*-toluidine (Limpricht). On reduction with stannous chloride in presence of alcoholic hydrochloric acid it yields a mixture (m.p. 97°) of monoamines, consisting of 62 p.c. of 5-nitro-*o*-toluidine and 38 p.c. of 6-nitro-*m*-toluidine, a little 2:5-diaminotoluene being formed also (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1053).

2:6-Dinitrotoluene; from 2:6-dinitro-*p*-toluidine by the diazo-reaction (Staedel, Ann. 1883, 217, 206; Rosenstiehl, Ann. Chim. 1872, [4] 27, 470; Cunerth, Ann. 1874, 172, 222; Claus and Becker, Ber. 1883, 16, 1597; Holleman and Boeseken, Rec. trav. chim. 1897, 16, 427); together with other products during the manufacture of trinitrotoluene (Molinari and Giua, Zeit. ges. Schiess. Sprengstoffw. 1914, 9, 239; cf. Haeussermann and Grell, Ber. 1894, 27, 2209). Glistening needles, m.p. 60°-61° (Staedel), or 65°-6° (H. and G.). On reduction with sulphuretted hydrogen in alcoholic ammonia a mixture, m.p. 68°, of 6-nitro-2-amino-*m*-cresol and 6-nitro-*o*-toluidine is formed, the former being produced by the action of the boiling hydrochloric acid (used to extract the amine) on the intermediate 6-nitro-*o*-tolylhydroxylamine (Cohen and Marshall, Chem. Soc. Trans. 1904, 85, 527). It condenses with dimethylaminobenzaldehyde to form a condensation product, bluish-violet needles (Sachs and Steinert, Ber. 1904, 37, 1745).

(*γ*) 3:4-Dinitrotoluene; together with 2:3-, 2:5-, and 3:6-dinitrotoluene by nitration of

m-nitrotoluene, and is readily separated from the mixture by fractional distillation *in vacuo* and freezing the distillate (Beilstein and Kuhlberg, Ann. 1870, 155, 25; Haeussermann and Grell, Ber. 1894, 27, 2209; Holleman and Sirks, Proc. K. Akad. Wetensch. Amsterdam, 1906, 9, 280; Sirks, Rec. trav. chim. 1907, 27, 208); from 3:4- or 4:5-dinitro-*o*-toluidine by elimination of the amino-group (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1139); from 5:6-dinitro-*m*-toluidine in a similar manner (Brady, Day and Rolt, *ibid.* 1922, 121, 531); from 3-nitro-*p*-toluidine by the diazo-reaction (Haeussermann and Grell, *l.c.*); conveniently by oxidising 3-nitro-*p*-toluidine by Caro's acid to 3-nitro-4-nitrosotoluene and completing the oxidation of the latter with nitric acid (Meisenheimer and Hesse, Ber. 1919, 52, 1161). Long needles, m.p. 50°-60° (M. and H.), or 61° (H. and G.). On reduction with stannous chloride in presence of absolute alcoholic hydrochloric acid, it yields a eutectic mixture (m.p. 40°) of 4-nitro-*m*-toluidine and 3-nitro-*p*-toluidine together with a little diamine (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1053).

3:5-Dinitrotoluene; from 3:5-dinitro-*o*- or *p*-toluidine by elimination of the amino-group (Staedel, Ann. 1883, 217, 189; Ber. 1881, 14, 909; Hübner, Ann. 1884, 222, 74; Neville and Winther, Ber. 1882, 15, 2984; Chem. Soc. Trans. 1882, 41, 416; Hönig, Ber. 1887, 20, 2418; Cohen and McCandlish, Chem. Soc. Trans. 1905, 87, 1270; Brady, Day and Rolt, *ibid.* 1922, 121, 528). It is best prepared by adding aceto-*p*-toluidide slowly to 8 times its weight of nitric acid (D. 1.79) below 0°, purifying the dinitro-derivative by extracting with hot benzene, hydrolysing with concentrated sulphuric acid (below 90°), diazotising the resulting base at -10° in concentrated sulphuric acid in presence of alcohol, warming and purifying the dinitrotoluene by extraction with alcohol (Kreman, Hönigsberg and Mauermann, Monatsh. 1923, 44, 65). Monoclinic needles or prisms readily volatile with steam, m.p. 92°-93°.

TRINITROTOLUENE.

The following method gives satisfactory results for the preparation of trinitrotoluene from toluene of about 99 p.c. purity. 50 grms. of toluene are added gradually with constant stirring to a mixture of 73.4 grms. of nitric acid (D. 1.42), and 146.8 grms. of sulphuric acid (D. 1.84), the temperature not being allowed to rise above 30°. The reaction is allowed to continue for half an hour after the addition of the toluene, and, after keeping, the spent acid is drawn off. The crude product (80-83 grms., consisting of about 60 p.c. of mono- and 40 p.c. of dinitrotoluene) is dissolved in 109.2 grms. of sulphuric acid (D. 1.84), the solution is heated to 50°, and a mixture of 54.6 grms. each of nitric acid (D. 1.5) and sulphuric acid (D. 1.84) is added gradually during a period of at least 1 hour, the temperature not exceeding 100°. The mixture is then heated for 2 hours at 90°-100°, after which it is cooled to 90°, and 145.6 grms. of oleum (15 p.c.) are added slowly followed by a mixture of 72.8 grms. each of oleum (15 p.c.) and nitric acid (D. 1.5). The addition of the acid takes 2 hours, and the temperature is not allowed

to exceed 115°. The mixture is then heated at 90°–117° for 2 hours. After keeping for at least 8 hours, the spent acid is drawn off, and the crude trinitrotoluene crushed and washed first with cold water and then several times in the molten state with hot water. A yield of 75 p.c. is obtained and the product melts at 78°–80°, a further yield of 8.5 p.c. (m.p. 69°–75°) can be recovered from the spent acid. If the product be purified by crystallising from, or washed with, a mixture of 9 volumes of 95 p.c. alcohol and 1 volume of benzene the yield is 69 p.c. (m.p. 79°–81°) and 7.5 p.c. (m.p. 78°–81°) (Hoffman, U.S. Bureau of Mines, Met. and Chem. Eng. 1916, 14, 467; cf. Humphrey, J. Ind. Eng. Chem. 1916, 8, 998; Langenscheidt, Z. ges., Schiess. u. Sprengstoffw. 1912, 7, 425). For the manufacture of TNT (trinitrotoluene) and its intermediate products, see Technical Methods of Explosives Supply, 1915–1918, No. 2, Ministry of Munitions and Department of Scientific and Industrial Research. An account of the minimum amount of water required to precipitate trinitrotoluene from its acid mother liquor is given by McHutchison and Wright (J. Soc. Chem. Ind. 1915, 34, 781).

For freezing-point solubility diagram of TNT and picric acid, see Taylor and Rinkenbach (J. Ind. Eng. Chem. 1923, 15, 795).

The specific heats of trinitrotoluene, tetryl and picric acid have been determined by Taylor and Rinkenbach (J. Amer. Chem. Soc. 1924, 46, 1504).

For quantitative experiments on the trinitration of toluene, see Gibson, Duckham and Fairbairn (Chem. Soc. Trans. 1922, 121, 282).

A review of the preparation of the six isomeric trinitrotoluenes up to date is given by Brunswick (Zeitsch. angew. Chem. 1923, 36, 75).

(a) 2:4:6-Trinitrotoluene; by prolonged boiling of toluene with nitric and sulphuric acids (Wilbrand, Ann. 1863, 128, 178) or from α - or β -dinitrotoluene in a similar manner; by treating 1 part of 2:4-dinitrotoluene dissolved in 4 parts of sulphuric acid (95–96 p.c. H_2SO_4) with $\frac{1}{2}$ parts of nitric acid (90–92 p.c. HNO_3), the mixture being heated gradually to 90°–95° with agitation for about 4–5 hours (Haeussermann, Zeitsch. angew. Chem. 1891, 5, 661); by boiling trinitrophenylacetic acid with water or alcohol (Jackson and Phinney, Ber. 1895, 28, 3067; Amer. Chem. J. 1899, 21, 431).

Pseudo-rhombic crystals, belonging to the prismatic class of the monoclinic system (Artini, Atti R. Accad. Lincei, 1915, [v.] 24, ii. 274; cf. Friedländer, Zeitsch. Kryst. Min. 1879, 3, 168), m.p. 80.52° (Mills, Phil. Mag. 1882, [5] 14, 27), 80.5° (Brunswick, Zeitsch. angew. Chem. 1923, 36, 75), 80.6° (Will, Ber. 1914, 47, 704), or 80.8°–80.85° (Rintoul, J. Soc. Chem. Ind. 1915, 34, 60). Electrical conductivity in liquid ammonia (Franklin and Kraus, Amer. Chem. J. 1900, 23, 294); cryoscopic behaviour (Bruni and Berti, Atti R. Accad. Lincei. 1900, [v.] 9, i. 274; Gazz. chim. ital. 1900, 30, 76); behaviour with methyl alcohol, &c. (Hantzsch and Kissel, Ber. 1899, 32, 3140); solubility in organic solvents (Taylor and Rinkenbach, J. Amer. Chem. Soc. 1923, 45, 44). It forms additive compounds with hydrocarbons and with aniline (Hepp, Ann. 1882, 215, 365). On reduction with alcoholic ammonium sulphide it yields 2:6-dinitro-*p*-

toluidine (Tiemann, Ber. 1869, 3, 218), whilst in hydrochloric acid solution in presence of cupric chloride it is reduced at a copper cathode to 2:6-dinitro-*p*-toluidine and 4:6-dinitro-*o*-toluidine (Brand and Eisenmenger, J. pr. Chem. 1913, ii. 87, 487). On oxidation with nitric acid at 180° it yields 1:3:5-trinitrobenzene with evolution of carbon dioxide (Claus and Becker, Ber. 1883, 16, 1597). With acetone and ammonia it gives a deep red coloration, and is not so sensitive to alkalis as the β - and γ -compounds. In alkaline alcoholic solutions it forms coloured salts which, under the simultaneous action of oxidising agents, yield a hexanitrodiphenylethane (m.p. 212°) (Will, *loc. cit.*; Giua, Atti R. Accad. Lincei. 1914, [v.] 23, ii. 484; Gazz. chim. ital. 1915, 45, 345). When exposed to light 2:4:6-trinitrotoluene forms two substances of the formula $C_7H_5O_6N_3$ (Schultz and Ganguly, Ber. 1925, 58, 702; see also Wichert and Donat, Zeitsch. ges. Schiess-Sprengstoffw. 1925, 20, 69).

2:4:6-Trinitrotoluene condenses with diazomethane (Heinke, Ber. 1898, 31, 1399); with nitrosodimethylamine to form the compound $C_6H_4(NO_2)_2 \cdot CH \cdot N \cdot C_6H_4 \cdot N(CH_3)_2$ (Sachs and Everding, Ber. 1903, 36, 959); it combines with dimethylaminobenzaldehyde (Sachs and Steinert, *ibid.* 1904, 37, 1733); and with α - and β -naphthylamine it yields compounds which melt at 113.5° and 141.5° respectively (Sudborough, Chem. Soc. Trans. 1901, 79, 522).

(b) 2:3:4-Trinitrotoluene; together with 3:4:6-trinitrotoluene by nitration of *m*-nitrotoluene (Hepp, Ann. 1882, 215, 366); by nitration of 2:3-dinitrotoluene, and to the extent of 17 parts together with 83 parts of 3:4:6-trinitrotoluene by the nitration of 3:4-dinitrotoluene (Brady; see also Gibson, Duckham and Fairbairn, Chem. Soc. Trans. 1922, 121, 282); by oxidation of 2:3-dinitro-*p*-toluidine in 80 p.c. sulphuric acid with Caro's acid, followed by treatment of the nitroso-derivative with nitric acid (Scott and Robinson, Chem. Soc. Trans. 1922, 121, 846); from 3:4-dinitro-*o*-toluidine in a similar manner (Brady and Williams, *ibid.* 1920, 117, 1140). Slender leaflets or flaky needles from alcohol or thick trimetric plates from acetone, m.p. 112°. On oxidation with chromic acid mixture it yields 2:3:4-trinitrobenzoic acid, m.p. 202° (Giua; Hepp; Brunswick). With acetone and ammonia it yields a greenish-yellow coloration (Will; Giua).

2:3:4-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution yields 4-nitro-1-hydroxy-5 (or 7)-methyl-1:2:3-benzotriazole, pale yellow hexagonal prisms + H_2O , m.p. 205° (decomp.) when anhydrous. On methylation this forms exclusively the *O*-ether, brownish-yellow needles, m.p. 152°, and on acetylation an acetyl-derivative, colourless monoclinic prisms, m.p. 182° (decomp.), is formed (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 894; Brady and Day, *ibid.* 1923, 123, 2258). Converted by aqueous sodium sulphite into sodium 2:4-dinitrotoluene 3-sulphonate (Brady, Hewatson and Klein, Chem. Soc. Trans. 1924, 125, 2400).

(c) 3:4:6-Trinitrotoluene; (see above); in a yield of 80 p.c. by adding a solution of 2 grms. of 4:5-dinitro-*o*-toluidine in 10 c.c. of 80 p.c.

sulphuric acid to Caro's acid, prepared from 10 grms. of ammonium persulphate and 7 c.c. of concentrated sulphuric acid, and pouring on to 20 grms. of crushed ice. On keeping over night and on further dilution the dinitro-nitrosotoluene separates and is oxidised by warming with 10 times its weight of nitric acid (D 1.5) (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1139); from 2:5-dinitro-*p*-toluidine in a similar manner (Scott and Robinson, *ibid.* 1922, 121, 845). Yellowish rhombohedral crystals from alcohol or rhombic plates from acetone, m.p. 104°. With alcoholic ammonia it yields 4:6-dinitro-*m*-toluidine, and with aniline, phenyl-dinitrotoluidine. With aqueous sodium sulphite it yields sodium 4:6-dinitrotoluene 3-sulphonate (Brady, Hewetson and Klein, *l.c.*). On oxidation with chromic acid mixture it yields 3:4:6-trinitrobenzoic acid, laminae, m.p. 190°–191° (decomp.) (Hepp; Giua). For the action of alkalis, aldehydes, and amines on α -, β -, and γ -trinitrotoluenes, see O'Riordan (Proc. Roy. Irish Acad. 1918, 34, 175). β - and γ -Trinitrotoluene react even with 1 p.c. sodium carbonate solution or lead oxide and alcohol with the formation of dinitrotoloxides. In all three cases the salts are very explosive. With acetone and ammonia it yields a blue coloration (Will, Ber. 1914, 47, 704; Giua, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 484; Gazz. chim. ital. 1915, 5, 345).

3:4:6-Trinitrotoluene when treated in boiling alcoholic solution with an excess of hydrazine hydrate yields 6-nitro-1-hydroxy-5-ethyl-1:2:3-benzotriazole, yellow prisms, m.p. 194° (decomp.). The latter compound on methylation yields a mixture of the O-methyl ether, long, pale canary-yellow needles, m.p. 35°, and the N-methyl ether, canary-yellow aethery tufts, m.p. 265° (decomp.), and on acetylation an acetyl derivative, faintly pink monoclinic needles, m.p. 166° (decomp.), is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; cf. Brady and Bowman, *ibid.* 1921, 119, 894).

(ξ) 2:3:5-Trinitrotoluene; from 3:5-dinitro-*o*-toluidine. Large, slightly yellow prisms, belonging to the bi-pyramidal class of the rhombic system. It melts at 97° (Brunswig, *Zeitsch. angew. Chem.* 1923, 36, 75). It dissolves in acetone containing a few drops of ammonia giving a rose-red coloured solution, which changes to red, then brown, and finally black. With chromic acid it yields 2:3:5-trinitrobenzoic acid, m.p. 82° (+2H₂O) or 171° (anhydrous) (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, i. 888). With aqueous sodium sulphite it yields sodium 3:5-dinitrotoluene 2-sulphonate (Brady, Hewetson and Klein, *l.c.*).

2:3:5-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution forms 6-nitro-1-hydroxy-4-methyl-1:2:3-benzotriazole, pale yellow prisms, m.p. 225° (decomp.). The latter on methylation yields a mixture of the O-ether, needles, m.p. 137°, and the N-ether, yellow needles, m.p. 220° (decomp.), and on acetylation an acetyl-derivative, almost colourless cubic crystals, m.p. 142°, is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; Brady and Bowman, *ibid.* 1921, 119, 894).

(ϵ) 2:3:6-Trinitrotoluene; by direct nitra-

tion of toluene (Drew, Chem. Soc. Trans. 1920, 117, 1615); together with 2:3:4- and 3:4:6-trinitrotoluene by nitration of *m*-nitrotoluene (Marqueyrol, Koehler and Jovinet, Bull. Soc. chim. 1920, [v.] 27, 420; Drew, *l.c.*; Brady, Chem. Soc. Trans. 1922, 121, 328); in a yield of 15 p.c. together with other products by nitration of 2:3- and 2:5-dinitrotoluene (Drew); from 2:4:6-trinitrotoluene by reduction, bromination, elimination of the amino-group, and replacement of the bromine atom by an amino-group, followed by conversion of the 2:6-dinitro-*m*-toluidine into 2:3:6-trinitrotoluene via the diazo-nitrate (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339); from 3:6- or 5:6-dinitro-*o*-toluidine by treatment with Caro's acid and oxidation of the dinitro-nitroso-toluene produced (Brady and Taylor, Chem. Soc. Trans. 1920, 117, 876); from 2:6-dinitro-*m*-cresol (Drew).

Molinari and Giua (Zeitsch. ges. Schiess-Sprengstoffw. 1914, 9, 239) obtained in the manufacture of trinitrotoluene a compound, m.p. 79.5°, which they stated might be 2:3:6-trinitrotoluene, together with 3- and 4-nitrotoluene, 2:4-, 2:5-, 2:6:3:4-dinitrotoluenes, and 2:4:6-trinitrotoluene. Brady and Taylor, however, showed that this compound was probably a mixture of 2:3:4- and 3:4:6-trinitrotoluenes.

The formation of 2:3:6-trinitrotoluene by the direct nitration of toluene has been questioned by Giua (Gazz. chim. ital. 1921, 51, ii. 113), but Drew's contention that 2:3:4-, 2:4:5-, and 2:3:6-trinitrotoluene are formed by the nitration of *m*-nitrotoluene is further supported by Brady (*l.c.*).

Shining white needles belonging to the prismatic class of the monoclinic system, m.p. 111°. By treatment with alcoholic ammonia in a sealed tube at 110°–120° it yields 3:6-dinitro-*o*-toluidine, m.p. 151°, and a complex mixture of substances, m.p. 128°. It yields 2:3:6-trinitrobenzoic acid, m.p. 55° (+2H₂O) or 160° (anhydrous), on oxidation with chromic acid (Körner and Contardi; cf. Brunswig, *l.c.*).

(δ) 3:4:5-Trinitrotoluene; from 3:5-dinitro-*p*-toluidine. Greenish-yellow transparent prisms or plates, belonging to the prismatic class of the monoclinic system, m.p. 137.5°. With chromic acid it yields 3:4:5-trinitrobenzoic acid (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 464; 1915, [v.] 24, i. 888; cf. Brunswig, *Zeitsch. angew. Chem.* 1923, 36, 75). With aqueous sodium sulphite it forms sodium 3:5-dinitrotoluene 4-sulphonate (Brady, Hewetson and Klein, Chem. Soc. Trans. 1924, 125, 2400).

3:4:5-Trinitrotoluene when boiled with hydrazine hydrate in alcoholic solution yields 4-nitro-1-hydroxy-6-methyl-1:2:3-benzotriazole, yellow needles, m.p. 241° (decomp.), the monohydrate of which, deep orange prisms, loses water at 90°–95°. The triazole on methylation yields exclusively the O-ether, yellow plates, m.p. 183°, and on acetylation an acetyl-derivative, colourless prismatic crystals, m.p. 210° (decomp.), is formed (Brady and Day, Chem. Soc. Trans. 1923, 123, 2258; cf. Brady and Bowman, *ibid.* 1921, 119, 894).

Up to the present, the formation of higher nitro-derivatives by the nitration of toluene has

failed, for if the reaction is promoted by heat or pressure either trinitrobenzoic acid or even tetranitromethane is obtained, whilst 3:5-dinitrotoluene could not be nitrated to yield any trinitro-derivative (Will, Ber. 1914, 47, 704).

o-Nitrobenzyl chloride; together with the *p*-isomeride by nitration of benzyl chloride (Noelting, Ber. 1884, 17, 385; Kumpf, Ann. 1884, 224, 100; Ber. 1884, 17, 1073; cf. Beilstein and Geitner, Ann. 1866, 139, 337); from *o*-nitrobenzyl alcohol and phosphorus pentachloride (Geigy and Königs, Ber. 1885, 18, 2401; Gabriel and Borgmann, Ber. 1883, 16, 2066); by the action of chlorine on a mixture of *o*-nitrotoluene and sulphur at 130°-140° (Haeussermann and Beck, Ber. 1892, 25, 2445). Calcespar-like crystals, m.p. 47.9°; n_D^{20} 1.5557 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). With potassium iodide it yields *o*-nitrobenzyl iodide. With stannous chloride and hydrochloric acid it is reduced to *o*-benzylamine (Lellmann and Stickel, Ber. 1886, 19, 1904; Thiele and Weil, Ber. 1895, 28, 1650), whilst on reduction with stannous chloride in presence of alcoholic hydrochloric acid *o*-amino-benzyl ethyl ether is obtained. By reduction with excess of stannous chloride in aqueous or ethereal solution in presence of hydrogen chloride, followed by treatment with hydrogen sulphide, *o*-diaminobenzyl sulphide is produced (Thiele and Dimroth, Ann. 1899, 305, 112, 122; Ber. 1895, 28, 914). With aluminium chloride in presence of benzene it yields *o*-nitrodiphenylmethane and other products (Freund, Monatsh. 1896, 17, 395). When reduced with sodium in methyl alcoholic solution *o*-nitrobenzyl chloride yields *o*-nitrobenzyl methyl ether (Thiele and Dimroth).

m-Nitrobenzyl chloride; from *m*-nitrobenzyl alcohol and phosphorus pentachloride (Gabriel and Borgmann, Ber. 1883, 16, 2064); together with *o*- and *p*-nitrobenzyl chloride by treating benzyl chloride in the cold with nitric acid (D 1.5) (Abelli, Gazz. chim. ital. 1883, 13, 98; Kumpf, l.c.). Yellow needles, volatile with steam, m.p. 44.8°, n_D^{20} 1.5577 (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1). When treated with sodium sulphite it yields the sodium salt of *m*-nitrobenzyl sulphonic acid (Purgotti and Monti, Gazz. chim. ital. 1900, 30, ii, 246).

p-Nitrobenzyl chloride; by nitration of benzyl chloride (Beilstein and Geitner, Ann. 1866, 139, 337; Strakosch, Ber. 1873, 6, 1056); by the action of 1 mol. of chlorine on *p*-nitrotoluene at 185°-190° (Wachendorff, Ann. 1877, 185, 271). Needles, m.p. 72.4°, n_D^{20} 1.5647 (Holleman, Vermeulen and de Mooy, l.c.). Chlorine at 180°-190° is without any action. It is oxidised by alkaline pyrogallol to *p*-nitrotoluene (Pellizzari, Gazz. chim. ital. 1884, 14, 481). For its reduction with stannous chloride under various conditions, see Thiele and Dimroth (l.c.); Roser, (Ann. 1887, 238, 364). With zinc and hydrochloric acid it is reduced to *p*-toluidine (Rudolph, D. R. P. 34234 of 1885). With sodium acetoxime in warm alcohol it yields *p*:*p*-dinitrostilbene (Schröter and Peschkes, Ber. 1900, 33, 1981). It forms colouring matters with primary, secondary, and tertiary amines, as well as with phenols in the presence of oxidising agents

(Greiff, D. R. P. 15120 of 1881; Lembach and Schleicher, D. R. P. 14945 of 1880).

2:4:6-Trinitrobenzyl chloride; m.p. 85° (Ganguly, Ber. 1925, 59, 708).

2:3:4-Trichloro-6-nitro-benzyl chloride.

Needles, m.p. 122° (Ganguly, l.c.).

o-Nitrobenzylidene chloride; in a yield of 23.3 p.c. by nitration of benzylidene chloride. M.p. 25.7° (Holleman, Vermeulen and de Mooy, Rec. trav. chim. 1914, 33, 1; cf. Kliegel, Ber. 1907, 40, 4937).

m-Nitrobenzylidene chloride; m.p. 64.5°. Yield 33.8 p.c. (Holleman, &c.).

p-Nitrobenzylidene chloride; m.p. 42.8°. Yield 42.9 p.c. (Holleman, &c.).

CHLORONITROTOLUENES.

The nitration of *o*-chlorotoluene leads to the formation of all the possible chloromononitro-derivatives, 2:3, 2:4, 2:5, and 2:6, although the 2:4-isomeride is difficult to detect. Using 10 grms. of *o*-chlorotoluene and nitrating with 40 grms. of nitric acid (D 1.52) at 0°, the percentage yields of the products in the above order are 19.2, 17.0, 43.3, and 20.5 respectively. In the case of *m*-chlorotoluene the 3:6, 3:5, 3:4, and 3:2-chloromononitrotoluenes are obtained in a yield of 58.9 p.c., very little, 32.3 p.c. and 8.8 p.c. respectively (Holleman and Wibaut, Proc. K. Akad. Wetensch. Amsterdam, 1912, 15, 594). The nitration of *o*-chlorotoluene with nitric and sulphuric acids primarily at 8°-10°, and finally at the temperature of the water-bath, leads to the formation of four isomeric dinitro-derivatives in the following proportions: 2-chloro-3:5-dinitrotoluene, 55-60 p.c.; 2-chloro-5:6-dinitrotoluene, 18-20 p.c.; 2-chloro-4:5-dinitrotoluene, 18-20 p.c.; 2-chloro-4:6-dinitrotoluene, 1-2 p.c. (Morgan and Drew, Chem. Soc. Trans. 1921, 117, 793).

2-Chloro-3-nitrotoluene; from 3-nitro-*o*-toluidine by the diazo-reaction (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151; cf. Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1127). M.p. 21° (Holleman, Rec. trav. chim. 1908, 27, 455), n_D^{20} 1.5327 (Wibaut, *ibid.* 1913, 32, 244).

2-Chloro-4-nitrotoluene; from *p*-nitrotoluene and phosphorus pentachloride (Lellmann, Ber. 1884, 17, 534) or antimony pentachloride (Wachendorff, Ann. 1877, 185, 273); in a yield of 95 p.c. by chlorination of *p*-nitrotoluene at 65°-75° in presence of antimony trichloride (Davies, Chem. Soc. Trans. 1921, 119, 868; 1922, 121, 809); from 4-nitro-*o*-toluidine (Green and Lawson, *ibid.* 1891, 59, 1017), or 6-chloro-4-nitro-*m*-toluidine (Morgan and Drew, *ibid.* 1920, 117, 789), or 2-chloro-4-nitro-*m*-toluidine (Morgan and Glover, *ibid.* 1921, 119, 1704) by the diazo-reaction. Long white pointed needles, m.p. 68° (Green and Lawson), or m.p. 62.3°, n_D^{20} 1.5470 (Wibaut, Rec. trav. chim. 1913, 32, 244), b.p. 257°-260°/756 mm. (Davies, l.c.). Volatile with steam and develops an intense red coloration with hot alcoholic sodium hydroxide.

2-Chloro-5-nitrotoluene; by nitration of *o*-chlorotoluene; from 5-nitro-*o*-toluidine (Goldschmidt and Hönig, Ber. 1886, 19, 2439; 1897, 30, 199), or 2-chloro-5-nitro-*p*-toluidine (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1334); together with 4-chloro-7-nitroindazole from

6-chloro-3-nitro-*o*-toluidine (Morgan and Drew, *ibid.* 1920, 117, 787) by the diazo-reaction. Yellowish pyramids, m.p. 44°, b.p. 248°/711 mm. (G. and H.), or m.p. 42-9°, n_D^{20} 1.5511 (Wibaut, *Rec. trav. chim.* 1913, 32, 244).

2-Chloro-6-nitrotoluene; from 6-nitro-*o*-toluidine (Green and Lawson, *l.c.*; Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 787) by the diazo-reaction; by the reduction of 2:6-dinitrotoluene by means of hydrogen sulphide in ammoniacal solution followed by the diazo-reaction (Wibaut, *Rec. trav. chim.* 1913, 32, 244); together with considerable amounts of 4-chloro-2-nitrotoluene by chlorination of *o*-nitrotoluene (Cohn, *Monatsh.* 1901, 22, 471; cf. Janson, D. R. P. 107505 of 1898). Needles, m.p. 35-3°, n_D^{20} 1.5377 (Wibaut), or m.p. 37° (Green and Lawson), b.p. 236°-238° (Janson). Readily volatile with steam. On reduction with zinc dust and sodium hydroxide it yields 6-chloro-*o*-toluidine, *o*-*o*-dichloroazotoluene, and *o*-*o*-dichlorotolidine (Cl:CH₂:NH₂=2:3:4) (Cohn, *l.c.*; cf. Akt. Ges. f. Anilfabr., D. R. P. 82140 of 1894).

3-Chloro-2-nitrotoluene; by chlorination of 6-nitro-*aceto-o*-toluidine in glacial acetic acid, followed by hydrolysis and elimination of the amino-group (Cohen and Hodsman, *Chem. Soc. Trans.* 1907, 91, 974). M.p. 23-4° (Holleman and Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 594), n_D^{20} 1.5204 (Wibaut, *Rec. trav. chim.* 1913, 32, 244). It may also exist in a metastable form. It is oxidised to 3-chloro-2-nitrobenzoic acid (Brand and Zöller, *Ber.* 1907, 40, 3324).

3-Chloro-4-nitrotoluene; from 5-chloro-4-nitro-*o*-toluidine. M.p. 24-2°, n_D^{20} 1.5428 (Wibaut, *l.c.*).

3-Chloro-5-nitrotoluene; from 5-nitro-*m*-toluidine by the diazo-reaction (Hönig, *Ber.* 1887, 20, 2419). Yellow needles, volatile with steam, m.p. 55° (Hönig), m.p. 58-4°, n_D^{20} 1.5404 (Wibaut, *Rec. trav. chim.* 1913, 32, 244), m.p. 61° (Wynne and Greeves, *Chem. Soc. Proc.* 1895, 11, 151).

3-Chloro-6-nitrotoluene; from 6-nitro-*m*-toluidine (Cohen and Hodsman, *Chem. Soc. Trans.* 1907, 91, 975) or 2-nitro-5-chloro-*p*-toluidine (Brand and Zöller, *l.c.*). It appears to exist in a stable form, m.p. 24-9°, and a metastable form, m.p. 24-2°, n_D^{20} 1.5495 (Wibaut, *l.c.*).

4-Chloro-2-nitrotoluene; together with the 4:3-isomeride by nitration of *p*-chlorotoluene (Engelbrecht, *Ber.* 1874, 7, 797; Goldschmidt and Hönig, *ibid.* 1886, 19, 2440; cf. Wroblewsky, *Ann.* 1873, 168, 203); from 2-nitro-*p*-toluidine by the diazo-reaction (Beilstein and Kuhlberg, *Ann.* 1871, 158, 336; Green and Lawson, *Chem. Soc. Trans.* 1891, 59, 1019). Long needles, m.p. 38°, b.p. 239°-240°/718 mm., readily volatile with steam. On reduction it yields *p*-chloro-*o*-toluidine (Goldschmidt and Hönig).

4-Chloro-3-nitrotoluene; together with the 4:2-isomeride by nitrating *p*-chlorotoluene (see under 4-chloro-2-nitrotoluene); from 3-nitro-*p*-toluidine by the diazo-reaction (Gattermann and Kaiser, *Ber.* 1885, 18, 2800). Oil which solidifies in a freezing mixture, m.p. 7°, b.p. 260°/745 mm., n_D^{20} 1.297 (Gattermann and Kaiser).

2-Chloro-3:4-dinitrotoluene; from 3:4-di-

nitro-*o*-toluidine by the Sandmeyer reaction. Colourless needles, m.p. 89°. With warm aqueous sodium hydroxide the following colour-changes occur; yellow, yellowish-brown, brownish-red; with alcoholic sodium hydroxide, pale green, dark green, greenish-blue, brownish-black, and after heating and keeping for 2 hours, pale red; with alcoholic ammonia, faint yellow (Morgan and Glover, *Chem. Soc. Trans.* 1921, 119, 1703).

2-Chloro-3:5-dinitrotoluene; from 3:5-dinitro-*o*-toluidine by the diazo-reaction (Körner and Contardi, *Atti R. Accad. Lincei*, 1915, [v.] 24, i. 888; Rabaut, *Bull. Soc. chim.* 1895, [3] 13, 634; *Compt. rend.* 1895, 120, 1123); together with other products by nitration of *o*-chlorotoluene (Nietzki and Rehe, *Ber.* 1893, 25, 3005; Borsche and Fiedler, *ibid.* 1911, 45, 270; Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 784); best prepared by heating 2-chloro-3-nitrotoluene or 2-chloro-5-nitrotoluene with a mixture of equal parts of sulphuric and fuming nitric acids for 2 hours on the water-bath (Borsche and Fiedler, *l.c.*). Stout yellow rhombs, or large prisms; m.p. 63°-64-5° (Borsche and Fiedler). With anhydrous liquid ammonia it yields an intense violet to bluish-violet colour (red by transmitted light) changing to greenish-black; with alcoholic ammonia a greenish to azure-blue colour changing to red; with alcoholic sodium hydroxide a pale yellow colour changing through greenish-blue to intense rose-red and on heating to bright orange-red (Morgan and Drew).

2-Chloro-4:5-dinitrotoluene; from 4:5-dinitro-*o*-toluidine by the Sandmeyer reaction (Morgan and Glover, *Chem. Soc. Trans.* 1921, 119, 1703); in 85 p.c. yield together with upwards of 4 p.c. of 2-chloro-4:6-dinitrotoluene by nitration of 2-chloro-4-nitrotoluene (Morgan and Challenor, *ibid.* 1921, 119, 1539); in 18-20 p.c. yield by direct nitration of *o*-chlorotoluene (Morgan and Drew, *ibid.* 1920, 117, 786, 792). Colourless hexagonal leaflets or prismatic needles, m.p. 88-5°. It yields a transparent orange-red colour with anhydrous liquid ammonia which changes to bluish- and brownish-black, a transparent orange-red coloration with alcoholic ammonia, and with alcoholic sodium hydroxide a pale yellow colour which changes through emerald-green to brownish-red (Morgan and Drew).

2-Chloro-4:6-dinitrotoluene; in a yield of about 1-2 p.c. by nitration of *o*-chlorotoluene; in a yield of 12 p.c. by nitration of 2-chloro-4-nitrotoluene (Morgan and Drew, *Chem. Soc. Trans.* 1920, 117, 786, 792); in small yield, together with 2-chloro-5:6-dinitrotoluene by nitration of 2-chloro-6-nitrotoluene (Morgan and Jones, *ibid.* 1921, 119, 187). Colourless rectangular prisms or prismatic needles, m.p. 49°. With anhydrous liquid ammonia it yields an intense violet coloration which changes to bluish-violet, magenta, and finally deep crimson; with alcoholic ammonia a bright red which changes to bluish-green, intense azure blue (red by transmitted light) to deep crimson, and with alcoholic sodium hydroxide an intense blue changing to greenish-blue and finally to black, and on heating to reddish-black and finally to transparent deep orange-red (Morgan and Drew).

2-Chloro-5:6-dinitrotoluene; as the chief product, together with a small amount of 2-chloro-4:6-dinitrotoluene, by the gradual addition of 2-chloro-6-nitrotoluene to a mixture of nitric acid (D 1.42) and sulphuric acid at 20°, the temperature being raised subsequently to 70° for 1 hour (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 187; cf. Janson, D. R. P. 107505 of 1898; Cohn, Monatsh. 1901, 22, 475; Morgan and Drew, Chem. Soc. Trans. 1920, 117, 787). Colourless needles or prisms, m.p. 106.5°. With anhydrous liquid ammonia it yields a transparent yellow colour which changes to orange-red, with alcoholic ammonia a transparent yellow colour, and with alcoholic sodium hydroxide a faint transparent yellow colour which on heating changes from orange to deep orange-red, fading to transparent brownish-yellow and finally to light orange (Morgan and Drew).

3-Chloro-2:4-dinitrotoluene; by the action of cupric chloride on 2:4-dinitro-*m*-tolyl-hydrazine. Long silky pale yellow needles, m.p. 92° (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 897). These authors consider that the compound, m.p. 73°, obtained by Borsche and Fiedler (Ber. 1913, 46, 2117) is identical with 3-chloro-2:6-dinitrotoluene.

3-Chloro-2:6-dinitrotoluene; large, almost colourless prisms, m.p. 75° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339; cf. Borsche and Fiedler, *l.c.*).

3-Chloro-4:6-dinitrotoluene; from 6-nitro-*m*-toluidine by replacement of the amino-group by chlorine, followed by nitration with fuming nitric acid and sulphuric acid; or by nitration of *m*-chlorotoluene (Reverdin and Crépieux, Ber. 1900, 33, 2506; Bull. Soc. chim. 1900, (3) 23, 838). Pale yellow needles, or shining leaflets, volatile with steam, m.p. 91°. When reduced with an alcoholic solution of ammonium sulphite it yields a chloronitrotoluidine (3:4:6- or 3:6:4-), yellow leaflets, m.p. 120°, acetyl derivative, m.p. 262° (Reverdin and Crépieux; cf. Borsche and Fiedler, Ber. 1913, 46, 2117). On nitration it yields 3-chloro-2:4:6-trinitrotoluene.

4-Chloro-2:3-dinitrotoluene; by nitration of *p*-chlorotoluene with nitric acid (D 1.4). Small yellow needles, m.p. 76° (Goldschmidt and Hönig, Ber. 1898, 19, 2439; Hönig, *ibid.* 1887, 20, 2420).

4-Chloro-2:5-dinitrotoluene; by oxidation of 4-chloro-2:5-dinitroetoluene with warm concentrated nitric acid. Short amber-yellow prisms, m.p. 107° (Kahrmann, Silva and Keleti, Ber. 1915, 48, 3021).

4-Chloro-2:6-dinitrotoluene; by nitration of 4-chloro-2-nitrotoluene with mixed acid. Long white needles, m.p. 101° (Hönig, Ber. 1887, 20, 2420).

4-Chloro-3:5-dinitrotoluene; by nitration of 4-chloro-3-nitrotoluene (Hönig, Ber. 1887, 20, 2420; Borsche and Fiedler, Ber. 1912, 45, 130; 1913, 46, 2117); in small quantity by the action of toluene *p*-sulphonyl chloride on 3:5-dinitro-*p*-cresol in presence of diethylaniline (Borsche and Fiedler). In preparing the compound by the first method, a substance, m.p. 108°, probably 4-chloro-2:5-dinitrotoluene, is formed simultaneously. 4-Chloro-3:5-dinitrotoluene is prepared also from the corresponding dinitrotoluenediazonium nitrate by the

action of cuprous or cupric chloride (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 22, ii. 464). Colourless needles, m.p. 118°-119° (Borsche and Fiedler), or stout yellow rhombic prisms, m.p. 114.5° (Körner and Contardi). Hönig gave the melting point as 48°.

3-Chloro-2:4:6-trinitrotoluene; by nitration of 3-chloro-4:6-dinitrotoluene at 150°-175°, or of 3-chlorotoluene with sulphuric acid (D 1.94) and nitric acid (D 1.51) (Reverdin, Drosel and Delétra, Bull. Soc. chim. 1904, [3] 31, 631); by condensation of trinitro-*m*-cresol with toluene *p*-sulphonyl chloride in presence of diethylaniline (Ullmann and Nádaí, Ber. 1908, 41, 1870). Long colourless needles or spangles, m.p. 148.5°.

2:3-Dichloro-4-nitrotoluene; by the action of cold fuming nitric acid on 2:3-dichlorotoluene. Fine needles, m.p. 50.5°-51.5° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1128; 1902, 81, 1327, 1347; cf. Seelig, Ann. 1887, 237, 163).

2:3-Dichloro-5-nitrotoluene; from 3-chloro-5-nitro-*o*-toluidine by the diazo-reaction (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151). Pale yellow needles, m.p. 83°.

2:4-Dichloro-5-nitrotoluene; by nitration of 2:4-dichlorotoluene with cold fuming nitric acid. Needles, m.p. 54°-55° (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1129; 1902, 81, 1334, 1348; cf. Seelig, *l.c.*).

2:5-Dichloro-3-nitrotoluene; from 5-chloro-3-nitro-*o*-toluidine by the diazo-reaction. Long slender needles, volatile with steam, m.p. 54°-55° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

2:5-Dichloro-4-nitrotoluene; by nitration of 2:5-dichlorotoluene (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1130; 1902, 81, 1347); from 6-chloro-4-nitro-*m*-toluidine by the diazo-reaction (Morgan and Drew, *ibid.* 1920, 117, 789). Fine needles, m.p. 50°-51° (C. and D.).

2:5-Dichloro-6-nitrotoluene, m.p. 68°-70°, from 5-chloro-6-nitro-*o*-toluidine by the diazo-reaction (Cohen and Hodsman, *ibid.* 1907, 91, 975).

2:6-Dichloro-3-nitrotoluene; m.p. 52°-53°, by nitrating 2:6-dichlorotoluene in the cold with fuming nitric acid (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1346).

2:6-Dichloro-4-nitrotoluene; together with other products in a yield of more than 30 p.c. by the monochlorination of 2-chloro-4-nitrotoluene in the presence of antimony trichloride or ferric chloride. Thick colourless faintly odorous blunt needles, m.p. 65°, b.p. 278°-279°/760 mm. It is very stable towards potassium permanganate solution (Davies, Chem. Soc. Trans. 1922, 121, 810).

3:4-Dichloro-5-nitrotoluene; from 3-chloro-5-nitro-*p*-toluidine by the diazo-reaction. Pale yellow needles, volatile with steam, m.p. 49°-50°. On further nitration it yields a dinitro-derivative, m.p. 80°-81° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1338, 1349).

3:4-Dichloro-6-nitrotoluene; by nitration of 3:4-dichlorotoluene. Fine long needles, m.p. 63°-64° (Cohen and Dakin, *ibid.* 1901, 79, 1133; 1902, 81, 1349).

3:5-Dichloro-2-nitrotoluene; by nitration of 3:5-dichlorotoluene. Needles, m.p. 62° (Cohen and Dakin, *ibid.* 1901, 79, 1134; 1902, 81, 1349).

A *dichloro-2-nitrotoluene*, m.p. 14°, b.p. 274°, d_4^{20} 1.458, is obtained from dichlorotoluene and fuming nitric acid as described by Wroblewsky (Ann. 1873, 163, 212).

The following dichlorodinitro-derivatives are obtained by nitrating the corresponding dichlorotoluenes (Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1111; 1902, 81, 1224, 1344; Cohen and Rodman, *ibid.* 1907, 91, 975; Davies, *ibid.* 1922, 121, 812; Seelig, Ann. 1887, 237, 129).

2:3-Dichloro-4:6-dinitrotoluene; m.p. 71°-72° (C. and D.).

2:4-Dichloro-3:5-dinitrotoluene; prisma, m.p. 103°-104° (C. and D.; S.).

2:5-Dichloro-4:6-dinitrotoluene; m.p. 100°-101° (C. and D.; C. and H.).

2:6-Dichloro-3:4-dinitrotoluene; by nitrating 2:6-dichloro-4-nitrotoluene with nitric acid (D 1.5) and concentrated sulphuric acid at the temperature of the water-bath for 1 hour. Long colourless needles, m.p. 130°-131° (D).

2:6-Dichloro-3:5-dinitrotoluene; colourless needles, m.p. 121° (C. and D.); also prepared from 2:6-dichloro-3-nitro-*p*-toluidine by eliminating the amino-group followed by nitration (D).

3:4-Dichloro-2:6-dinitrotoluene; long, almost colourless needles, m.p. 91.5°-92.5° (C. and D.).

3:5-Dichloro-2:6-dinitrotoluene, long white needles, m.p. 99°-100° (C. and D.).

3:5-Dichloro-2:4:6-trinitrotoluene; by heating ethyldichlorotrinitrophenyl acetate in a sealed tube with concentrated hydrochloric acid at 150°-160°. Long flat white prisms, m.p. 200°-201° (Jackson and Smith, Amer. Chem. J. 1904, 32, 168).

2:6-Dichloro-3:4:5-trinitrotoluene; by prolonged nitration of 2:6-dichloro-3:5-dinitrotoluene with a mixture of nitric acid (D 1.5) and fuming sulphuric acid (20 p.c. SO_3) at 155°-160°. Small colourless needles, m.p. 160°-161° (Davies, Chem. Soc. Trans. 1922, 121, 812).

The following trichloronitrotoluenes have been obtained by nitrating the corresponding dichlorotoluenes (Seelig, Ann. 1887, 237, 140; Cohen and Dakin, Chem. Soc. Trans. 1902, 1224, 1344).

2:3:4-Trichloronitrotoluene; white needles, m.p. 60°-61° (S.).

2:3:5-Trichloronitrotoluene; felted needles, m.p. 58°-59° (C. and D.).

2:3:6-Trichloronitrotoluene; long needles, m.p. 57°-58° (C. and D.).

2:4:5-Trichloronitrotoluene; needles or prisms, m.p. 91°-92° (S.) (cf. Beilstein and Kuhlberg, Ann. 1869, 162, 240; Schultz, Ann. 1871, 277).

2:4:6-Trichloro-3-nitrotoluene; m.p. 54° (Seelig) (C. and D.).

2:5:6-Trichloro-3-nitrotoluene; prisma, m.p. 81°-82° (C. and D.).

The following tetrachlorodinitrotoluenes have been obtained by nitrating the corresponding dichlorotoluenes (Seelig, Ann. 1887, 237, 140; Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1224, 1344).

2:3:4:6-Tetrachloro-5-nitrotoluene; small needles, m.p. 141°-142° (C. and D.).

2:3:5:6-Tetrachloro-4-nitrotoluene; small needles, m.p. 140°-142° (C. and D.).

2:3:5-Trichloro-4:6-dinitrotoluene; prisma, m.p. 140°-142° (C. and D.).

2:4:5-Trichloro-3:6-dinitrotoluene; small needles, m.p. 227° (S.).

2:4:6-Trichloro-3:5-dinitrotoluene; m.p. 178°-180° (C. and D.).

3:4:5-Trichloro-2:6-dinitrotoluene, prismatic needles, m.p. 163°-164° (C. and D.).

The following tetrachloronitrotoluenes have been obtained in a similar manner (Cohen and Dakin, *ibid.* 1904, 85, 1274; 1906, 89, 1483).

2:3:4:5-Tetrachloro-6-nitrotoluene; m.p. 159°.

2:3:4:6-Tetrachloro-5-nitrotoluene; m.p. 131°-134° (not pure).

2:3:5:6-Tetrachloro-4-nitrotoluene; small hexagonal plates, m.p. 150°-152°.

2-Bromo-4-nitrotoluene, by elimination of the amino-group from 6-bromo-4-nitro-*m*-toluidine (Neville and Winther, Chem. Soc. Trans. 1881, 39, 85; Ber. 1881, 14, 418); by heating *p*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 171); by the action of hydrobromic acid on *p*-nitrotoluene-*o*-diazopiperidine (Wallach, Ann. 1886, 235, 248). Needles, m.p. 77.5° (S.) or 74°-75° (N. and W.).

2-Bromo-5-nitrotoluene; from 5-nitro-*o*-toluidine (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429); by heating *m*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 180); from 2-bromo-5-nitro-*p*-toluidine or 6-bromo-3-nitro-*o*-toluidine by the diazo-reaction (Blaskowa, Chem. Weekblad. 1912, 9, 968). It melts at 78° (S.).

2-Bromo-6-nitrotoluene; from 6-nitro-*o*-toluidine (Friedländer, Bruckner and Deutsch, Ann. 1912, 388, 23; Nötting, Ber. 1904, 37, 1015). Yellowish-white needles, m.p. 41° (N.) or 36° (F. B. and D.).

3-Bromo-2-nitrotoluene; from 2-nitro-3-bromo-*m*-toluidine by the diazo-reaction. Liquid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 430; Ber. 1880, 13, 1945).

3-Bromo-5-nitrotoluene; from 3-bromo-5-nitro-*p*-toluidine, 5-bromo-3-nitro-*o*-toluidine, or 3-bromo-5-nitro-*o*-toluidine by the diazo-reaction. Prisma, m.p. 81.4°-81.6° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429; Ber. 1880, 13, 564) or m.p. 86°, b.p. 267°-270° (Wroblewsky, Ann. 1878, 192, 203).

4-Bromo-2-nitrotoluene; from 2:4-dinitrotoluene by replacing the *p*-nitro-group by bromine (Beilstein and Kuhlberg, Ann. 1871, 158, 340); together with 4-bromo-3-nitrotoluene by nitrating *p*-bromotoluene (Wroblewsky, Ann. 1873, 168, 176); by the action of bromine on *o*-nitrotoluene in presence of iron (Glad, Rep. 1915, 48, 433). Slender yellowish needles or large monoclinic tables, m.p. 45.4° (Blaskowa and Rose, Ber. 1873, 6, 699), m.p. 43°, b.p. 257°-257° (Wroblewsky), d_4^{20} 1.3759 (Blaskowa, Rec. trav. chim. 1915, 34, 263). Its reaction with sulphuric acid on electrolysis yields chloro-*o*-amino-3-ene (Gattermann, Ber. 1904, 37, 1921).

4-Bromo-3-nitrotoluene; together with 4-bromo-2-nitrotoluene by nitrating *p*-bromotoluene (Wroblewsky, Ann. 1873, 168, 176).

(D 152) cooled in ice a mixture of 4-bromo-2-nitrotoluene and 4-bromo-3-nitrotoluene, in the relative proportions of 56.3 : 43.7, is obtained. Analysis by decomposition with sodium methoxide showed the mixture to contain 41.5 p.c. of the 3:4-isomeride, whilst calculation from theoretical considerations gave the relative proportions as 2:4/3 = 52.4 : 47.6 (Holleman, *Rec. trav. chim.* 1915, 34, 283); from 3-nitro-*p*-toluidine by the diazo-reaction (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 442; *Ber.* 1880, 13, 972); by treating *m*-nitrotoluene with bromine in presence of ferrous bromide (Scheufelen, *Ann.* 1885, 231, 180). M.p. 33°. n_D^{20} 1.5682 (Holleman; cf. Hübner and Rods), b.p. 255°-256°, D_4^{20} 1.631 (Wroblewsky). By the electrolysis of its solution in sulphuric acid, 4-bromo-5-amino-2-cresol is obtained (Gatterman, *Ber.* 1893, 27, 1931).

2-Bromo-3:5-dinitrotoluene; slender white prisms or large prisms, m.p. 86.2° (Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v.] 25, ii. 339; *Blanksma, Rec. trav. chim.* 1901, 20, 425).

3-Bromo-4:6-dinitrotoluene; by nitrating *m*-bromotoluene or *m*-bromomononitrotoluene with fuming nitric acid (Grete, *Ann.* 1873, 168, 258; *Ber.* 1875, 8, 567; Bentley and Warren, *Amer. Chem. J.* 1890, 12, 1); by the decomposition of ethyl bromodinitrophenylmalonate (Jackson and Robinson, *Amer. Chem. J.* 1889, 11, 541). Long pale yellow prisms or needles, m.p. 103°-104° (G.).

4-Bromo-3:5-dinitrotoluene; from 3:5-dinitro-*p*-toluidine by the diazo-reaction; by nitration of 4-bromo-3-nitrotoluene with nitric acid (D 152). Yellow prisms, m.p. 118.4° (Jackson and Ittner, *Amer. Chem. J.* 1897, 19, 7, 199, 205; Körner and Contardi, *Atti R. Accad. Lincei*, 1914, [v.] 23, ii. 464).

3-Bromo-2:4:6-trinitrotoluene; by boiling 10 grms. of 3-bromo-4:6-dinitrotoluene with 20 c.c. of a mixture of 1 vol. of concentrated sulphuric acid and 2 vols. of concentrated nitric acid (Bentley and Warren, *Amer. Chem. J.* 1890, 12, 4); from 3-bromo-2:6-dinitro-*p*-toluidine (Körner and Contardi, *Atti R. Accad. Lincei*, 1916, [v.] 25, ii. 339). Small needles, m.p. 143°. With alcoholic ammonia it yields 2:4:6-trinitro-*m*-toluidine.

2:3-Dibromo-4- (or 6) nitrotoluene; by nitrating 2:3-dibromotoluene. Needles, m.p. 56.5°-57.5° (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 434; *Ber.* 1881, 14, 419) or 59° (Wroblewsky, *Ann.* 1873, 168, 184).

2:3-Dibromo-5-nitrotoluene; from 3-bromo-5-nitro-*o*-toluidine by the diazo-reaction. It melts at 105.4° (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 429; *Ber.* 1880, 13, 965; Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 512).

2:4-Dibromo-5-nitrotoluene; by nitration of 2:4-dibromotoluene (Davis, *Chem. Soc. Trans.* 1902, 81, 872; cf. Neville and Winther, *l.c.*); from 2-bromo-5-nitro-*p*-toluidine by the diazo-reaction. Colourless needles; m.p. 85° (Blanksma, *Chem. Weekblad.* 1912, 9, 968) or 81°-82° (Davis).

2:4-Dibromo-6-nitrotoluene (?); by nitrating dibromotoluene derived from dibromo-*m*-toluidine (m.p. 75°). It melts at 80°-81° (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 441; *Ber.* 1881, 39, 86; *Ber.* 1881, 14, 419).

2:5-Dibromo-3-nitrotoluene; from 5-bromo-3-nitro-*o*-toluidine by the diazo-reaction. It melts at 69.5°-70.2° (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 448; *Ber.* 1881, 39, 86; *Ber.* 1880, 13, 974; *Ber.* 1881, 14, 419).

2:5-Dibromo-4-nitrotoluene; by nitrating 2:5-dibromotoluene; from 6-bromo-4-nitro-*m*-toluidine by the diazo-reaction (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 445; *Ber.* 1881, 39, 86); together with other products by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids (Claus, *J. pr. Chem.* 1888, [2] 37, 18). Needles, m.p. 87°-89° (N. and W.), 89° (C.).

2:6-Dibromo-3-nitrotoluene; by nitration of 2:6-dibromotoluene with nitric acid (D 145) the 3-nitro-compound is formed and not the 4-nitro-derivative as stated by Neville and Winther; from 6-bromo-3-nitro-*o*-toluidine. Pale yellow crystals, m.p. 50° (Blanksma, *l.c.*, cf. Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 502).

2:6-Dibromo-4-nitrotoluene; from *p*-nitrotoluene by the action of bromine in presence of ferrous bromide (Scheufelen, *Ann.* 1885, 231, 178); from 2:6-dibromo-4-nitro-*m*-toluidine (Neville and Winther). Needles, m.p. 57°-58° (S.) or 56.8°-57° (N. and W.).

3:4-Dibromo-5-nitrotoluene; from 3-bromo-5-nitro-*p*-toluidine. Leaflets, m.p. 62°-63.6° (Neville and Winther, *l.c.*) or 63°-65° (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 510).

3:4-Dibromo-6-nitrotoluene; by nitration of 3:4-dibromotoluene (Wroblewsky, *Ann.* 1873, 168, 184; Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 429; *Ber.* 1881, 39, 86; *Ber.* 1881, 14, 417); from 5-bromo-2-nitro-*p*-toluidine (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 515). Needles, m.p. 86.5°-87.5° (Neville and Winther) or 83.5°-84.5° (Cohen and Dutt).

3:5-Dibromonitrotoluene; by nitration of 3:5-dibromotoluene. Prisms, m.p. 124° (Wroblewsky, *Ann.* 1873, 168, 189).

3:5-Dibromo-2-nitrotoluene; obtained together with a *by-product* of higher melting-point by the diazotisation of 3:5-dibromo-2-nitro-*p*-toluidine. It melts at 67°, and on nitration with nitric acid (D 152) it yields a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene, but in presence of sulphuric acid 3:5-dibromo-2:4:6-trinitrotoluene is obtained (Blanksma, *Chem. Weekblad.* 1909, 6, 728).

3:5-Dibromo-4-nitrotoluene; obtained together with a *compound*, m.p. about 250°, from 3:5-dibromo-4-nitro-*o*-toluidine by the diazo-reaction. Colourless crystals, m.p. 84° (Blanksma, *l.c.*).

2:4-Dibromo-3:5-dinitrotoluene; by nitration of 2:4-dibromotoluene or 2:4-dibromo-5-nitrotoluene. Light yellow prisms, m.p. 127.5° (Davis, *Chem. Soc. Trans.* 1902, 81, 873) or 130° (Blanksma, *Chem. Weekblad.* 1912, 9, 968).

2:5-Dibromo-4:6-dinitrotoluene; by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids. Small acicular needles, or large yellow prisms, m.p. 142°. It sublimes readily in leaflets (Claus, *J. pr. Chem.* 1888, [2] 37, 16).

2:6-Dibromodinitrotoluene; by nitration of 2:6-dibromotoluene. It melts at 161.6°-162.2°

(Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 448; *Ber.* 1881, 39, 86; *Ber.* 1880, 13, 974; *Ber.* 1881, 14, 419).
2:5-Dibromo-4-nitrotoluene; by nitrating 2:5-dibromotoluene; from 6-bromo-4-nitro-*m*-toluidine by the diazo-reaction (Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 445; *Ber.* 1881, 39, 86); together with other products by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids (Claus, *J. pr. Chem.* 1888, [2] 37, 18). Needles, m.p. 87°-89° (N. and W.), 89° (C.).
2:6-Dibromo-3-nitrotoluene; by nitration of 2:6-dibromotoluene with nitric acid (D 145) the 3-nitro-compound is formed and not the 4-nitro-derivative as stated by Neville and Winther; from 6-bromo-3-nitro-*o*-toluidine. Pale yellow crystals, m.p. 50° (Blanksma, *l.c.*, cf. Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 502).
2:6-Dibromo-4-nitrotoluene; from *p*-nitrotoluene by the action of bromine in presence of ferrous bromide (Scheufelen, *Ann.* 1885, 231, 178); from 2:6-dibromo-4-nitro-*m*-toluidine (Neville and Winther). Needles, m.p. 57°-58° (S.) or 56.8°-57° (N. and W.).
3:4-Dibromo-5-nitrotoluene; from 3-bromo-5-nitro-*p*-toluidine. Leaflets, m.p. 62°-63.6° (Neville and Winther, *l.c.*) or 63°-65° (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 510).
3:4-Dibromo-6-nitrotoluene; by nitration of 3:4-dibromotoluene (Wroblewsky, *Ann.* 1873, 168, 184; Neville and Winther, *Chem. Soc. Trans.* 1880, 37, 429; *Ber.* 1881, 39, 86; *Ber.* 1881, 14, 417); from 5-bromo-2-nitro-*p*-toluidine (Cohen and Dutt, *Chem. Soc. Trans.* 1914, 105, 515). Needles, m.p. 86.5°-87.5° (Neville and Winther) or 83.5°-84.5° (Cohen and Dutt).
3:5-Dibromonitrotoluene; by nitration of 3:5-dibromotoluene. Prisms, m.p. 124° (Wroblewsky, *Ann.* 1873, 168, 189).
3:5-Dibromo-2-nitrotoluene; obtained together with a *by-product* of higher melting-point by the diazotisation of 3:5-dibromo-2-nitro-*p*-toluidine. It melts at 67°, and on nitration with nitric acid (D 152) it yields a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene, but in presence of sulphuric acid 3:5-dibromo-2:4:6-trinitrotoluene is obtained (Blanksma, *Chem. Weekblad.* 1909, 6, 728).
3:5-Dibromo-4-nitrotoluene; obtained together with a *compound*, m.p. about 250°, from 3:5-dibromo-4-nitro-*o*-toluidine by the diazo-reaction. Colourless crystals, m.p. 84° (Blanksma, *l.c.*).
2:4-Dibromo-3:5-dinitrotoluene; by nitration of 2:4-dibromotoluene or 2:4-dibromo-5-nitrotoluene. Light yellow prisms, m.p. 127.5° (Davis, *Chem. Soc. Trans.* 1902, 81, 873) or 130° (Blanksma, *Chem. Weekblad.* 1912, 9, 968).
2:5-Dibromo-4:6-dinitrotoluene; by treating dibromo-*p*-cymene with a mixture of nitric and sulphuric acids. Small acicular needles, or large yellow prisms, m.p. 142°. It sublimes readily in leaflets (Claus, *J. pr. Chem.* 1888, [2] 37, 16).
2:6-Dibromodinitrotoluene; by nitration of 2:6-dibromotoluene. It melts at 161.6°-162.2°

(Neville and Winther, Chem. Soc. Trans. 1880, 37, 437; Ber. 1880, 13, 967).

2:6-Dibromo-3:5-dinitrotoluene; by nitration of 2:6-dibromo-3-nitrotoluene. Colourless crystals, m.p. 161° (Blanksma, l.c.).

3:5-Dibromo-2:4-dinitrotoluene; when 3:5-dibromotoluene is added slowly to four times its weight of nitric acid (D 1.52) and the mixture is warmed for 10 minutes at 100°, 3:5-dibromo-2:4-dinitrotoluene, needles, m.p. 157°, is obtained, together with a product, cubes, m.p. 106°-108°, which appears to be a mixture of the above substance with the 2:6-isomeride (Blanksma, Rec. trav. chim. 1904, 23, 125; cf. Neville and Winther, l.c.); also prepared by nitration of 3:5-dibromo-4-nitrotoluene and, together with the 2:6-isomeride, by nitration of 3:5-dibromo-2-nitrotoluene (Blanksma, Chem. Weekblad, 1909, 6, 728).

3:5-Dibromo-2:6-dinitrotoluene; (see above); from 3:5-dibromo-2:6-dinitro-*p*-toluidine. White needles or flat plates, m.p. 120° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339) or 117° (Blanksma, l.c.).

3:5-Dibromo-2:4:6-trinitrotoluene; by nitration of 3:5-dibromotoluene in presence of sulphuric acid (Blanksma, Rec. trav. chim. 1904, 23, 125); by nitration of 3:5-dibromo-4-nitrotoluene, 3:5-dibromo-2:4-dinitrotoluene, and of 3:5-dibromo-2-nitrotoluene, the nitration in the last case being carried out in presence of sulphuric acid (Blanksma, Chem. Weekblad, 1909, 6, 728); from 3:5-dibromo-2:6-dinitro-*p*-toluidine by the action of nitrous gases on a suspension in concentrated nitric acid at 0° (Körner and Contardi, l.c.). White flat needles, m.p. 240°; Palmer (Ber. 1888, 21, 3501; 1896, 29, 1346) describes it as long yellow prisms, m.p. 229°-230°.

2:3:4-Tribromonitrotoluene; by nitration of 2:3:4-tribromotoluene. M.p. 107°-108° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 446; Cohen and Dutt, l.c.).

2:3:5-Tribromonitrotoluene; on nitration 2:3:5-tribromotoluene yields two mononitro-derivatives, m.p. 67°-68° and 88°-89° respectively, the former in greater quantity (Cohen and Dutt, l.c.).

2:3:6-Tribromonitrotoluene; m.p. 91°-92° (C. and D.; N. and W.).

2:4:5-Tribromonitrotoluene; colourless crystals, m.p. 131°-131.5° (C. and D.).

2:4:6-Tribromonitrotoluene; m.p. 215° (Wroblewsky, Ann. 1873, 168, 195).

2:4:6-Tribromonitrotoluene; colourless crystals, m.p. 74°-75.5° (C. and D.).

2:5:6-Tribromo-4-nitrotoluene; from 2:6-dibromo-4-nitro-*m*-toluidine. It melts at 106°-107° (C. and D.; N. and W.).

3:4:5-Tribromonitrotoluene; colourless crystals, m.p. 104°-105° (C. and D.).

3:5:6-Tribromo-2-nitrotoluene; from 3:5-dibromo-6-nitro-*o*-toluidine. It melts at 93° (Blanksma, Chem. Weekblad, 1914, 11, 185).

2:3:4-Tribromodinitrotoluene; m.p. 197°-199° (C. and D.).

2:3:5-Tribromodinitrotoluene; m.p. 209°-210° (C. and D.).

2:3:6-Tribromodinitrotoluene; light yellow prisms, m.p. 202°-203° (C. and D.).

2:4:5-Tribromodinitrotoluene; colourless crystals, m.p. 278°-279° (C. and D.).

2:4:6-Tribromodinitrotoluene; colourless crystals, m.p. 217°-218° (C. and D.; N. and W.).

3:4:5-Tribromodinitrotoluene; colourless prisms, m.p. 211.5° (C. and D.).

3:5:6-Tribromodinitrotoluene; by nitration of 3:5:6-tribromo-2-nitrotoluene. Colourless crystals, m.p. 208° (Blanksma, Chem. Weekblad, 1914, 11, 185).

2:3:4:5-Tetrabromo-6-nitrotoluene, m.p. 212° (N. and W.).

2:3:4:6-Tetrabromo-5-nitrotoluene, m.p. 215°-216° (N. and W.).

2:3:5:6-Tetrabromo-4-nitrotoluene; by nitration of 2:3:5:6-tetrabromotoluene (Neville and Winther, Chem. Soc. Trans. 1880, 37, 450); from 2-bromo-4-nitrotoluene by bromination in presence of ferrous bromide (Scheufelen, Ann. 1885, 231, 179). It melts at 213° (Neville and Winther) or 227° (Scheufelen).

m-Chloro-*p*-bromonitrotoluene; by nitration of chlorinated *p*-bromotoluene. Needles, m.p. 61° (Willgerodt and Salzmann, J. pr. Chem. 1880, [2] 39, 478).

o-Chlorobromonitrotoluene; by nitration of brominated *o*-chlorotoluene. Needles, m.p. 68° (W. and S.).

Dichloro-*p*-bromonitrotoluene; by nitration of dichloro-*p*-bromotoluene. Pearly leaflets, m.p. 106° (W. and S.).

Trichloro-*p*-bromonitrotoluene; by nitration of trichloro-*p*-bromotoluene. Needles, m.p. 162° (W. and S.).

2-Iodonitrotoluene; by nitration of 2-iodotoluene. Microscopic needles, m.p. 103°-104° (Beilstein and Kuhlberg, Ann. 1871, 158, 347).

2-Iodo-3-nitrotoluene; from 3-nitro-*o*-toluidine. Light yellow plates, m.p. 67°-68° (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441).

2-Iodo-4-nitrotoluene; from 4-nitro-*o*-toluidine. Yellowish plates, m.p. 51° (Reverdin, Ber. 1897, 30, 3000) or rhombic plates, m.p. 58° (Willgerodt and Kok, Ber. 1908, 41, 2077). It yields a dichloride, sulphur-yellow prisms, m.p. 83°, which on treatment with sodium carbonate or sodium hydroxide yields 2-iodo-4-nitrotoluene, yellowish-white powder, exploding at 180°-181°. The latter on treatment with hypochlorous acid is converted into 2-iodoxy-4-nitrotoluene, white flocculent precipitate, exploding at 204° (Willgerodt and Kok, l.c.).

2-Iodo-5-nitrotoluene; from 5-nitro-*o*-toluidine by the diazo-reaction (Reverdin); by gradual treatment of *o*-iodo-toluene with nitric acid (D 1.51) (Reverdin; Beilstein and Kuhlberg, Ann. 1871, 158, 347). It melts at 103°-104° and forms a dichloride, m.p. 102° (decomp.), when chlorine is passed into a saturated solution in chloroform (McCrae, Chem. Soc. Trans. 1878, 73, 693).

2-Iodo-6-nitrotoluene; from 6-nitro-*o*-toluidine. It forms thick yellowish-white crystals, m.p. 35.5° (Nölting, Ber. 1904, 37, 1018) or yellow needles, m.p. 34°-35° (Cohen and Meyer, Chem. Soc. Trans. 1904, 85, 1627).

3-Iodo-2-nitrotoluene; from 5-iodo-6-nitro-*o*-toluidine. Colourless prismatic plates, m.p. 65°, volatile with steam (Wheeler and Brantlecht, Amer. Chem. J. 1910, 44, 126).

3-Iodo-5-nitrotoluene; from 5-nitro-*m*-toluidine. Yellow rectangular prisms, m.p. 77°

(Wheeler and Scholes, Amer. Chem. J. 1910, 44, 126).

3-Iodo-6-nitrotoluene; from 6-nitro-*m*-toluidine. Orange needles, volatile with steam, m.p. 84° (Artmann, Monatsh. 1905, 26, 1091).

3-Iodo-nitrotoluene; by nitration of 3-iodotoluene. Small needles, m.p. 108°–109° (Beilstein and Kuhlberg).

4-Iodo-2-nitrotoluene; from 2:4-dinitrotoluene by replacing the *p*-nitro-group by iodine (Heynemann, Ann. 1871, 158, 337); together with other products by the nitration of *p*-iodotoluene (Reverdin, Ber. 1897, 30, 3001). Pale yellow crystals, m.p. 60°–61°, b.p. 286° (decomp.).

4-Iodo-3-nitrotoluene; from 3-nitro-*p*-toluidine. Flat yellow needles, m.p. 55°–56° (Beilstein and Kuhlberg, Ann. 1871, 158, 344). Yields a dichloride, large yellow plates, m.p. 71° (Willgerodt and Simonis, Ber. 1906, 39, 269).

2-Iodo-3:5-dinitrotoluene; from 3:5-dinitrotoluene-2-diazonium nitrate and cupric iodide. Small lemon-yellow plates or long prisms, m.p. 119°–5° (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, i. 888).

3-Iodo-2:4-dinitrotoluene; by boiling an alcoholic solution of 2:4-dinitro-3-tolylhydrazine with excess of iodine. Yellow leaflets, m.p. 117° (Brady and Bowman, Chem. Soc. Trans. 1921, 119, 897).

3-Iodo-2:6-dinitrotoluene; large aggregates of small colourless plates, m.p. 90° (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339).

4-Iodo-3:5-dinitrotoluene; by nitration of *p*-iodotoluene (Glassner, Ber. 1875, 8, 561); from 3:5-dinitro-*p*-toluidine. Lemon-yellow needles, m.p. 158° (Körner and Contardi, Atti R. Accad. Lincei, 1914, [v.] 23, ii. 464); Glassner gave m.p. 137°–138°.

Di-iodonitrotoluene (?); formed together with other products by nitration of *p*-iodotoluene with nitric acid (D 151); m.p. 112° (Reverdin, l.c.).

2:3-Di-iodo-4-nitrotoluene; from 3-iodo-5-nitro-*o*-toluidine. Light brown prismatic needles, m.p. 143° (Wheeler, etc., Amer. Chem. J. 1910, 44, 126, 493).

2:5-Di-iodo-3-nitrotoluene; from 5-iodo-3-nitro-*o*-toluidine. Colourless prisms, m.p. 95° (Wheeler, etc.).

2:5-Di-iodo-4-nitrotoluene; from 5-iodo-4-nitro-*o*-toluidine. Buff coloured prismatic plates, m.p. 117° (Wheeler, etc.).

2:5-Di-iodo-6-nitrotoluene; from 5-iodo-6-nitro-*o*-toluidine. Colourless needles, m.p. 105° (Wheeler, etc.).

3:4-Di-iodo-5-nitrotoluene; from 3-iodo-5-nitro-*p*-toluidine. Rectangular orange prisms, m.p. 84°–85° (Wheeler, etc.).

3-Bromo-2-iodonitrotoluene; by nitration of 3-bromo-2-iodotoluene. Prisms (Wroblewsky, Ann. 1873, 168, 165).

2-Bromo-4-iodonitrotoluene; by nitration of *o*-bromo-*p*-iodotoluene. Yellow needles, m.p. 92° (Hirtz, Ber. 1896, 29, 1405).

3-Bromo-4-iodonitrotoluene; by nitration of 3-bromo-4-iodotoluene. Needles, m.p. 118° (Wroblewsky, Ann. 1873, 168, 160).

3:5-Dibromo-4-iodo-2-nitrotoluene; by nitration of 3:5-dibromo-4-iodotoluene. Large needles, volatile with steam, m.p. 69° (Wroblewsky, Ann. 1878, 192, 210).

3:5-Dibromo-2:4-di-iodonitrotoluene; by nitration of 3:5-dibromo-2:4-di-iodotoluene (m.p. 68°). Plates, m.p. 129° (Wroblewsky).

SULPHINIC AND SULPHONIC ACID DERIVATIVES.

Toluene *o*-sulphinic acid; by boiling *o*-tolyltoluenesulphazide with baryta water (Limpricht, Ber. 1887, 20, 1241); by dropping toluene *o*-sulphonyl chloride into a warm mixture of zinc dust and water (Troeger and Voigtländer, J. pr. Chem. 1896, [2] 54, 513); by treating an ice-cold solution of *o*-toluenediazonium sulphate in sulphuric acid saturated with sulphur dioxide with copper (Gattermann, Ber. 1899, 32, 1140; Fr. Bayer & Co., Eng. Pat. 26139 of 1896; Fr. Pat. 252787 and addn.; D. R. P. 95830 of 1896); by the action of sulphur dioxide on an ethereal solution of *o*-tolyl magnesium bromide (Rosenheim and Singer, Ber. 1904, 37, 2152). Long needles, m.p. 80° (Limpricht). $\text{NaA} + 4\text{H}_2\text{O}$, glistening plates; $\text{CaA}_2 + 3\text{H}_2\text{O}$, crystalline powder; $\text{BaA}_2 + 3\text{H}_2\text{O}$, nodules; $\text{SrA}_2 + 3\text{H}_2\text{O}$, crystalline powder. On passing hydrogen sulphide into the methyl alcoholic solution, a mixture of *o*-tolyl tetra- and penta-sulphide is formed. On boiling with water for about 3 hours, the sulphinic acid is converted into *o*-toluic disulphoxide and toluene *o*-sulphonic acid (T. and V.). For its behaviour with diazo-compounds, see Troeger and Ewers (J. pr. Chem. 1900, [2] 62, 369).

Toluene *m*-sulphinic acid; from diazotised *m*-toluidine, sulphur dioxide and copper powder. Unstable oil (Troeger and Hill, J. pr. Chem. 1905, (2) 71, 201).

Toluene *p*-sulphinic acid; prepared as in the case of the *o*-sulphinic acid (Limpricht); by treating toluene *p*-sulphonyl chloride with sodium amalgam, zinc-dust or sodium sulphite (Otto, Ann. 1867, 142, 92; 1868, 145, 19; Ber. 1876, 9, 1586; Bloomstrand, Ber. 1899, 32, 1141); by the action of sulphur dioxide and aluminium chloride on toluene or its halogen derivatives at low temperatures (Knoevenagel and Kenner, Ber. 1908, 41, 3315). Plates, m.p. 86°–87° (Thomas, Chem. Soc. Trans. 1909, 95, 344). $\text{KA} + 2\text{H}_2\text{O}$, leaflets (Casanova, Ber. 1887, 20, 2088); $\text{CaA}_2 + 4\text{H}_2\text{O}$; BaA_2 , small leaflets; $\text{ZnA}_2 + 2\text{H}_2\text{O}$ (Otto); NH_4A , small needles, m.p. 175°; *hydrazine salt*, glistening plates, decomposing at 140°; *aniline salt*, m.p. 118°; *o*-toluidine salt, m.p. 124°; *p*-toluidine salt, m.p. 140°; *m*-xylylidine salt, m.p. 129°–5° (Hälsig, J. pr. Chem. 1897, [2] 56, 213); *phenylhydrazine salt*, m.p. 114° (Köhler and Reimer, Amer. Chem. J. 1904, 31, 163; cf. Hälsig). On electrolytic oxidation it yields *p*-sulphobenzoic acid (Sebor, Zeitsch. Elektrochem. 1903, 9, 370). When treated with an excess of thionyl chloride, it yields the *suphiny*l chloride, m.p. 54°–58° (Hilditch and Smiles, Ber. 1908, 41, 4113). When ammonia is passed into an alcoholic or ethereal solution of toluene *p*-sulphinic acid, the corresponding ammonium salt is formed, whilst in benzene solution a mixture of *p*-tolyl disulphoxide and toluene *p*-sulphonic acid is produced (Heiduschke, Verh. Ges. deut. Naturforsch. Aerzte, 1907, 11, 170; Hälsig, J. pr. Chem. 1897, 56, 213).

For the action of toluene *p*-sulphinic acid on nitrosobenzene and phenylhydroxylamine, see

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Bamberger and Rising (Ber. 1901, 34, 228, 241), and for further reactions, see Kohler and Macdonald (Amer. Chem. J. 1899, 22, 235), von Meyer, Nacke and Gmeiner (J. pr. Chem. 1901, 63, 167), von Meyer (*ibid.* 1903, 68, 263), Hälsig (*ibid.* 1897, 56, 213), Troeger and Ewers (*ibid.* 1900, 62, 389), Hantzsch and Horn (Ber. 1902, 35, 877), Ullmann and Lehner (*ibid.* 1905, 38, 729), Kohler and Reimer (Amer. Chem. J. 1904, 31, 163).

Toluene p-sulphinic anhydride; melts at 75° (Knoevenagel and Polaek, Ber. 1908, 41, 3323).

Methyl ester; a very unstable yellow oil. Oxidation yields the corresponding sulphonate (Otto, J. pr. Chem. 1893, [2] 47, 166).

Ethyl ester; from sodium toluene *p*-sulphinic acid and ethyl chlorocarbonate. Oil, D₂₀ 1.1212. On treatment with hydrogen sulphide, (CH₃)C₆H₄SO₃H, C₂H₅SH, (CH₃)C₆H₄SH, [(CH₃)C₆H₄]₂S₂ and sulphur are produced (Otto and Bössing, Ber. 1885, 18, 2504; 1886, 19, 1226; 1887, 20, 2278; 1893, 26, 310).

Nitrotoluene sulphinic acid; from *o*(?)-nitrotoluene *p*(?)-sulphonic acid and sodium amalgam in ethereal solution. Crystals, NaA' + $\frac{1}{2}$ H₂O (Otto and Grüber, Ann. 1868, 145, 24).

2:6-Dinitrotoluene 4-sulphinic acid; from the corresponding sulphonyl chloride and zinc dust. Solidifies after prolonged keeping over sulphuric acid. KA', crusts; BaA' + xH₂O, pearly leaflets; PbA' + 3H₂O, microscopic prisms (Perl, Ber. 1885, 18, 71).

Toluene 2:4-disulphinic acid; obtained as its zinc salt by the action of zinc dust on the corresponding disulphonyl chloride. The free acid is an oil, zinc salt, white needles, sodium and barium salts, white crystals. When heated with water the free acid yields toluene 2:4-disulphonic acid and toluene-toluene-2:4-dithio-sulphonate, C₆H₄(SO₂S)₂:C₆H₄ (Tröger and Meine, J. pr. Chem. 1903, [2] 68, 313).

Benzyl sulphinic acid; by treating benzyl sulphonyl chloride with zinc dust or sodium amalgam. The free acid is very unstable and is readily decomposed with evolution of sulphur dioxide; NaA', small leaflets (Otto and Lüders, Ber. 1880, 13, 1287).

Sulphonation of toluene: The quantities of the three isomeric monosulphonic acids produced are dependent upon the temperature, the concentration, and the amount of the sulphonating agent. Increase of temperature favours the production of toluene *p*- and *m*-sulphonic acids. The concentration of acid between the limits of 96-100 p.c. appears to be without influence. Increase in the amount of acid favours the production of the *o*-isomeride at low temperatures, but this influence is neutralised at higher temperatures by the effect due to rise of temperature. The addition of potassium sulphate, mercurous sulphate, and silver sulphate has no effect. At 35° and 75° the transformation of the *o*- and *p*-isomerides into one another occurs very slowly, whilst toluene *m*-sulphonic acid is unaltered after heating with sulphuric acid for 6 hours at 100°. With chlorosulphonic acid the chief product is also the *p*-isomeride (Holleman, Culand, van der Linden and Wibaut, Ber. 1911, 44, 2504). If fuming sulphuric acid be used and the temperature of the reaction is kept at the b.p.

of toluene, the main product is the *p*-acid, but if the temperature be not allowed to rise above 100° and ordinary concentrated acid is employed, 40-50 p.c. of the *o*-sulphonic acid is obtained (Fahlberg, Fr. Pat. 163797; D. R. P. 35211 of 1884; Fabr. de Thann, Eng. Pat. 14390 of 1901; Fr. Pat. 312797; D. R. P. 137935 of 1901; Eng. Pat. 10810 of 1897; Norton and Otten, Amer. Chem. J. 1885, 10, 140; Bourgeois, Chem. Zentr. 1900, i. 253; Reverdin, Ber. 1909, 42, 1523).

Toluene o-sulphonic acid; in small quantity together with the *p*-isomeride by dissolving toluene in hot fuming sulphuric acid (Engelhardt and Latschinoff, Zeit. f. Chem. 1869, (2) 5, 617; Wolkoff, *ibid.* (2) 6, 321; Bourgeois, Rec. trav. chim. 1899, 18, 436); by gradual addition of concentrated sulphuric acid to boiling toluene only the *p*-isomeride is formed (Chrutschoff, Ber. 1874, 7, 1167), whilst, according to Fahlberg (Ber. 1879, 12, 1048) no *m*-sulphonic acid is produced; in a yield of 40-50 p.c. by sulphonating below 100° with concentrated sulphuric acid with efficient agitation (Fahlberg and List; cf. D. R. PP. 35211, 35717 of 1884, and 137935 of 1901); from the sulphonyl chloride obtained together with the *m*- and *p*-isomerides by the action of chlorosulphonic acid on toluene (Klason and Vallin, Ber. 1879, 12, 1848; Noyes, Amer. Chem. J. 1886, 8, 176; Gilliard, Monnet and Cartier, D. R. P. 98030 of 1894); from 4-bromotoluene 2-sulphonic acid by reduction with sodium amalgam (Terry, Ann. 1873, 169, 27); from 4-nitrotoluene 2-sulphonic acid by elimination of the nitro-group (Jenssen, Ann. 1874, 172, 235); by treating diazo-derivatives of *o*-toluidine with sulphurous acid (Müller and Wiesinger, Ber. 1879, 12, 1348); by treatment of *p*-diazo-toluene *o*-sulphonic acid with sodium methoxide in methyl alcoholic solution (Moale, Amer. Chem. J. 1898, 20, 298); by warming the salts of *o*-sulphotoluene-*p*-hydrazine sulphonic acid, (CH₃)C₆H₄(SO₂H)·NH·NH·SO₂H, with potassium hydroxide (Ges. f. Chem. Ind. D. R. P. 68708 of 1892). For separation of the *o*- and *p*-acids by means of magnesium and zinc salts, see Fahlberg (Eng. Pat. 17401 of 1896; D. R. PP. 103299 of 1898, and 103943 of 1899), or by means of sulphuric acid, see Lange (Fr. Pat. 232539; D. R. P. 57391 of 1890).

Free acid, thin leaflets containing 2H₂O; NH₄A', thin leaflets; NaA' + H₂O, tables; KA' + H₂O, monoclinic plates; KA', needles; CaA₂, leaflets; BaA₂ + H₂O, plates;

ZnA₂ + 7H₂O; CdA₂ + 2H₂O; PbA₂ + 4H₂O, needles (Terry; Hübner and Post); +H₂O (Klason and Vallin); MnA₂ + 2H₂O; CuA₂ + 4H₂O; AgA₂; MnA₂ + 2H₂O; ZnA₂ + 7H₂O; MgA₂ + 7H₂O (Klason and Vallin, *loc. cit.*; Hübner and Post, Ann. 1873, 169, 1).

Chloride; by the action of chlorine on toluene *o*-sulphinic acid in presence of dilute sodium hydroxide or hydrochloric acid at temperatures below 35° (Basler Chemische Fabrik, Eng. Pat. 4525 of 1900, and 12585 of 1900; U.S. Pat. 667861; D. R. P. 124407 of 1900), or on potassium toluene *o*-sulphinic acid in aqueous solution (Ullmann and Lehner, Ber. 1905, 38, 729). Oil, b.p. 126°/10 mm., D₁₇ 1.3443 (U. and L.), or b.p. 151°/33 mm., 154°/36 mm. (Davies, Chem.

Soc. Trans. 1921, 119, 878). See also Fahlberg and List (l.c.), and Majert and Ebers (D. R. P. 95338 of 1898); Fabr. de Thann, Eng. Pat. 14390 of 1901; U.S. Pat. 692598; Fr. Pat. 312797; D. R. P. 142116 of 1901; Eng. Pat. 2304 of 1905; M. L. B., D. R. P. 154493 of 1902; Eng. Pat. 6581 of 1897; 4525 of 1900; 11077 and 11078 of 1898; 16299 of 1903.

Bromide; by the action of bromine on an aqueous solution of toluene *o*-sulphinic acid. M.p. 13°, b.p. 137.5°–138°/10 mm.

Tröger's compound (J. pr. Chem. 1896, [2] 54, 523) contains some of the *p*-isomeride (Ullmann and Lehner, l.c.).

Amide; octahedra, m.p. 154° (Noyes, m.p. 156.3° (McKie, Chem. Soc. Trans. 1918, 113, 799; cf. Wolkoff, l.c.; Klason and Vallin, Ber. 1879, 12, 1850; Heffter, Ann. 1883, 221, 208; Miller, Chem. Soc. Trans. 1892, 61, 1030; Thomas, *ibid.* 1909, 95, 343; Noyes, l.c.; Fahlberg and List, l.c.). It can be separated from the *p*-isomeride by fractional precipitation from an alkaline solution by means of acids or by fractional crystallisation of the sodium salts (von Heyden, D. R. P. 76881 of 1892, and 77435 of 1894; cf. Barger and Givaudan, Eng. Pat. 848 of 1903; D. R. P. 154655 of 1903). When oxidised in alkaline solution with potassium manganate or potassium permanganate it yields *o*-sulphaminobenzoic acid, in neutral solution benzoic sulphinide is the chief product, whilst in acid solution the product is *o*-sulphobenzoic acid (Fahlberg and List, Ber. 1888, 21, 242; cf. Fahlberg and Remsen, Ber. 1879, 12, 469). It is converted in 4*N*-ammoniacal solution in the presence of ammonium sulphate at 40° at a platinum gauze anode into 'saccharin'; the material yield being 43.7 p.c. and the current yield 9.2 p.c. The most favourable results, however, (material yield 75.4 p.c., current yield 42.6 p.c.) are obtained by the electrolysis of a suspension in 2*N*-sodium carbonate solution at about 60° with a platinum gauze anode and a rotating lead cathode (Fichter and Löwe, Helv. Chim. Acta, 1922, 5, 60; *vide* SACCHARIN).

Methylamide, thin striated plates, m.p. 73°–76°, when oxidised with alkaline potassium permanganate yields potassium *o*-methylsulphaminobenzoate (Remsen and Clark, Amer. Chem. J. 1903, 30, 247).

Toluene *m*-sulphonic acid; in small quantities by sulphonation of toluene (Holleman and co-workers, l.c.); from *o*-bromotoluene *m*-sulphonic acid (Müller, Ann. 1873, 169, 47) or 4-bromotoluene 3-sulphonic acid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 628) and sodium amalgam; or from 2-bromotoluene 5-sulphonic acid and zinc dust in alkaline solution (Miller, Chem. Soc. Trans. 1892, 61, 1030); from *p*-toluidine 3-sulphonic acid (Pechmann, Ann. 1874, 173, 202; Neville and Winther, l.c.), *o*-toluidine *m*-sulphonic acid (Pagel, Ann. 1875, 176, 297) or *o*-toluidine 5-sulphonic acid (Neville and Winther, l.c.); by treating *m*-toluidine diazo-salts with sulphur dioxide (Müller and Wiesinger, Ber. 1879, 12, 1348); from *p*-diazo-toluene *m*-sulphonic acid by treatment with zinc dust in ethyl alcoholic solution (Griffin, Amer. Chem. J. 1897, 19, 173, 189).

The free acid forms thin deliquescent scales + H_2O (Klason and Vallin); NH_4A , scales;

$\text{NaA} + \frac{1}{2}\text{H}_2\text{O}$ (Miller), $+ \frac{1}{2}\text{H}_2\text{O}$ (Vallin, Ber. 1886, 19, 2953), $+ \text{H}_2\text{O}$ (G.); $\text{KA} + \frac{1}{2}\text{H}_2\text{O}$, scales (M.), $+ \text{H}_2\text{O}$ (K. and V.); $\text{CaA} + 2\frac{1}{2}$ or $5\text{H}_2\text{O}$ (V.), $+ 3\text{H}_2\text{O}$ (K. and V.), $+ 2\text{H}_2\text{O}$, tables (G.); $\text{BaA} + \text{H}_2\text{O}$, rectangular tables (G.); $\text{ZnA} + 7\text{H}_2\text{O}$, thin rectangular plates (K. and V.), $+ 6\text{H}_2\text{O}$, long thin prisms; $\text{CdA} + 6\text{H}_2\text{O}$ (V.), $+ 7\text{H}_2\text{O}$, tables (K. and V.); $\text{PbA} + \text{H}_2\text{O}$ (Peckmann), $+ 2\text{H}_2\text{O}$ (M.; Pagel; V.), $+ 3\text{H}_2\text{O}$ (K. and V.); $\text{MnA} + 6\text{H}_2\text{O}$ (V.), $+ 7\text{H}_2\text{O}$ (K. and V.); $\text{CuA} + 7\text{H}_2\text{O}$ (V.), $+ 4\text{H}_2\text{O}$ (K. and V.), $+ \frac{1}{2}\text{H}_2\text{O}$ (G.); AgA , glistening prisms (V.), rectangular tables (G.).

Chloride; oil.

Amide; monoclinic needles or tables (Noyes and Walker, Amer. Chem. J. 1886, 8, 168), hexagonal scales, fernlike aggregates from water, or monoclinic prisms from alcohol (Griffin); m.p. 108° (Klason and Vallin, l.c.; Klason, Ber. 1886, 19, 2887; Griffin, Amer. Chem. J. 1897, 19, 176) or 91° (Noyes, Amer. Chem. J. 1886, 8, 177). According to Noyes, the amide, m.p. 108°, is a mixture of the *o*- and *p*-isomerides. On oxidation with potassium permanganate or chromic acid mixture it yields *m*-sulphaminobenzoic acid.

Toluene *p*-sulphonic acid; chief product of sulphonation of boiling toluene (Dewille, Ann. Chim. 1841, (3) 3, 172; Fittig and Tollens, Ann. 1864, 131, 310; Märcker, *ibid.* 1865, 136, 85; Engelhardt and Latschinoff, Zeit. f. chem. 1869 (2) 5, 617; Jaworski, *ibid.* 1865, 221; Otto and Grüber, Ann. 1867, 142, 92; 1868, 145, 10; Chrutschoff, Ber. 1874, 7, 1167; Fahlberg, Ber. 1879, 12, 1048); from toluene and chlorosulphonic acid (Klason and Vallin, Ber. 1879, 12, 1848); by the action of sulphurous acid on *p*-diazo-toluene salts (Müller and Wiesinger). Thick plates or flat prisms + H_2O (K. and V.), m.p. 92° (Norton and Otten, Amer. Chem. J. 1888, 10, 140), or 35°, b.p. 146°–147°/0 mm. (Krafft and Wilke, Ber. 1900, 33, 3208). Fusion with potash yields *p*-cresol and *p*-hydroxybenzoic acid. Fusion with sodium formate yields *p*-toluic acid (Remsen, Ber. 1875, 8, 1412). Hydrolysis with steam commences at 150° (Armstrong and Miller, Chem. Soc. Trans. 1884, 45, 148). On electrolytic oxidation in 10–20 p.c. sulphuric acid using a lead anode at 70°, it yields *p*-sulphobenzoic acid (Sebor, Zeitsch. Elektrochem. 1903, 9, 370).

NH_4A (K. and V.); $\text{NaA} + 2\text{H}_2\text{O}$, or $+ 4\text{H}_2\text{O}$, rectangular tables (Vallin, Ber. 1886, 19, 2953); $\text{KA} + \text{H}_2\text{O}$, six-sided plates, prisms or trimetric crystals (Otto and Köbig, Ber. 1886, 19, 1834); BaA , crystallises in anhydrous leaflets above 30° and as needles + $3\text{H}_2\text{O}$ below 30° (Kelbe, Ber. 1883, 16, 622); $\text{CaA} + 4\text{H}_2\text{O}$, monoclinic prisms (K. and V.); $\text{MgA} + 6\text{H}_2\text{O}$, large tables (K. and V.); $\text{ZnA} + 6\text{H}_2\text{O}$, tables (K. and V.); $\text{CdA} + 6\text{H}_2\text{O}$, tables (K. and V.); PbA , long needles (K. and V.); $\text{MnA} + 6\text{H}_2\text{O}$, tables (K. and V.); $\text{CuA} + 6\text{H}_2\text{O}$, tables or needles (K. and V.); AgA , large tables (K. and V.).

The following salts with organic bases are described by Norton and Otten (l.c.): $\text{NH}_4(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SO}_3$, rosettes, m.p. 128°; $\text{NH}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SO}_3$, m.p. 78°; $\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{SO}_3$, m.p. 92°; $\text{NH}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_4\text{SO}_3$, m.p. 111°; $\text{NH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4\text{SO}_3$, m.p. 88°; $\text{N}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_4\text{SO}_3$, m.p. 66°.

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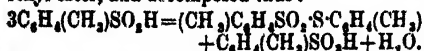
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Chloride; rhombic tablets or triclinic crystals (Otto and Köhlig, Ber. 1886, 19, 1835), m.p. 69°, b.p. 145°-146°/15 mm. (Kraft and Roos, Ber. 1892, 25, 2259), 136°-1°/11 mm., 151°-6°/20 mm. (Bourgeois, Rec. trav. chim. 1899, 18, 436), 164°/33 mm. (Davies, Chem. Soc. Trans. 1921, 119, 878), 80°/0 mm. (Kraft and Wilke, l.c.). On warming with alkaline solutions, or better, by boiling with 80 p.c. sulphuric acid, it yields *o*-chlorotoluene (Ges. für. Chem. Ind., D. R. P. 133000 of 1901). Toluene *p*-sulphonyl chloride when heated with ethylene chlorohydrin yields β -chloroethyltoluene *p*-sulphonate, b.p. 210°/21 mm., which is a valuable reagent for introducing the chloroethyl-group into amines and phenols (Clemo and W. H. Perkin, Chem. Soc. Trans. 1922, 121, 642; B. D. C., W. H. Parkin and Clemo, Eng. Pat. 193618 of 1922).

Toluene *p*-sulphonyl chloride when treated at 70°-75° with antimony pentachloride yields a mixture of the 2:6-di- and 2:3:6-trichloro-derivatives, converted on hydrolysis into the corresponding sulphonic acids, or, on removing the acyl-group into a mixture of 2:6-di- and 2:3:6-trichlorotoluene (Geigy & Co., D. R. P. 210856 of 1908). When electrolysed in 2*N*. alcoholic hydrochloric acid solution it yields as the main product, the corresponding sulphonic acid, which is partially converted into its ethyl-ester, and decomposed thus:



In the presence of titanium trichloride using a nickel gauze cathode, the main product is *p*-tolyl mercaptan, which is also produced by reducing a suspension of the sulphonyl chloride in aqueous sulphuric acid at 80° at a lead cathode (Fichter and Bernouilli, Zeitsch. Elektrochem. 1907, 13, 310). Toluene *p*-sulphonyl chloride on nitration on the water-bath with fuming nitric and concentrated sulphuric acids yields 2:6-dinitrotoluene 4-sulphonic acid in almost theoretical yield (Reverdin and Crépieux, Ber. 1901, 34, 2992).

Bromide; from toluene *p*-sulphonic acid and bromine. Monoclinic prisms, μ .p. 96° (Otto, Ann. 1867, 142, 98) or 93°-94° (Zincke and Frohneberg, Ber. 1910, 43, 837).

Iodide; from sodium toluene *p*-sulphinate and iodine. Yellow powder, m.p. 84°-85°. By heating with water or alcohol it is decomposed into toluene *p*-sulphonic acid, iodine and little *p*-toluene disulphoxide, whilst by heating with potassium hydroxide it yields toluene *p*-sulphonic acid. Zinc-ethyl yields the zinc sulphinate (Otto and Trüger, Ber. 1891, 24, 479).

Ethyl ester; from the chloride (Jaworski, Zeit. f. chem. 1865, 1221) or the bromide (Otto, Ann. 1867, 142, 100); by treating the ethyl ester of toluene *p*-sulphonic acid with potassium permanganate and acetic acid (Otto and Böding, Ber. 1896, 19, 1236). Monoclinic crystals, m.p. 32°-33°, b.p. 73°/15 mm., D_{20}^{25} 1.1736, D_{20}^{30} 1.1678 (Kraft and Roos, Ber. 1892, 25, 2259). The phenyl-, *o*-, *m*-, and *p*-tolyl- esters melt at 95°-96°, 84°-55°, 51°, and 69°-70° respectively (Reverdin and Crépieux, Bull. Soc. chim. 1901, (3) 25, 1044; 1902, (3) 27, 741; Ber. 1908, 41, 214, 1483). For other esters, see Reverdin and Crépieux (l.c.); Bomberger and Rieck (Ann. 1901, 34, 336). For the use of

methyl- and ethyl-toluene *p*-sulphonates as alkylating agents, see Ullmann and Wenner (Ann. 1903, 327, 120); Finzi (Annali. Chim. Appl., 1925, 15, 41).

Anhydride; formed together with the chloride by heating toluene *p*-sulphonic acid with pure thionyl chloride. Crystals, m.p. 122°-125° (Meyer and Schlegel, Monatsh. 1913, 34, 561).

Amide; leaflets, m.p. 137°-137.5° (Clæsson and Wallin, Ber. 1879, 12, 1853; McKie, Chem. Soc. Trans. 1918, 113, 799). It forms a potassium salt, $\text{C}_6\text{H}_4\text{SO}_3\text{NHK}$ (Wolkoff, Ber. 1872, 5, 140; Zeit. f. Chem. 1870, (2) 6, 323, 580). **Methylamide**, m.p. 76°-77°; **ethylamide**, m.p. 64°; **dimethylamide**, m.p. 76°; **diethylamide**, m.p. 59°-60°; **anilide**, m.p. 103°; **methylanilide**, m.p. 95°; **ethylanilide**, m.p. 88°; ***p*-toluidide**, m.p. 118° (van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1902, 616; cf. Rec. trav. chim. 1884, 3, 7; Jaeger, Proc. K. Akad. Wetensch. Amsterdam, 1920, 23, 347; Remsen and Palmer, Amer. Chem. J. 1896, 8, 241; Marckwald and von Droste-Hulshoff, Ber. 1898, 31, 3262; 1899, 32, 561; D. R. P. 105870 of 1897); **propylamide**, m.p. 52° (Marckwald, Ber. 1899, 32, 3509); **propylisobutylamide**, m.p. 59° (M.); **bromoallylamide**, m.p. 45°-46° (Rudziak, Ber. 1901, 34, 3543); **benzylamide**, m.p. 116° (Chattaway, Chem. Soc. Trans. 1905, 87, 145); **benzylmethylamide**, m.p. 95° (Holmes and Ingold, Chem. Soc. Trans. 1925, 127, 1813); **anilide**, m.p. 103° (R. and P.); **3-iodoanilide**, m.p. 128° (Ullman, Ann. 1904, 332, 38); **2:4-dinitroanilide**, m.p. 219°; ***o*-toluidide**, m.p. 106°, on nitration yields the 5-nitro-*o*-toluidide, and a little 3-nitro-*o*-toluidide and 3:5-dinitro-*o*-toluidide, which, on hydrolysis, yield 5-nitro-*o*-toluidine, 3-nitro-*o*-toluidine, and 3:5-dinitro-*o*-toluidine, respectively; ***m*-toluidide**, m.p. 114°; ***p*-toluidide**, m.p. 117°, on nitration yields the 3-nitro-*p*-toluidide; ***p*-phenetide**, m.p. 106°-107°; the amides with *o*-, *m*-, and *p*-phenylenediamine melt at 201°-202°, 172° and above 250°, respectively; ***di-p*-toluenesulphonbenzide**, m.p. 243°, and its **dimethyl-derivative**, m.p. 235° (Reverdin and Crépieux; Willstätter and Kalb, Ber. 1904, 37, 3761). For other derivatives, see Esch and Marckwald (Ber. 1900, 33, 762); Howard and Marckwald (l.c.); von Meyer (J. pr. Chem. 1901, 63, 167). For *N*-halogen derivatives of the amides see Chattaway (Chem. Soc. Trans. 1905, 87, 145).

Benzylsulphonic acid; by oxidising benzyl disulphide with nitric acid (Barbaglia, Ber. 1872, 5, 270, 688); by boiling benzyl chloride with aqueous potassium or sodium sulphite (Böhler, Ann. 1870, 154, 50; 1883, 221, 215; Mohr, ibid. 1883, 221, 216; Otto and Lüdern, Ber. 1880, 13, 1286); by heating benzyl methyl ketone with sulphuric acid (Krekelus, Ber. 1886, 19, 3625). Very hygroscopic crystals. The potassium salt when heated with phosphorus pentachloride yields benzotrichloride; with potassium cyanide it yields benzyl cyanide (Barbaglia, l.c.), and on fusion with potassium hydroxide it yields toluene and benzoic acid (Otto, Ber. 1893, 13, 1258).

$\text{NH}_4\text{A}'$; $\text{KA}' + \text{H}_2\text{O}$, rhombic tablets; $\text{CaA}' + 2\text{H}_2\text{O}$, crystalline scales; $\text{BaA}' + 2\text{H}_2\text{O}$, plates; $\text{PbA}' + \text{Pb(OH)}_2$, crystalline plates.

tate; PbA' , plates; AgA' , crystalline scales (Böhler, Lc.).

The *o*-chloro-derivative, obtained by treating *o*-chlorobenzyl chloride with sulphites, forms a dinitro-derivative whose calcium salt forms needles. The free acid on heating with ammonia at 135° – 140° yields a nitroaminohydroxybenzyl sulphonic acid (Kalle and Co., D. R. P. 141783 of 1902).

Chloride; prisms, m.p. 92° . Decomposes on heating into benzyl chloride and sulphur dioxide (Pechmann, Ber. 1873, 6, 534; Otto and Lüders, Ber. 1880, 13, 1286).

Amide; small prisms, m.p. 102° (O. and L.) or 105° (P.).

(a) *Toluene 2:4-disulphonic acid*; by sulphonation of toluene, toluene-*o*- or *p*-sulphonic acid (Hakansson, Ber. 1872, 5, 1085; Claesson and Berg, *ibid.* 1880, 13, 1170; Gnehm and Forrer, *ibid.* 1877, 10, 542, 1276; Klason, *ibid.* 1887, 20, 354; Senhofer, Ann. 1872, 164, 126); by the action of iodine and potassium iodide on potassium toluene disulphate (Tröger and Meine, J. pr. Chem. 1903, (2) 68, 313); by heating toluene *p*-sulphonyl chloride with sulphuric acid (Fahlberg, Ber. 1879, 12, 1052; Amer. Chem. J. 1879, 1, 170; 1880, 2, 182); from *p*-toluidine 2-sulphonic acid and *o*-toluidine 4-sulphonic acid by the xanthate method (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 754).

$(\text{NH}_4)_2\text{A}'' + \text{H}_2\text{O}$; $\text{K}_2\text{A}'' + \text{H}_2\text{O}$; $\text{BaA}'' + \text{H}_2\text{O}$, silky needles (W. and B.) or $\text{BaA}'' + (7/2)\text{H}_2\text{O}$, prisms (H.); $\text{ZnA}'' + 8\text{H}_2\text{O}$; $\text{CuA}'' + 8\text{H}_2\text{O}$, four-sided prisms; $\text{As}_2\text{A}'' + 2\text{H}_2\text{O}$ (Senhofer).

Chloride; elongated prisms or prismatic needles, m.p. 56° (W. and B.) or 51° – 53° (H.).

Bromide; white solid, m.p. 78° (Tröger and Meine).

Amide; prisms, m.p. 185° – 186° . On oxidation with potassium permanganate it yields disulphaminobenzoic acid (Fahlberg).

Anilide; small prisms or tufts of needles, m.p. 187° (W. and B.).

o-Toluidide; m.p. 170° – 171° (T. and M.).

m-Toluidide; m.p. 138° (T. and M.).

(β) *Toluene 2:5-disulphonic acid*; by sulphonation of toluene; by heating toluene *o*-sulphonic acid with fuming sulphuric acid at 160° (Hakansson, Lc.), or toluene *m*-sulphonic acid with sulphuric acid at 180° (Klason, Lc.); from *o*-toluidine 5-sulphonic acid by replacing the amino-group by a mercaptan group and oxidising the thiocresol sulphonic acid obtained with permanganate (Klason, Ber. 1887, 20, 354); from *p*-toluidine 2:5-disulphonic acid by conversion into the hydrazine and treatment of the latter with copper sulphate, or from *o*-toluidine 5-sulphonic acid by the xanthate method (Wynne and Bruce).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$; $\text{BaA}'' + \text{H}_2\text{O}$.

Chloride; four-sided plates or prisms, m.p. 98° (W. and B.).

Amide; microscopic prisms, m.p. 224° (K.).

Anilide; slender prismatic needles, m.p. 178° (W. and B.).

(γ) *Toluene 2:6-disulphonic acid*; by reduction of 4-bromo- or 4-chlorotoluene 2:6-disulphonic acid with sodium amalgam (Kornatzki, Ann. 1883, 221, 199; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 771).

$\text{K}_2\text{A}''$, anhydrous flat prisms; $\text{BaA}'' + 2\text{H}_2\text{O}$,

rhombs (above 50°), or $+4\text{H}_2\text{O}$, flat needles (below 50°).

Chloride; monoclinic prisms, m.p. 88° .

Amide; long slender needles, melting above 260° (Kornatzki).

Anilide; minute diamond-shaped prisms, m.p. 162° (W. and B.).

Toluene 3:4-disulphonic acid; from *p*-toluidine 3-sulphonic acid by conversion into *p*-thiocresol 3-sulphonic acid and oxidation of the latter with potassium permanganate (Klason, Ber. 1887, 20, 356), or by diazotisation, treatment with potassium xanthate, saponification and oxidation with potassium permanganate (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 751).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, needles; $\text{BaA}'' + 2\text{H}_2\text{O}$, prisms.

Chloride; scales, m.p. 111° , or prismatic crystals, m.p. 70° – 80° , from benzene, containing benzene of crystallisation, which is lost rapidly on exposure to air when the melting-point rises to 111° (Klason; Wynne and Bruce).

Amide; m.p. 235° – 239° (slight decomp.) (Klason).

Anilide; small prisms or clusters of minute plates, m.p. 190° (W. and B.).

(γ or δ) *Toluene 3:5-disulphonic acid*; from *o*-toluidine 3:5-disulphonic acid by conversion into the hydrazine and treatment with copper sulphate (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 748); together with the 2:5-acid by sulphonation of toluene *m*-sulphonic acid (Klason, Ber. 1886, 19, 2889; 1887, 20, 352); by treatment of *p*-iodotoluene disulphonic acid with sodium amalgam (Limprieth and Richter, Ber. 1885, 18, 2179; Richter, Ann. 1885, 230, 326).

$\text{K}_2\text{A}''$, anhydrous microscopic scales; $\text{BaA}'' + 3\frac{1}{2}\text{H}_2\text{O}$, small scales, becoming anhydrous on exposure to air (W. and B.). The product obtained by Richter is the 3:5-disulphonic acid and not the 2:6- or 2:3-isomeride, as he was led to believe from the experiments of Hasse (Ann. 1885, 230, 286), whilst the compound described by Hasse is not the 3:5-acid.

Chloride; pale yellow prismatic crystals, m.p. 95° (W. and B.) (Hasse gives m.p. 132°).

Amide; short prisms, m.p. 214° (K.) or 216° (R.) (Hasse gives m.p. above 230°).

Anilide; thin scales, m.p. 153° (W. and B.).

Toluene 2:4:6-trisulphonic acid; by heating 1 mol. of potassium toluene 2:4-disulphonate with 3 mols. of chlorosulphonic acid at 240° . The product is converted, *vis* the barium and potassium salts, into the sulphonyl chloride, which is then heated with 12 parts of water at 130° – 140° .

Long slender needles $+6\text{H}_2\text{O}$, which lose $3\text{H}_2\text{O}$ at 100° and melt at 145° .

$\text{KA}'' + 3\frac{1}{2}\text{H}_2\text{O}$, large rhombic tables; $\text{Ba}_2\text{A}'' + 14\text{H}_2\text{O}$; $\text{Pb}_2\text{A}'' + 8\text{H}_2\text{O}$, amorphous crystals (Klason, Ber. 1881, 14, 307).

Chloride; tables, m.p. 153° (K.).

Amide; microscopic crystals, m.p. above 300° (K.).

4-Fluorotoluene 2-sulphonic acid; from *p*-toluidine 2-sulphonic acid.

$\text{KA}'' + 2\text{H}_2\text{O}$, large scales; $\text{BaA}'' + \text{H}_2\text{O}$, small scales.

Chloride; oil, b.p. 145° – $150^\circ/20$ mm.

Amide; large prisms or long white needles, m.p. 140° or 155° . When oxidised with per-

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manganate it yields *p*-chlorobenzoic sulphinide, 'fluoraccharin,' colorless needles or rhombs, m.p. 200°, which is very sweet but has a somewhat bitter after-taste (Roode, Amer. Chem. J. 1891, 13, 219; Hölleman, Rec. trav. chim. 1906, 25, 330).

p-Chlorotoluene on sulphonation yields chiefly 4-chlorotoluene 3-sulphonic acid together with 4-chlorotoluene 2-sulphonic acid (Wynne, Chem. Soc. Trans. 1892, 61, 1082; Wynne and Bruce, Chem. Soc. Proc. 1895, 11, 152; Vogt and Henninger, Ann. Chim. 1865, (4) 27, 133; Ann. 1873, 165, 362), whilst toluene *o*-sulphonic acid or its soluble salts when chlorinated in cold aqueous solution yields a mixture of 4- and 6-chlorotoluene *o*-sulphonic acids. The latter mixture is readily separable owing to the much greater insolubility of the salts of the 4-chloro-acid. Chlorination in more dilute solution at a temperature not exceeding 60° yields a mixture of dichloro- and trichlorotoluene *o*-sulphonic acids (B. D. C., Green and Herbert, Eng. Pat. 170056 of 1920).

On disulphonation with 20 p.c. fuming sulphuric acid *p*-chlorotoluene yields a mixture of the 2:6- and 2:5-disulphonic acids in the proportion of about 3 parts of the former to 1 part of the latter, together with some of the 3:5-disulphonic acid. A similar mixture is obtained also when 4-chlorotoluene 2-sulphonic acid is treated in this manner (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 768).

3-Chlorotoluene *o*-sulphonic acid; from *m*-chlorotoluene and 100 p.c. sulphuric acid.

$\text{NaA}' + \text{H}_2\text{O}$, monosymmetric rhombs; KA' , monosymmetric rhombs; $\text{BaA}'_2 + \text{H}_2\text{O}$, small nacreous plates (Wynne, Chem. Soc. Trans. 1892, 61, 1075).

Chloride; orthorhombic prisms, m.p. 53° (W.).

Amide; thin scales, m.p. 182° (W.).

4-Chlorotoluene 2-sulphonic acid; sulphonation of *p*-chlorotoluene (above) or chlorination of toluene *o*-sulphonic acid (above); from *p*-toluidine 2-sulphonic acid by the diazo-reaction (Jensen, Ann. 1874, 172, 239; Roode, Amer. Chem. J. 1891, 13, 221; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 761; cf. Wynne, *ibid.* 1892, 61, 1078).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, rectangular scales; KA' , anhydrous prismatic needles (W. and B.; R.), $+ \text{H}_2\text{O}$ (Hübner and Majert, Ber. 1873, 6, 793); $\text{BaA}'_2 + \text{H}_2\text{O}$, microscopic plates (H. and M.), or prismatic aggregates (W. and B.; Jensen); $\text{CaA}'_2 + 6\text{H}_2\text{O}$ (H. and M.); $\text{PbA}'_2 + 8\text{H}_2\text{O}$ (H. and M.); $\text{CuA}'_2 + 7\text{H}_2\text{O}$ (H. and M.).

Chloride; large four-sided elongated plates, m.p. 24° (W. and B.).

Amide; slender needles, m.p. 142° (W. and B.; Heffer, Ann. 1883, 221, 209, gives m.p. 138°).

Anilide; monosymmetric plates, m.p. 144° (W. and B.).

When oxidised with potassium permanganate it yields *p*-chlorobenzoic sulphinide, pearly scales, m.p. 218°, with a sweet taste but bitter after-taste (R.). On heating at 150° with 20 p.c. fuming sulphuric acid the free acid yields a mixture of the 2:5- and 2:6-disulphonic acids in the approximate proportions of 1:3 (W. and B.).

4-Chlorotoluene 3-sulphonic acid; by sul-

phonation of *p*-chlorotoluene (Vogt and Henninger, l.c.); from *p*-toluidine 3-sulphonic acid by diazotisation and treatment with cuprous chloride (Wynne and Bruce, l.c.).

$\text{NaA}' + \text{H}_2\text{O}$, long needles or flat prisms (Wynne); $\text{NaA}' + 5\text{H}_2\text{O}$ (Hübner and Majert, l.c.); $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$ (Wynne), $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, laminae, $\text{KA}' + \text{H}_2\text{O}$, rectangular plates or prismatic needles (W. and B.); $\text{BaA}'_2 + \frac{1}{2}\text{H}_2\text{O}$ (H. and M.), $\text{BaA}'_2 + \text{H}_2\text{O}$, thin scales, $\text{BaA}'_2 + 2\text{H}_2\text{O}$, rectangular prisms (W. and B.), $\text{BaA}'_2 + 7\text{H}_2\text{O}$ (Engelbrecht, Ber. 1874, 7, 796); $\text{CdA}'_2 + 2\text{H}_2\text{O}$; $\text{PbA}'_2 + 6\text{H}_2\text{O}$; $\text{CuA}'_2 + 10\text{H}_2\text{O}$. When heated with 20 p.c. fuming sulphuric acid at 150° it yields a mixture of the 2:5- and 3:5-disulphonic acids.

Chloride; large elongated hexagonal plates, m.p. 56° (W. and B.).

Amides; spear-shaped crystals, m.p. 156° (W. and B.).

Anilide; small monosymmetric prisms or needles, m.p. 188° (W. and B.).

6-Chlorotoluene 2-sulphonic acid; non-deliquescent laminae, m.p. about 72°, is obtained from the sulphonyl chloride which is produced in a yield of 38.6 p.c., together with other isomerides, by chlorinating toluene *o*-sulphonyl chloride at 75°-90° in presence of antimony pentachloride.

$\text{NaA}' + \text{H}_2\text{O}$, large laminae; $\text{BaA}'_2 + \text{H}_2\text{O}$, small lustrous flakes.

Chloride; large thick white prisms or plates, softening at 71°, m.p. 72°.

Amide; glistening scales, m.p. 180°. On oxidation with alkaline permanganate at 96°-97° in the presence of carbon dioxide, it yields 6-chloro-*o*-benzoic sulphinide ('6-chloro-saccharin'), small plates, m.p. 210°-212°. The latter product is more than half as sweet as saccharin, but has a somewhat astringent taste except in very great dilution (Davies, Chem. Soc. Trans. 1921, 119, 878).

6-Chlorotoluene 3-sulphonic acid; from *o*-chlorotoluene and fuming sulphuric acid (Hübner and Majert, l.c.; Wynne, Chem. Soc. Trans. 1892, 61, 1073); from *o*-toluidine 5-sulphonic acid by the diazo-reaction (Wynne, l.c., 1040). It crystallises with $\frac{1}{2}\text{H}_2\text{O}$.

$\text{NH}_4\text{A}' + \text{H}_2\text{O}$; $\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, thin plates; $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, large quadric tables or scales; $\text{CaA}'_2 + 2\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, leaflets or long thin prisms; $\text{PbA}'_2 + 2\text{H}_2\text{O}$; $\text{CuA}'_2 + \frac{1}{2}\text{H}_2\text{O}$.

The potassium salt on sulphonation with 20 p.c. fuming sulphuric acid at 150° yields *o*-chlorotoluene 3:5-disulphonic acid, which is also produced by sulphonating *o*-chlorotoluene under similar conditions.

Chloride; long, pearly prisms, m.p. 60° or 65°.

Bromide; thin flat prisms, m.p. 67.5°.

Amide; thin glistening scales, m.p. 123°.

Anilide; thin irregular scales or anorthic plates, m.p. 92° (Wynne, l.c.; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 731).

2-Chlorotoluene 4-sulphonic acid; from *o*-toluidine 4-sulphonic acid by diazotisation and treatment with cuprous chloride (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 766); by hydrolysis of the amide with hydrochloric acid at 150° (Payan, Ann. 1883, 221, 213).

$\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, large hexagonal plates (W. and B.); anhydrous pearly needles (P.); $\text{BaA}'_2 + \frac{1}{2}\text{H}_2\text{O}$.

small scales; $\text{BaA}'_2 + \text{H}_2\text{O}$, thin scales (W. and B.), anhydrous (P.); CaA'_2 , glistening rhombic leaflets (P.).

Chloride; long massive prisms, m.p. 37° , b.p. $178^\circ/36$ mm. (W. and B.; Davies, Chem. Soc. Trans. 1921, 119, 860).

Amide; in the usual manner (W. and B.) or by treating the sulphonamide of diazoaminotoluene with hydrochloric acid (P.). Long slender needles, m.p. 137° (Davies).

Anilide; rhomb-shaped plates, m.p. 96° (W. and B.).

On sulphonation with 35 p.c. fuming sulphuric acid at 150° potassium *o*-chlorotoluene 4-sulphonate yields a mixture of the 4:5- and 4:6-disulphonic acids (W. and B.).

2:3-Dichlorotoluene sulphonic acid; 2:3-dichlorotoluene is stated by Wynne and Greeves (Chem. Soc. Proc. 1895, 11, 151) and Wynne (Chem. Soc. Trans. 1892, 61, 1045) to yield two sulphonic acids on sulphonation, which are separated by their barium salts. The acid from the less soluble barium salt yields a very soluble *chloride*, radiating needles, m.p. 45° , and an *amide*, m.p. 221° , whilst that from the more soluble barium salt is the 5-sulphonic acid, and yields a *chloride*, prisms, m.p. 85° , *amide*, m.p. 183° . Cohen and Dakin (Chem. Soc. Trans. 1901, 79, 1129) could only isolate one sulphonic acid, forming the sulphonamide, m.p. 222° .

$\text{NaA}' + \text{H}_2\text{O}$, large pearly leaflets; $\text{CaA}'_2 + \text{H}_2\text{O}$, leaflets; $\text{BaA}'_2 + \text{H}_2\text{O}$, leaflets (Seelig, Ann. 1887, 237, 159).

2:4-Dichlorotoluene 5-sulphonic acid; by sulphonation of 2:4-dichlorotoluene.

$\text{NaA}' + 1\frac{1}{2}\text{H}_2\text{O}$, long thin needles; $\text{CaA}'_2 + 3\text{H}_2\text{O}$, long thin needles; $\text{BaA}'_2 + 2$ or $4\text{H}_2\text{O}$ (Seelig; Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151; Cohen and Dakin).

Chloride; elongated scales or hard prisms, m.p. 71° (W. and G.; C. and D.); *amide*, m.p. 176° - 177° (W. and G.; C. & D.).

2:5-Dichlorotoluene *p*-sulphonic acid; (see 2:3:6-trichlorotoluene *p*-sulphonic acid); by chlorination of toluene *p*-sulphonic acid (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920). *Chloride* is formed together with 2:6-dichlorotoluene *p*-sulphonyl chloride by chlorination of 2-chlorotoluene *p*-sulphonyl chloride (Davies, Chem. Soc. Trans. 1921, 119, 874).

2:5-Dichlorotoluene sulphonic acid; by sulphonation of 2:5-dichlorotoluene.

KA' , long needles which break up into a crystalline powder; $\text{NaA}' + 1\frac{1}{2}\text{H}_2\text{O}$, long slender needles; $\text{BaA}'_2 + \text{H}_2\text{O}$, diamond-shaped plates and large prismatic needles (Wynne, l.c.).

Chloride; brownish coloured tables, m.p. 43° (W.) or colourless plates, m.p. 46° (C. and D.).

Amide; long thin flat needles, m.p. 191° - 192° (W.; C. and D.; cf. Seelig, Ann. 1887, 237, 159).

2:6-Dichlorotoluene *p*-sulphonic acid; colourless deliquescent plates.

$\text{NaA}' + \text{H}_2\text{O}$, colourless fan-like needles; $\text{BaA}'_2 + 3\text{H}_2\text{O}$, minute silky needles.

Chloride; by chlorinating at 65° - 70° a fused mass of 2-chloro-*p*-toluene sulphonyl chloride for 2 hours until the necessary increase in weight has been attained. Large flat plates, m.p. 69° . A substance, hair-like colourless needles, m.p. 218° , apparently pentachlorotoluene, is obtained as a by-product.

Amide; scales, m.p. 191° (Davies, Chem. Soc. Trans. 1921, 119, 871).

2:6-Dichlorotoluene sulphonic acid; by sulphonation of 2:6-dichlorotoluene.

Chloride; prismatic needles, m.p. 60° .

Amide; m.p. 204° (Wynne and Greeves, l.c.; cf. Cohen and Dakin, l.c.).

3:4-Dichlorotoluene sulphonic acid; from 3:4-dichlorotoluene and 5 p.c. fuming sulphuric acid.

KA' , long thin prismatic needles; NaA' , long slender brittle needles; $\text{BaA}'_2 + 2(1)\text{H}_2\text{O}$, long slender needles.

Chloride; long monosymmetric prisms, m.p. 82° .

Amide; elongated prisms, m.p. 189° (Wynne, Chem. Soc. Trans. 1892, 61, 1060) or 190° - 191° (Cohen and Dakin, l.c.).

3:5-Dichlorotoluene sulphonic acid; by sulphonation of 3:5-dichlorotoluene.

Chloride; thick prisms, m.p. 45° .

Amide; needles, m.p. 168° - 169° (Wynne and Greeves; Cohen and Dakin).

2-Chlorotoluene 3:5-disulphonic acid; by sulphonating 2-chlorotoluene 5-sulphonic acid and from *o*-toluidine 3:5-disulphonic acid by the diazo-reaction. Very small needles.

$\text{K}_2\text{A}'' + 2\frac{1}{2}\text{H}_2\text{O}$, massive irregular crystals, or $+2\text{H}_2\text{O}$, small needles; $\text{BaA}'' + 4\frac{1}{2}\text{H}_2\text{O}$, minute needles.

Chloride; short slender needles, m.p. 85° .

Anilide; small elongated flat prisms, m.p. 183° (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 750).

2-Chlorotoluene 4:5-disulphonic acid; by sulphonation of potassium *o*-chlorotoluene-4-sulphonate and from *o*-toluidine 4:5-disulphonic acid by the diazo-reaction.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, long prismatic needles; $\text{BaA}'' + 2\text{H}_2\text{O}$, small rectangular prisms (W. and B.).

Chloride; plates or monosymmetric prisms, m.p. 158° .

Anilide; small prisms, m.p. 183° (W. and B.).

2-Chlorotoluene 4:6-disulphonic acid; from 2-chlorotoluene 4-sulphonic acid and 35 p.c. fuming sulphuric acid at 150° .

$\text{K}_2\text{A}'' + 2\text{H}_2\text{O}$, large prisms; $\text{BaA}'' + 6\text{H}_2\text{O}$, microscopic prisms; $\text{BaA}'' \cdot \text{K}_2\text{A}'' + 3\text{H}_2\text{O}$, very small needles.

Chloride; octahedral prisms or four-sided plates, m.p. 88° .

Anilide; small plates, m.p. 180° (W. and B.).

4-Chlorotoluene 2:5-disulphonic acid; from *p*-toluidine 2:5-disulphonic acid. Small scales.

$\text{K}_2\text{A}'' + 2\text{H}_2\text{O}$, small scales; $\text{BaA}'' + \text{H}_2\text{O}$, minute prisms.

Chloride; very small prisms, m.p. 144° .

Anilide; small diamond-shaped scales or large prisms, m.p. 245° (W. and B.).

4-Chlorotoluene 2:6-disulphonic acid; by sulphonation of 4-chlorotoluene 2-sulphonic acid with 20 p.c. fuming sulphuric acid at 150° .

$\text{K}_2\text{A}''$, anhydrous scales; $\text{BaA}'' + 2\frac{1}{2}\text{H}_2\text{O}$, small prisms.

Chloride; large prisms or large pale-yellow monosymmetric plates, m.p. 108° .

Anilide; small lustrous scales, m.p. 188° (W. and B.).

4-Chlorotoluene 3:5-disulphonic acid; from *p*-toluidine 3:5-disulphonic acid. Long colourless needles.

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rapidly becomes anhydrous on exposure to air; $\text{BaA}' + 3\text{H}_2\text{O}$, prisms.

Chloride; small monosymmetric prisms from benzene, containing $\frac{1}{2}\text{C}_6\text{H}_5$, which is lost rapidly at 140° , or plates from light petroleum. Both forms melt at 118° with previous softening (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 740; Pope, Z. f. Krist., 1900, 31, 128).

2:3:4-Trichlorotoluene; when shaken with fuming sulphuric acid at 60° yields two sulphonic acids, α -acid, $\text{NaA}' + 4\frac{1}{2}\text{H}_2\text{O}$, fine needles or leaflets, and the β -acid, $\text{NaA}' + \text{H}_2\text{O}$, leaflets (Seelig, Ann. 1887, 237, 136).

2:3:6-Trichlorotoluene 4-sulphonic acid; obtained together with the 2:5-dichloro-isomeride by neutralising 680 grams of toluene p -sulphonic acid with sodium hydroxide dissolved in sufficient water to make about 11 litres and chlorinating until 10 c.c. of the solution have acquired an acidity equivalent to 5.5 c.c. of N -alkali. Nearly the whole of the sodium trichlorosulphonate crystallises, and the dichlorosulphonate is recovered practically pure by evaporating the mother-liquor (B. D. C., Green and Clibbens, Eng. Pat. 169025 of 1920).

3:4:5-Trichlorotoluene sulphonic acid; $\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, needles; KA' , scales; $\text{BaA}' + \text{H}_2\text{O}$, scales.

Chloride; short needles, m.p. 88° (Wynne, Chem. Soc. Trans. 1892, 61, 1069).

2-Bromotoluene 4-sulphonic acid; from o -toluidine 4-sulphonic acid by the diazo-reaction (Hayduck, Ann. 1874, 172, 205); together with p -bromotoluene and p -bromobenzyl bromide by brominating potassium toluene p -sulphonate (Miller, Chem. Soc. Trans. 1892, 61, 1027).

KA' , white plates (M.); $\text{BaA}' + 2\text{H}_2\text{O}$, plates (M.) or microscopic tables (H.);

$\text{PbA}' + 2\frac{1}{2}\text{H}_2\text{O}$ (H.).

Chloride; m.p. 54° (H.).

Amide; microscopic prisms, m.p. 151° (H.).

2-Bromotoluene 5-sulphonic acid; from o -bromotoluene by sulphonation (Miller, Chem. Soc. Trans. 1892, 61, 1029; Hübner and Post, Ann. 1873, 169, 31; cf. Dmochowsky, Ber. 1872, 5, 333); from brominated p -toluidine 3-sulphonic acid by elimination of the amino-group (Fechmann, Ann. 1874, 173, 212); from o -toluidine by sulphonation and replacement of the amino-group by bromine (Pagel, Ann. 1875, 176, 394; Neville and Winther, Chem. Soc. Trans. 1880, 37, 628; Ber. 1880, 13, 1943; Wynne, Chem. Soc. Trans. 1892, 61, 1041; cf. Gerver, Ann. 1873, 169, 384).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, striated prisms; $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}' + 2\text{H}_2\text{O}$, rhomboidal tables; $\text{PbA}' + 2\text{H}_2\text{O}$ (H. and P.) or $3\text{H}_2\text{O}$ (P.).

Chloride; elongated flat prisms, m.p. 61° (W.), 56° (N. and W.), 53° (P.).

Bromide; glistening scales, m.p. 63.5° (W.). *Amide*, needles, m.p. 147° (W.; N. and W.) or 135° (P.).

2-Bromotoluene 6-sulphonic acid; in small yield, together with 2-bromotoluene 5-sulphonic acid by sulphonating o -bromotoluene. The two acids are separated by means of their barium salts, when the barium salt of the 5-acid crystallises first.

KA' ; $\text{BaA}' + \text{H}_2\text{O}$, minute scales (Miller, l.c.).

According to Wroblewsky (Ann. 1873, 168, 186), m -bromotoluene when dissolved in fuming

sulphuric acid yields three sulphonic acids of which the α -acid is formed in greatest quantity. Separation is effected by means of their barium salts.

Grete (Ber. 1874, 7, 795; 1875, 8, 565; Ann. 1875, 177, 233) only obtained one acid corresponding to the α -acid of Wroblewsky.

α -Acid or 3-bromotoluene 2-sulphonic acid; $\text{BaA}' + \text{H}_2\text{O}$; $\text{CaA}' + 2\text{H}_2\text{O}$; $\text{SrA}' + \text{H}_2\text{O}$; $\text{MgA}' + 6\text{H}_2\text{O}$; $\text{PbA}' + 3\text{H}_2\text{O}$; $\text{CuA}' + 4\text{H}_2\text{O}$.

β -Acid or 3-bromotoluene 6-sulphonic acid; KA' ; $\text{CaA}' + 2\frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}' + 1\frac{1}{2}\text{H}_2\text{O}$; $\text{PbA}' + 3\text{H}_2\text{O}$.

γ -Acid; formed in smallest quantity; $\text{BaA}' + 2\frac{1}{2}\text{H}_2\text{O}$.

m -Bromotoluene o -sulphonic acid; by bromination of p -toluidine 2-sulphonic acid, followed by elimination of the amino-group (Weckwarth, Ann. 1874, 172, 191).

$\text{NaA}' + \frac{1}{2}\text{H}_2\text{O}$, scales or nodules; $\text{KA}' + \text{H}_2\text{O}$, yellow rhombic plates; $\text{SrA}' + 2\frac{1}{2}\text{H}_2\text{O}$, yellow needles; $\text{BaA}' + 2\frac{1}{2}\text{H}_2\text{O}$, scales or plates; $\text{PbA}' + 3\frac{1}{2}\text{H}_2\text{O}$, grouped prisms; $\text{PbA}' + 5\text{H}_2\text{O}$, yellow prisms; $\text{CuA}' + \frac{1}{2}\text{H}_2\text{O}$; yellowish-green plates or thick prisms.

Chloride; liquid, solidifying in a freezing mixture.

Amide; thick yellow needles from chloroform, m.p. 162° – 165° .

This acid appears to be identical with Wroblewsky's β -acid, although some of the salts differ in the content of water of crystallisation.

3-Bromotoluene 5-sulphonic acid; from 3-bromo- o -toluidine 5-sulphonic acid or 5-bromo- p -toluidine 3-sulphonic acid by elimination of the amino-group (Neville and Winther, Chem. Soc. Trans. 1880, 41, 420; Ber. 1880, 13, 1944).

Chloride; m.p. 52° (N. and W.).

Amide; m.p. 138° – 139° (N. and W.).

Bromotoluene sulphonic acid; from toluene by sulphonation, nitration, reduction and replacement of the amino-group by bromine (Weckwarth, Ann. 1874, 172, 193; Hayduck, *ibid.* 1875, 177, 57). $\text{BaA}' + \text{H}_2\text{O}$.

Chloride; oil, solidifying on cooling.

Amide; nodules, which do not melt at 230° .

4-Bromotoluene 2-sulphonic acid; chief product, together with the 3-acid by sulphonating p -bromotoluene (Hübner and Post, Ann. 1873, 169, 6; Zeit. f. Chem. 1871, (2) 7, 618; Miller, Chem. Soc. Trans. 1892, 61, 1026) from p -toluidine 2-sulphonic acid by the diazo-reaction (Jensen, Ann. 1874, 172, 237). Free acid, large plates. Oxidised by chromic acid mixture to p -bromosulphobenzoic acid and reduced to toluene o -sulphonic acid by sodium amalgam.

$\text{NaA}' + \text{H}_2\text{O}$; $\text{KA}' + \text{H}_2\text{O}$, scales (Roode, Amer. Chem. J. 1891, 13, 222); $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$ (Miller); $\text{MgA}' + 8\frac{1}{2}\text{H}_2\text{O}$?; $\text{CaA}' + 4\text{H}_2\text{O}$, rhombic needles; $\text{SrA}' + \text{H}_2\text{O}$; $\text{BaA}' + \text{H}_2\text{O}$; $\text{BaA}' + 2\text{H}_2\text{O}$ (M.); $\text{PbA}' + 3\text{H}_2\text{O}$, needles; $\text{PbA}' + 2\text{H}_2\text{O}$ (M.); $\text{CuA}' + 7\text{H}_2\text{O}$.

Chloride; plates, m.p. 35° (H. and P.).

Amide; long fine needles, m.p. 166° – 167° (H. and P.). When oxidised with permanganate it yields p -bromobenzoic sulphimide, which is somewhat sweet with a bitter after-taste (R.).

4-Bromotoluene 3-sulphonic acid; (see above); by sulphonation of p -bromotoluene; from p -toluidine 3-sulphonic acid by replacing the amino-group by bromine (R. Richter, Ann. 1885, 230, 319; Post and Baer, Ann. 1873,

186, 7; Pechmann, *ibid.* 1874, 173, 208; Neville and Winther, Chem. Soc. Trans. 1880, 37, 631). Lamine + H_2O , m.p. $105^\circ\text{--}110^\circ$ (P.). Oxidation with chromic acid mixture yields *p*-bromobenzoic-*m*-sulphonic acid.

$\text{BaA}'_2 + 7\text{H}_2\text{O}$, long rhombic needles; $\text{SrA}'_2 + 7\text{H}_2\text{O}$; $\text{PbA}'_2 + 3\text{H}_2\text{O}$.

Chloride; oil, solidifying on keeping, m.p. 62° (P.; N. and W.).

Amide; long needles, m.p. $151^\circ\text{--}152^\circ$ (H. and P.).

2-Bromotoluene 3:5-disulphonic acid; from *o*-toluidine 3:5-disulphonic acid by the Sandmeyer reaction (Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 749; Hasse, Ann. 1885, 230, 295).

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, small needles; $\text{BaA}'' + 4\text{H}_2\text{O}$, short slender needles (W. and B.).

Chloride; white needles, m.p. 102° .

Anilide; small square prisms or irregular needles, m.p. 194° (W. and B.); the products obtained by Hasse were impure).

4-Bromotoluene disulphonic acid; by passing sulphur trioxide into a mixture of *p*-bromotoluene and sulphuric acid (Kornatzki, Ann. 1883, 221, 192). Very deliquescent crystals. On boiling with nitric acid it yields dibromonitrotoluene disulphonic acid, nitrotoluene disulphonic acid, and disulphobromobenzoic acid.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, fine needles or large rhombic prisms; $\text{BaA}'' + 5\text{H}_2\text{O}$, thick prisms or fine needles or plates; $\text{PbA}'' + 2\text{H}_2\text{O}$, glistening needles.

Chloride; large rhombic plates, m.p. 99° (K.).

Amide; irregular crystals, m.p. above 260° (K.).

p-Bromotoluene disulphonic acid; from *p*-toluidine disulphonic acid by replacement of the amino-group by bromine (Limprieth, Ber. 1885, 18, 2179; Richter, Ann. 1885, 230, 324). Crystalline mass.

$\text{K}_2\text{A}'' + \text{H}_2\text{O}$, silky felted needles; $\text{BaA}'' + 6\text{H}_2\text{O}$, silky needles.

Chloride; prisms, m.p. 133° (R.).

Amide; long prisms, m.p. above 240° .

2:1-Dibromotoluene 5-sulphonic acid; from 2-bromotoluene 5-sulphonic acid by nitration and replacement of the nitro-group by bromine (Schäfer, Ann. 1874, 174, 365). Syrup.

$\text{NaA}' + 2\text{H}_2\text{O}$; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$ (S.).

5:6-Dibromotoluene 3-sulphonic acid; from 3-bromo-*o*-toluidine 5-sulphonic acid by the Sandmeyer reaction (Wynne, Chem. Soc. Trans. 1892, 61, 1038).

$\text{NaA}' + \text{H}_2\text{O}$, long flat needles; KA' , long needles; $\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, long thin needles.

Chloride; small four-sided prisms or needles, m.p. 93° (W.).

Bromide; needles, m.p. 97° (W.).

Amide; small prisms, m.p. 214° (W.).

2:3:5-Tribromotoluene 4-sulphonic acid; from *o*-toluidine *p*-sulphonic acid by dibromination and replacement of the amino-group by bromine (Hayduck, Ann. 1874, 174, 354); or from 3:5-dibromo-*o*-toluidine 4-sulphonic acid by replacement of the amino-group by bromine (Claus and Immel, Ann. 1891, 265, 677). Free acid is deliquescent.

KA' , white needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, white mammillary mass (H.).

Chloride; syrup.

Amide; amorphous powder, charring without melting when heated.

2-(or 6)-Nitrotoluene 3-sulphonic acid; from *p*-toluidine *m*-sulphonic acid by nitration, reduction and elimination of the amino-group (Pechmann, Ann. 1874, 173, 214).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, plates.

Chloride, m.p. 58.5° (Foth, Ann. 1885, 230, 308).

Amide; m.p. 163.5° (F.).

2-Nitrotoluene 4-sulphonic acid; together with other products by nitrating *o*-nitrotoluene *p*-sulphonamide (Reverdin and Crépieux, Ber. 1901, 34, 2992); by sulphonating *o*-nitrotoluene or nitrating toluene *p*-sulphonic acid (Beilstein and Kuhlberg, Ann. 1871, 155, 18; Engelhardt and Bek, Zeit. f. Chem. 1869, (2) 5, 209; Kornatzki, Ann. 1883, 221, 180).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, scales; $\text{PbA}'_2 + 2\text{H}_2\text{O}$. On electrolysis in sulphuric acid solution it yields 6-amino-3-cresol 4-sulphonic acid (Gattermann, Ber. 1894, 27, 1938).

Chloride, by nitration of toluene *p*-sulphonyl chloride. M.p. 45° (van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, 1902, 616; cf. Otto and Grüber, Ann. 1868, 145, 23) or 36° (Reverdin and Crépieux). A suspension in alcoholic sulphuric acid is readily reduced at a lead electrode below 20° . The product is 2-aminotolyl-4-mercaptan sulphate which readily changes to the sulphate of 2-aminotolyl-4-disulphide on keeping in a loosely closed vessel (Fichter and Bernouilli, Ber. 1909, 42, 4308).

Amide; four-sided rhombic columns, m.p. 128° (O. and G.), 139° (K.), 144° (Reverdin and Crépieux, Ber. 1901, 34, 2992, 2996; Neale, Ann. 1880, 203, 73). When heated with fuming nitric acid two mononitrotoluene sulphonic acids, of which one is 2-nitrotoluene 4-sulphonic acid, and a dinitrotoluene sulphonic acid are obtained (Reverdin and Crépieux, *l.c.*).

For the preparation and properties of the *anilide*, *p*-toluidide, 2:4-dinitroanilide, α - and β -naphthalide, the diamide of *o*-, *m*-, and *p*-phenylenediamine; and also the esters of *phenol*, *o*-, *m*-, and *p*-cresol, *p*-nitrophenol, *resorcinol* and *nitroresorcinol*, &c., see Reverdin and Crépieux (Ber. 1901, 34, 2992, 2996; 1902, 35, 314, 1439; Bull. Soc. chim. 1901, (3) 25, 1044; 1902, (3) 27, 745). For the *N*-halogen derivative of the amides, see Chattaway (Chem. Soc. Trans. 1905, 87, 145).

2-Nitrotoluene 5-sulphonic acid; by heating the diazo-compound of 2-nitro-*p*-toluidine 5-sulphonic acid with absolute alcohol at 100° (Foth, Ann. 1885, 230, 305).

KA' , reddish-yellow thick prisms; barium and lead salts, readily soluble in water and alcohol.

Chloride; thick prisms, m.p. 50° (F.).

Amide; long glistening needles, m.p. 133.5° (F.).

m-Nitrotoluene sulphonic acid; by sulphonating *m*-nitrotoluene (Beilstein and Kuhlberg, Ann. 1870, 155, 27).

$\text{BaA}'_2 + 2\text{H}_2\text{O}$, nodules; $\text{PbA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, small granules.

von Pagel (Ann. 1875, 176, 304) has described a nitrotoluene sulphonic acid obtained by nitrating *p*-toluidine *o*-sulphonic acid and eliminating the amino-group.

$\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, tufts of red needles.

4-Nitrotoluene 2-sulphonic acid; by nitrating toluene *o*-sulphonic acid or by sulphonating

p-nitrotoluene (Jaworsky, *Zeit. f. Chem.* 1865, 1, 222; Beilstein and Kuhlberg, *l.c.*; Jensen, *Ann.* 1874, 172, 230; Hart and Kernen, *Ber.* 1877, 10, 1046; *Amer. Chem. J.* 1879, 1, 349; Schwanert, *Ann.* 1877, 186, 351; *Ber.* 1877, 10, 29; Noyes, *Amer. Chem. J.* 1886, 8, 168; Haussner, *Bull. Soc. chim.* 1890, (3) 3, 797; by sulphonating *p*-cymene to its *o*-sulphonic acid and treating the sulphonation mixture at 40°–60° with nitric and sulphuric acids (Hintikka, *Eng. Pat.* 123548 of 1918; *Can. Pat.* 200291; *cf.* Osaakeytio, *D. R. P.* 327051 of 1918). Prisms or rhombic tables + 2H₂O, or prisms + aq., m.p. 133.5° (Hintikka, *Ann. Acad. Sci. Fennicae*, 1917 (A), 10, 1).

For the action of sodium hydroxide, see Fischer and Hepp, *Ber.* 1893, 26, 2233; 1895, 28, 2281; Bender, *ibid.* 1895, 28, 422; Green and Wahl, *ibid.* 1897, 30, 3099; Kalle & Co., *D. R. P.* 79241 of 1892; Cassella & Co., *D. R. P.* 75369 of 1893; Leonhardt & Co., *D. R. PP.* 96107 of 1893, 46252 of 1888, and 38735 of 1886; for the action of zinc and sodium hydroxide, see Neale, *Ann.* 1880, 203, 80; Kornatzki, *Ann.* 1883, 221, 182; Bender and Schultz, *Ber.* 1886, 19, 3235; for the action of sodium hypochlorite, see Ris and Simon, *Ber.* 1897, 30, 2618; 1898, 31, 354; Geigy & Co., *Fr. Pat.* 269466; *D. R. P.* 98760 of 1897; Green and Wahl, *Ber.* 1897, 30, 3097; 1898, 31, 1078; Levinstein, *D. R. P.* 106961 of 1897; Green, *Chem. Soc. Trans.* 1904, 85, 1424; for dye formation by condensation with *p*-diamines in presence of alkalis, see Geigy & Co., *Eng. Pat.* 15671 of 1890; *U.S. Pat.* 455952; *Fr. Pat.* 208626; *D. R. PP.* 50290 of 1890, 75326 of 1893.

NH₄A', long prisms not decomposed by sulphuric acid at 100°; NaA' + 2H₂O, prisms (Haussner); KA' (Noyes); CaA' + H₂O (Schwanert), or + 4H₂O, needles (H. and R.), or + 6H₂O (Hart); BaA' + 3H₂O (Jaworsky); PbA' + 3H₂O, needles (Beilstein and Kuhlberg), or + 2H₂O (Schwanert).

Chloride; rhombic tables, m.p. 43°–44.5°.

Amide; long needles, m.p. 186°. With permanganate it is oxidised to anhydro-*p*-nitro-sulphaminobenzoic acid (Noyes).

o-Nitrobenzyl sulphonic acid; by boiling *o*-nitrobenzyl chloride with sodium sulphite solution (*Eng. Fischer*, *Fr. Pat.* 193686; *D. R. P.* 58722 of 1888; Marckwald and Frahn, *Ber.* 1898, 31, 1855). Very hygroscopic crystals.

NaA' + H₂O, silver-white scales; BaA' + 3H₂O; AgA' + H₂O, needles.

m-Nitrobenzyl sulphonic acid; from *m*-nitrobenzyl chloride and sodium sulphite (Purgotti and Monti, *Gazz. chim. ital.* 1900, 30, ii. 247). White crystals + H₂O, m.p. 74°.

NaA' + H₂O, needles; BaA' + 3H₂O; PbA', needles; AgA', leaflets.

Chloride; m.p. 100°.

Amide; m.p. about 159° (decomp.).

Methyl ester; m.p. 77°.

p-Nitrobenzyl sulphonic acid; from *p*-nitrobenzyl chloride and alkali sulphites (Dahl & Co., *D. R. P.* 55138 of 1889; Purgotti and Monti, *l.c.*); by nitration of barium benzyl sulphonic acid (Böhler, *Ann.* 1870, 154, 55). A little acid is formed also (Mohr, *ibid.* 1883, 221, 46). If the crude mixture is oxidised with alkaline potassium permanganate *p*-nitrobenzoic acid and a little *o*-nitrobenzoic acid are formed.

The following salts are described by Böhler, and are probably those of *p*-nitrobenzyl sulphonic acid.

BaA' + 2H₂O, needles; PbA' + 3H₂O, needles; PbOHA', crystals.

Chloride; oil.

Amide; prisms, m.p. 204° (Mohr).

Nitrotoluene disulphonic acid; together with other acids by boiling *p*-bromotoluene disulphonic acid with fuming nitric acid (Kornatzki, *Ann.* 1883, 221, 198).

K₂A', fine needles.

The same acid (?) is obtained by warming toluene disulphonic acid, obtained from *p*-bromotoluene disulphonic acid and sodium amalgam, with nitric acid for 2 hours (Kornatzki, *l.c.*, 201).

K₂A'', fine needles; BaA'' + 3H₂O, small needles.

2:6-Dinitrotoluene 4-sulphonic acid; by nitration of toluene *p*-sulphonic acid (Beilstein and Kuhlberg, *Ann.* 1870, 155, 21; Schwanert, *Ann.* 1877, 186, 342; *Ber.* 1877, 10, 28; *cf.* Marckwald, *Ann.* 1893, 274, 349) in almost theoretical yield by nitrating toluene *p*-sulphonyl chloride with fuming nitric and concentrated sulphuric acids (Reverdin and Crépieux, *Ber.* 1901, 34, 2992; *Bull. Soc. chim.* 1901, (3) 25, 1043).

Pale yellow flat rhombic prisms + 2H₂O, m.p. 165° (anhydrous) (Schwanert).

NH₄A', flat rhombic prisms; KA', CaA' + 2H₂O, needles or scales; BaA' + 4H₂O, prisms; PbA' + 2H₂O, clumps of needles; PbA' + 3H₂O, laminae (Schwanert).

Chloride; rhombic needles, m.p. 125° (S.).

Amide; white needles or laminae, m.p. 203° (S.).

Dinitrobenzyl sulphonic acid; by warming nitrobenzyl sulphonic acid with nitric and sulphuric acids (Mohr, *Ann.* 1883, 221, 225).

KA', yellow leaflets; BaA' + 4H₂O, yellowish nodules; PbA' + 4H₂O, yellow crystals.

Chloronitrotoluene sulphonic acid; from liquid (α)-chloronitrotoluene and fuming sulphuric acid (Wroblewsky, *Ann.* 1873, 168, 204).

BaA' + 4H₂O, needles.

5-Chloro-4-nitrotoluene 2-sulphonic acid; by successive sulphonation and nitration of *m*-chlorotoluene.

BaA' + 2H₂O, yellowish-brown plates or needles (Schraube and Romig, *Ber.* 1893, 26, 579).

6-Chloro-4-nitrotoluene 2-sulphonic acid; slightly hygroscopic, colourless flattened needles (Davies, *Chem. Soc. Trans.* 1921, 119, 881, 885).

NaA' + H₂O, plates; BaA' + H₂O, needles.

Chloride; formed in about 60 p.c. yield together with about 40 p.c. of 6-chloro-3-nitrotoluene *o*-sulphonyl chloride by nitrating 6-chlorotoluene *o*-sulphonyl chloride at 20°–30° (D.).

Amide; minute needles, m.p. 161°. A red colour is formed by boiling for a few minutes with ammonia solution (D.).

6-Chloro-3-nitrotoluene *o*-sulphonic acid (see above). Very deliquescent microscopic prisms.

NaA' + 3H₂O, needles; BaA' + 7H₂O, small needles, decomposing at about 140°.

Chloride; long colourless needles, m.p. 60°. When boiled with sodium hydroxide the sulphonyl group is replaced by hydroxyl (Davies, *l.c.*).

2. *Chloro-5-nitrotoluene p-sulphonic acid*; small non-deliquescent crystals which after drying at 120° melt at 123°–128° (Davies).

$\text{NaA}' + 2\text{H}_2\text{O}$, pale yellow or colourless needles; $\text{BaA}' + 2\text{H}_2\text{O}$, colourless scales.

Chloride; formed together with 2-chloro-6-nitrotoluene *p*-sulphonyl chloride by gradual addition of 2-chlorotoluene *p*-sulphonyl chloride with stirring to a cold mixture of nitric acid (D 1.5) and sulphuric acid.

Large colourless prisms, m.p. 99.2° (D.).

Amide, small needles, m.p. 181° (D.).

2-*Chloro-6-nitrotoluene p-sulphonic acid* (see above); deliquescent plates.

NaA' , colourless microscopic plates; KA' , colourless laminæ; $\text{BaA}' + 3\text{H}_2\text{O}$, colourless leaflets (Davies).

Chloride; long colourless needles, m.p. 70° (D.).

Amide; needles or scales, m.p. 182° (D.).

o-Bromonitrotoluene m-sulphonic acid; by nitration of barium *o*-bromotoluene sulphonate (Müller, Ann. 1873, 169, 42; Pagel, *ibid.* 1875, 176, 299).

Free acid is crystalline and very deliquescent.

$\text{NaA}' + \text{H}_2\text{O}$; KA' ; $\text{BaA}' + \text{H}_2\text{O}$, small needles or nodules; $\text{PbA}' + 2\text{H}_2\text{O}$, microscopic crystals.

o-Bromonitrotoluene p-sulphonic acid; by nitration of barium *o*-bromotoluene-*p*-sulphonate with nitric acid (D 1.5) (Hayduck, Ann. 1874, 174, 347); from *o*-toluidine *p*-sulphonic acid by nitration and replacement of the amino-group by bromine (Hayduck, *ibid.* 1874, 172, 219). Microscopic needles.

$\text{BaA}' + 3\text{H}_2\text{O}$, needles.

Chloride; crystals which do not melt at 220°.

Amide; does not melt at 200°.

m-Bromonitrotoluene o-sulphonic acid; by nitration of barium (β) *m*-bromotoluene *o*-sulphonate (Wroblewsky, Ann. 1873, 168, 169).

$\text{CaA}' + 4\frac{1}{2}\text{H}_2\text{O}$, large prismatic crystals; $\text{BaA}' + 3\frac{1}{2}\text{H}_2\text{O}$, needles; $\text{PbA}' + 3\text{H}_2\text{O}$, prismatic crystals.

m-Bromonitrotoluene o-sulphonic acid; by nitration of *m*-bromotoluene *o*-sulphonic acid (Weckwarth, Ann. 1874, 172, 200).

NaA' , yellow granules; $\text{CaA}' + 5\text{H}_2\text{O}$, pale yellow prisms; $\text{BaA}' + 3\frac{1}{2}\text{H}_2\text{O}$, yellow needles.

Nitro-p-bromotoluene o-sulphonic acid; by nitrating *p*-bromotoluene *o*-sulphonic acid (Hässelbarth, Ann. 1873, 169, 22). Deliquescent laminæ.

$\text{BaA}' + 2\text{H}_2\text{O}$; $\text{SrA}' + 7\text{H}_2\text{O}$; $\text{PbA}' + 3\text{H}_2\text{O}$; $\text{CuA}' + 6\text{H}_2\text{O}$; AgA' .

Nitro-p-bromotoluene m-sulphonic acid; by nitrating barium *p*-bromotoluene *m*-sulphonate (Hässelbarth, *l.c.*). Small deliquescent needles.

$\text{BaA}' + 5\text{H}_2\text{O}$ or H_2O ; $\text{SrA}' + 5\text{H}_2\text{O}$;

$\text{PbA}' + 2\frac{1}{2}\text{H}_2\text{O}$.

Dibromonitrotoluene sulphonic acid; together with other acids by boiling *p*-bromotoluene disulphonic acid with nitric acid (Kornatzki, Ann. 1883, 221, 197).

$\text{KA}' + \text{H}_2\text{O}$, nodules; $\text{BaA}' + 3\frac{1}{2}\text{H}_2\text{O}$, thin plates.

AMINO DERIVATIVES.

o-Toluidine; by reduction of *o*-nitrotoluene (Beilstein and Kuhlberg, Ann. 1871, 158, 77);

by catalytic reduction by passing the vapours mixed with hydrogen over heated reduced copper or nickel (Sabatier and Senderens, Compt. rend. 1901, 133, 321); and by other methods of catalytic reduction (Hänke and Browne, J. Physikal. Chem. 1923, 27, 52); by heating 1 part of *o*-cresol with 1 part of ammonium chloride and 4 parts of ammonium-zinc chloride for 40 hours at 330°–340° (Merz and Müller, Ber. 1887, 20, 547); together with *p*-toluidine by the action of hydroxylamine on toluene in presence of aluminium or ferric chloride (Graebe, Ber. 1901, 34, 1778). Colourless, thick, refractive liquid, which does not solidify at –20°, b.p. 199.7°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 621) or 198.4°–198.5°/736.4 mm. (Brühl, Ann. 1880, 200, 189); D_4^{25} 1.0112; D_{15}^{25} 1.0031; D_{25}^{25} 0.997; D_{50}^{25} 0.9852 (Perkin, Chem. Soc. Trans. 1896, 69, 1245); D_{50}^{25} 1.003; D_{55}^{25} 0.998 (B. and K.); magnetic rotatory power at 15° 17.18 (Perkin); heat of combustion at constant volume 963.8 Cal.; at constant pressure 964.7 Cal. (Petit, Ann. Chim. 1889, [6] 18, 152; Compt. rend. 1888, 107, 266); refractive index, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 216); surface tension, Dutoit and Friderich (Compt. rend. 1900, 130, 328); cryoscopic behaviour, Ampola and Rimatori, (Gazz. chim. ital. 1897, 27, 1, 43, 63). May be separated from *p*-toluidine by means of the acid oxalates (Ihle, J. pr. Chem. 1876, (2) 14, 449; Bindschedler, Ber. 1873, 6, 448; Miniati, Booth and Cohen, J. Soc. Chem. Ind. 1887, 6, 418); by freezing (Rosenstiehl, Bull. Soc. chim. 1871, (2) 17, 7); by means of the nitrate (Schad, Ber. 1873, 6, 1361); by means of the hydrochloride, sulphates or phosphates (Lewy, Zeitsch. anal. Chem. 1884, 23, 269; Ber. 1886, 19, 1717, 2728; D. R. P. 22139 of 1882; cf. Wülling, Ber. 1886, 19, 2132). The crude product contains about 63 p.c. *o*-, 2 p.c. *m*-, and 35 p.c. *p*-toluidine.

According to Friewell (J. Soc. Chem. Ind. 1908, 27, 258) the best method of separation is to freeze in presence of water or ice. *p*-Toluidine forms a hydrate (Walker and Beveridge, Chem. Soc. Trans. 1907, 91, 1797) which can be readily separated from the other isomerides. A full description of the method and apparatus is given by Friewell.

The proof that 2-aminotoluene is identical with 6-aminotoluene is given by Wroblewsky (Ann. 1878, 192, 213).

Estimation of aniline and *o*- and *p*-toluidine, see Reinhardt, Zeitsch. anal. Chem. 1894, 33, 90; Dobriner and Schranz, *ibid.* 1895, 34, 734; Liebmann and Studer, J. Soc. Chem. Ind. 1899, 18, 111; for estimation of small quantities of *p*-toluidine in *o*-toluidine, see Haasemann, Zeitsch. anal. Chem. 1887, 26, 750; estimation of *o*- and *p*-toluidine by specific gravity determination, see Zeitsch. anal. Chem. 1885, 24, 459; by solidification point of the mixed acetyl derivatives (Holleman, Rec. trav. chim. 1903, 27, 438; Proc. K. Akad. Wetensch. Amsterdam, 1904, 7, 395).

For other methods, see Raabe, Chem. Zeit. 1891, 15, 116, 179. For the two modifications of *o*-toluidine, see Ostrowski, Zeitsch. physikal. Chem. 1906, 57, 341).

A colour test to distinguish between aniline

and the three toluidines is described by Murray (Chem. News, 1923, 130, 23).

Salts (see Reilstein and Kuhlberg, Ann. 1870, 156, 75; Rosenstiehl, *l.c.*), $B'HCl + H_2O$, scales, m.p. $214.5-215^\circ$, b.p. $240.2^\circ/728$ mm. or $243.2^\circ/760$ mm. (Ullmann, Ber. 1898, 31, 1699); $B'_2H_3Cl, CuCl_2$ (Pomey, Compt. rend. 1887, 104, 365); $B'HB$, trimetric prisms (Stadel, Ber. 1883, 16, 28); $B'HI$, slender rhombic prisms (Stadel); $B'HNO_3$, leaflets; $B'_2H_3SO_4$, small crystals; $B'_2H_3SO_4$ (Wellington and Tollens, Ber. 1885, 18, 3313); $B'_2H_3SO_4 + H_2O$ (Hitzel, Bull. Soc. chim. 1894, (3) 11, 1054); $B'_2H_3PO_4$ (Lewy, Ber. 1886, 19, 1718); $B'_2H_3ClO_4$, m.p. 95° (Reisser, Ber. 1888, 21, 1260); oxalate, small plates; $B'_2H_3FeC_2N_6$ (Eisenberg, Ann. 1880, 205, 271; Ber. 1879, 12, 2234); $B'_2H_3SnCl_4$, silky needles, m.p. 164° ; $B'_2H_3SnCl_4 + H_2O$, short pale pink needles, beginning to decompose at 210° (Druce, Chem. Soc. Trans. 1918, 113, 716); $(B'HCl)_2ZnCl_2 + 2H_2O$, tables (Base, Amer. Chem. J. 1898, 20, 653); $B'_2H_3HgCl_2$, plates (Swan, *ibid.* 1898, 20, 622); $B'HCl \cdot HgCl_2$ (Swan); $(B'HCl)_2HgCl_2$ (Swan); $B'HCl \cdot HgBr_2$ (Swan); $B'HClSnCl_2 + \frac{1}{2}H_2O$, colourless prisms (Slagle, Amer. Chem. J. 1898, 20, 640); $(B'HCl)_2SnCl_2 + 2H_2O$ (Slagle); $(B'HCl)_2SbCl_3$ (Higbee, *ibid.* 1900, 23, 150); $(B'HCl)_2BiCl_3$ (Hauser and Vanino, Ber. 1900, 33, 2271); $(B'HBBr)_2ZnBr_2 + 2H_2O$ (Base); $(B'HBBr)_2SbBr_3$ (Higbee); $B'_2H_3PtCl_6$, decomposed by boiling water, unlike the salt of *p*-uidine (de Coninck, Bull. Soc. chim. 1886, 45, 131); $B'_2ZnCl_2 + 2H_2O$ (Lachovich, *ibid.* 1888, 9, 513); B'_2HgCl_2 , m.p. 115° (lein, Ber. 1878, 11, 743); B'_2MnCl_2 ; $HgBr_2$, leaflets, m.p. 104° (Klein, Ber. 1879, 835); B'_2ZnBr_2 (Leeds, Jahresbericht, 82, 503); B'_2ZnI_2 ; B'_2CdI_2 ; $B'_2HgC_2N_6$; $B'_2HgC_2N_6$; $B'_2HgCu(SO_4)_2$ (Deniges, Compt. *ibid.* 1870, 112, 870); $B'_2HgH_3(SO_4)_2 + H_2O$; H_3PO_4 and $B'_2H_3PO_4$ could not be prepared; $HSCN(CrSCN) \cdot 2NH_3$, red plates (Christensen, pr. Chem. 1892, (2) 45, 362); *picrate* mononitric crystals, m.p. $212-215^\circ$ (Jerusalem, Chem. c. Trans. 1909, 95, 1284; Carrasso and Padoa, ti R. Accad. Lincei, 1906, (v.) 15, i, 699); $HISbI_3$, red needles (Higbee); $(B'HI)_2(SbI_3)_2$, onze leaflets (H.); B'_2MgCl_2 (Tombeck, mpt. rend. 1896, 124, 963, 1532; Ann. Chim. 00, (7) 21, 397); B'_2ZnBr_2 (Tombeck, Ann. im. 1900, (7) 21, 466); B'_2CdCl_2 ; B'_2CdBr_2 ; $CdSO_4$; B'_2AgNO_3 ; $B'_2Ag_2SO_4$; $3B' + 2SiF_6$ (Pomey and Jackson, Amer. Chem. J. 1888, 10, 2). **Chlorate**, white plates exploding at 88° (atta and Choudhury, J. Amer. Chem. Soc. 16, 88, 1079); B'_2CdCl_2 , tables (Lachowicz, *ibid.* 1889, 10, 898); B'_2HgCl_2 (Lachowicz); B'_2HgCl_2 (?), m.p. $113-115^\circ$ (Klein, Ber. 1878, 744); $2B'_2HgBr_2$, laminated crystals, m.p. 104° (Klein, Ber. 1880, 13, 835); $2B'_2HgI_2$, decomposes at $40-50^\circ$ (Klein); $4B' + AgNO_3$; $B' + AgNO_3$ (Lachowicz, Monath. 1889, 10, 7); $3B' + 2CuSO_4 + H_2O$ (Lachowicz); B'_2ZnBr_2 ; $2B'_2ZnI_2$; $2B'_2CdI_2$; $2B'_2HgCl_2$; $B'_2Hg(CN)_2$; $2B'_2MnCl_2$ (Leeds). **Benzene sulonic acid salt**, m.p. 137° (Norton and Westcott, Amer. Chem. J. 1888, 10, 135); **toluene p-sulphonic acid salt**, long prisms, m.p. 180° (Norton and Otten, *ibid.* 144); **amide-sulphonate**, $C_6H_5NOHSO_3NH_2$, prisms, m.p. 131° (Norton and Otten, *ibid.* 144); **amide-sulphonate**, $C_6H_5NOHSO_3NH_2$, prisms, m.p. 131° (Norton and Otten, *ibid.* 144); **amide-sulphonate**, $C_6H_5NOHSO_3NH_2$, prisms, m.p. 131° (Norton and Otten, *ibid.* 144).

succinic acid salt, $(C_6H_5N)_2C_4H_4Cl_2O_4 + C_2H_5OH$, crystalline powder (van der Riet, Ann. 1894, 280, 232); **toluene p-sulphonic acid salt**, needles, m.p. 124° (Hälsig, J. pr. Chem. 1897, (2) 56, 217); B'_2Ca (Erdmann and Smitten, Ann. 1906, 361, 52).

o-Toluidine forms precipitates with salts of the rare metals (Jefferson, J. Amer. Chem. Soc. 1902, 25, 540).

o-Toluidine dissolved in diluted sulphuric acid and treated with chromic acid and sulphuric acid yields a blue colour, converted into red-violet on dilution (Rosenstiehl, Bull. Soc. chim. 1868, (2) 10, 200), whilst a solution of *o*-toluidine in diluted sulphuric acid gives an orange coloration with nitric acid (Lorenz, Ann. 1874, 172, 180). When an equal volume of water is added to a solution of the base in ether, and a very dilute solution of bleaching powder is added drop by drop, the aqueous layer is coloured yellow or brown, and the ethereal layer on shaking with sulphuric acid colours this reddish-violet (Rosenstiehl). If a trace of a salt of *o*-toluidine is added to a solution of a salt of 2:5-tolylenediamine, followed by ferric chloride, potassium dichromate, or manganese dioxide, a green colour is formed (distinction from *m*- and *p*-toluidine) (Nietzki, Ber. 1877, 10, 1157).

When passed through a hot tube *o*-toluidine is converted into ditolylamine, with evolution of ammonia and hydrogen (Seyberth, Ber. 1896, 29, 2594), whilst under the influence of an electric discharge it yields a little ammonia and forms a strongly basic polyamine (Berthelot, Compt. rend. 1898, 126, 780). It is oxidised in alkaline solution forming azotoluene, oxalic acid and ammopla, whilst in acid solution it forms quinones. Azoderivatives are formed also with nitric acid (Nietzki, Ber. 1877, 10, 662; Ullmann and Forgan, Ber. 1901, 34, 3805; cf. Bradshaw, Amer. Chem. J. 1906, 35, 326). Its hydrochloride when electrolysed or when treated with potassium dichromate yields dyestuffs (Goppelsroeder, Dingl. poly. J. 1877, 223, 347, 634; Coninck, Compt. rend. 1898, 127, 1221).

o-Toluidine printed on the fibre can be oxidised to a moderately permanent dark violet dye by means of sodium chlorate and potassium ferrocyanide; *m*-toluidine under these conditions yields a blackish-violet colour and *p*-toluidine a chestnut-brown colour (Kirpitschnikoff, Zeitsch. Farb. Text. Ind. 1905, 4, 233).

It gives a violet colouring matter with thallium chloride (Renz, Ber. 1902, 35, 2768). When treated with hydrogen in the presence of reduced nickel it yields methyl cyclo-hexylamine (Sabatier and Senderens, Bull. Soc. chim. 1904, (3) 31, 769).

It reacts with diazo-compounds (Mehner, J. pr. Chem. 1902, 65, 401); with methylene iodide (Senier and Goodwin, Chem. Soc. Trans. 1902, 81, 290); with phenyl urethane (Dixon, *ibid.* 1901, 79, 102); with phosphoryl trithiocyanate (*ibid.* 541); with a number of aldehydes (Eibner and Peltzer, Ber. 1900, 33, 3490; Fosse, Bull. Soc. chim. 1901, (3) 25, 375; Etard, *ibid.* 1883, (2) 39, 530; Picot, Ber. 1898, 18, 1663; Sachs and Kempf, Ber. 1902, 35, 2704; Ochs and Blas, Monath. 1904, 25, 365; Walthers and Rastan, J. pr. Chem. 1902, 65, 253).

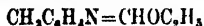
o-Toluidine on treatment with acetic anhydride

cyanate either at 1°-3° or at the boiling point yields chiefly acetyl-*o*-tolylthiocarbamide, m.p. 184° (Doran and Dixon, Chem. Soc. Trans. 1905, 87, 338). With dichloroacetic acid, *o*-toluidine yields chiefly *o*-methylaminophenyl-*o*-toluidine-acetic acid, prismatic needles, m.p. 239°-240°, as well as some *o*-tolyl-*o*-methylmesatin C_8H_7ON , golden-yellow leaflets, m.p. 225° (Ostromisslensky, Ber. 1907, 40, 4972; cf. Meyer, Ber. 1883, 16, 2261). The magnesium iodide derivative of *o*-toluidine reacts with ethyl chloracetate to yield iodoaceto-*o*-toluidide, long white needles, m.p. 142° (decomp.) (Bodroux, Compt. rend. 1905, 141, 195), and with α -iodopropionate and α -iodobutyrate to form α -iodopropion-*o*-toluidide, m.p. 148°, and α -iodobutyr-*o*-toluidide, m.p. 138°-139°, respectively (Bodroux and Taboury, *ibid.* 1907, 144, 1437).

The diazoamino-compounds derived from the three toluidines and diphenylamine are described by Vignon and Simonet (Compt. rend. 1905, 140, 788).

Formyl-derivative; by continuous boiling of *o*-toluidine with formic acid (Ladenburg, Ber. 1877, 10, 1129; Tobias, *ibid.* 1882, 15, 2446). Plates, m.p. 62° (Nef, Ann. 1892, 270, 310), b.p. 288°. When boiled for a long time it decomposes into *o*-toluidine, methenylditolylamine, carbon monoxide and carbon dioxide. For solid and liquid modifications, see Orloff (J. Russ. Phys. Chem. Soc. 1905, 37, 439).

Silver salt, amorphous precipitate (Comstock and Clapp, Amer. Chem. J. 1891, 13, 526); *sodium salt* (Wheeler, *ibid.* 1900, 23, 466); *ethyl-*o*-tolylformimino ether*,



from silver *o*-formotoluidide and chloroformic ester, liquid, b.p. 101°/12 mm. (Wheeler and Boltwood, Amer. Chem. J. 1896, 18, 389); *methylether*; from the silver salt and methyl iodide. Liquid, b.p. 211°-213° (C. and C.).

Thioformyl-derivative; by heating the formyl-derivative with phosphorus pentasulphide at 120°. Another method of preparation is given by Nef (Ann. 1892, 270, 313). Yellow needles, m.p. 96° (Senier), or colourless needles, m.p. 100°-101° (Nef). On distillation *in vacuo* it forms methenyldi-*o*-tolylamine. On heating under pressure for 7 hours at 190° it yields a crystalline compound, $C_{14}H_{14}N_2S$, m.p. 160° (Senier, Ber. 1885, 18, 2292; Chem. Soc. Trans. 1885, 47, 762).

Acetyl-derivative; by heating the base with acetic acid (Beilstein and Kuhlberg, Ann. 1870, 156, 77; Alt, *ibid.* 1889, 252, 318), or by shaking with water and acetic anhydride (Hinsberg, Ber. 1890, 23, 2962). See also Lumière and Barbier (Bull. Soc. chim. 1905, (3) 33, 784; Pawlewski (Ber. 1902, 35, 110). Long monoclinic crystals, m.p. 110° (Alt; Sudborough, Chem. Soc. Trans. 1901, 79, 537) or 107°-109° (Bedson and King, Chem. Soc. Trans. 1890, 37, 753), b.p. 296° (Beilstein and Kuhlberg).

With potassium permanganate it yields acetyl-*o*-aminobenzoic acid and with phosphorus pentachloride an unstable iminochloride, $CH_3COCl=NC_6H_4$, which on careful heating yields a base $C_8H_7N=C(CH_3)CH_2$, $CCl=NC_6H_4$, m.p. 53°. When treated hot with bromine it yields the derivative $CH_3C_6H_4BrNHCH_2C_6H_4BrO$, whilst bromine in acetic acid solution yields the

6-bromo-derivative. When treated with a mixture of hydrochloric and nitric acids it yields a dichloroaceto-*o*-toluidide, m.p. 155°-156° (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii, 20).

Aceto-*o*-toluidide forms compounds with sodium hydroxide, $C_8H_7ON+NaOH$, with sodium methoxide, $C_8H_7ON+CH_3ONa$, and with sodium ethoxide, $C_8H_7ON+C_2H_5ONa$ (Cohen, Archdeacon and Brittain, Chem. Soc. Trans. 1896, 69, 93; 1898, 73, 161).

With methyl iodide in presence of dry silver oxide, aceto-*o*-toluidide yields a mixture of methyl aceto-*o*-toluidide and *N*-*o*-tolylacetimino-methylether, whilst with ethyl iodide it yields *N*-*o*-tolylacetimino-ethylether (Lander, Chem. Soc. Trans. 1901, 79, 690). Chloroacetylchloride in the presence of aluminium chloride yields chloroacetyl-*o*-toluidine, m.p. 180° (Kunckell, Ber. 1900, 33, 2644). On heating with diacetylhydrazine, aceto-*o*-toluidide yields 1-*o*-tolyl-2,4,5-dimethyl-1:3:4-triazole (Pellizzari and Alciatore, Atti R. Accad. Lincei, 1901 [v.] 10, 444).

N-Chloro-derivative, $CH_3C_6H_4NCIClOCH_3$, from aceto-*o*-toluidide and potassium hypochlorite at the ordinary temperature. Prisms or plates, m.p. 43°. At 160°, or when a drop of sulphuric acid is added to its solution in acetic acid, 5-chloro-aceto-*o*-toluidide is formed (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790).

N-Bromo-derivative; formed by the action of potassium hypobromite on a suspension of the acetyl-derivative in sodium bicarbonate solution at 0°. Yellow, four-sided plates, m.p. 100.5°. On keeping at the ordinary temperature for a few seconds, it is transformed into 5-bromoaceto-*o*-toluidide (Chattaway and Orton).

Chloroacetyl-derivative



by the action of chloroacetyl chloride on a well-cooled solution of *o*-toluidine in benzene (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 299; cf. Bischoff and Walden, Ann. 1894, 279, 62; Grothe, Archiv. der. Pharmacie, 1889, 238, 588). Slender needles, m.p. 111°-112°. For the corresponding bromo-, dichloro-, trichloro-, and thioacetyl-derivatives, see Rugheimer and Hoffmann, Ber. 1885, 18, 2987; Cloke, Ann. Chim. 1880, (6) 9, 215; Abenius and Widman, *l.c.*; Wallach, Ber. 1890, 13, 529; 1883, 16, 147).

Propionyl-derivative; from *o*-toluidine and propionic acid (Pictet and Duparc, Ber. 1887, 20, 3421). Needles, m.p. 87°, b.p. 299°/730 mm. Oxidised by potassium permanganate to propionyl-*o*-amino-benzoic acid.

Benzoyl-derivative; long broad needles, m.p. 131° (Gudeman, Ber. 1893, 21, 2553) or 143° (Brückner, Ann. 1890, 205, 130). Phosphorus pentachloride yields $C_8H_7N=CCl_2C_6H_5$ (Just, Ber. 1896, 19, 982).

Oxalyl-derivative; plates, m.p. 131° (Bladis, Bull. Soc. chim. 1884, (2) 41, 130).

Phthalyl-derivative; needles, m.p. 162°, b.p. about 360° (Fröhlich, Ber. 1884, 17, 2679).

Diacetyl-derivative; by heating 1 part of aceto-*o*-toluidide with 1 part of acetylchloride at 170°-190° (Kay, Ber. 1893, 26, 2235); from the monoacetyl-compound and acetic anhydride at 200°-205° (Bistrzycki and Ullrich, Ber. 1894, 27, 91). Oil (Kay). crystals, m.p. 16° (Ullrich).

Ber. 1895, 28, 1665; Clayton, Ber. 1895, 28, 1665; Sudborough, Chem. Soc. Trans. 1901, 79, 537).

4-Chloro-o-toluidine; by reduction of 4-chloro-2-nitrotoluene (Goldschmidt and Hönig, Ber. 1886, 19, 2441; Cohn, Monath. 1901, 22, 473; cf. Engelbrecht, Ber. 1874, 7, 797); from 2:4-dinitrotoluene (Beilstein and Kuhlberg, Ann. 1871, 158, 337). M.p. 21°–22°, b.p. 237°/722 mm. (G. and H.). B'HCl, needles; (B'HCl), PtCl₄ + 2H₂O, slender yellow needles.

Acetyl-derivative, leaflets, m.p. 139°–140° (E.) or 130°–131° (G. and H.). Oxidised by permanganate in presence of magnesium sulphate to 4-chloro-2-acetylamino-benzoic acid (Cohn).

5-Chloro-o-toluidine; by chlorination of aceto-o-toluidide followed by hydrolysis (Lellmann and Klotz, Ann. 1885, 231, 317); by the action of sulphuryl chloride on aceto-o-toluidide in carbon disulphide solution followed by hydrolysis with hydrochloric acid (Wynne, Chem. Soc. Trans. 1892, 61, 1045). The same (?) chlorotoluidine is obtained together with o-toluidine by reducing o-nitrotoluene with tin and hydrochloric acid (Beilstein and Kuhlberg, Ann. 1870, 156, 81). Thin plates, m.p. 29°–30° (W.; B. and K.; L. and K.), b.p. 241° (B. and K.), 236°–238°/730 mm. (L. and K.), or 246°/746 mm. (W.). B'HCl, small tables; B'HNO₃, leaflets.

Acetyl-derivative; by chlorination of aceto-o-toluidide (L. and K.); by the action of an aqueous solution of bleaching powder on an ice-cold solution of aceto-o-toluidide in diluted acetic acid solution (Claus and Stapelberg, Ann. 1893, 274, 286; cf. Chattaway and Orton, l.c., and Cohen and Dakin, *ibid.* 1902, 81, 1329); or by chlorination using sodium chlorate and hydrochloric acid (Reverdin and Crépieux, Ber. 1900, 33, 2497). Small slender needles, m.p. 129°–140° (W.; C. and O.). **N-Chloro-derivative**; four or six-sided prisms, m.p. 66°. On heating, solution in acetic acid 3:5-dichloroaceto-o-toluidide is formed (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 790).

6-Chloro-o-toluidine; 6-nitro-o-toluidine is converted into 6-chloro-2-nitrotoluene and the latter is reduced (Reverdin and Crépieux; cf. Wynne and Greeves; Nölting; Cohn). Liquid at the ordinary temperature, m.p. 2°–8°, and darkens rapidly in the air (Wibaut, Rec. trav. chim. 1913, 32, 244), b.p. 242°–244°. B'HCl, silvery leaflets, decomposing at 250°–252°; H₂SO₄, silvery needles, decomposing at 250°–252°.

Acetyl-derivative; needles, m.p. 156° (Wibaut), 170°–189° (Janson, D. R. P. 107505 of 1898; Ann. Monath. 1901, 22, 473); (Hönig, Ber. 1877, 20, 2417 gave 136°). **Benzoyl-derivative**; m.p. 170°–171° (Wibaut; Cohn) or 173° (N.).

3-Bromo-5-bromo-o-toluidine; by bromination of aceto-o-toluidide, followed by chlorination and hydrolysis. Colourless needles, m.p. 60° (Cohen and Murray, Chem. Soc. Trans. 1915, 19, 847).

Acetyl-derivative; m.p. 171°; **diacetyl-derivative**; m.p. 80°–85° (C. and M.).

3-Chloro-5-bromo-o-toluidine; by reducing 3-chloro-5-bromo-2-nitrotoluene with tin and hydrochloric acid; from aceto-o-toluidide by successive chlorination, hydrolysis, and bromina-

Acetyl-derivative; colourless needles, m.p. 187°; **diacetyl-derivative**, m.p. 85° (C. and M.).

5(?)-Iodoaceto-o-toluidide; by treating aceto-o-toluidide with iodine monochloride in glacial acetic acid. It melts at 169°–5° and yields a **dichloride**, which decomposes at 109°, and an **iodoso-derivative** (Willgerodt and Heusner, Ber. 1907, 40, 4077).

3:5-Dichloro-o-toluidine; by chlorination of aceto-o-toluidide, followed by hydrolysis (Claus and Stapelberg, Ann. 1893, 274, 291); readily obtained by Chattaway and Orton's method (above) (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1329). Glistening needles, m.p. 53° (C. and S.).

Acetyl-derivative; needles or columns, m.p. 186°. **N-chloro-derivative**, four-sided prisms, m.p. 78° (Chattaway and Orton l.c.).

4:5-Dichloro-o-toluidine; by reducing 3:4-dichloro-6-nitrotoluene with stannous chloride. Plates with a silky lustre, m.p. 100°–101° (Cohen and Dakin).

4:6-Dichloro-o-toluidine (?); by reducing dichloronitrotoluene (Wroblewsky, Ann. 1873, 168, 213). Leaflets, m.p. 88°, b.p. 259°. Does not form salts.

2:4-Dichlorotoluidine (?); by reducing β-dichloronitrotoluene. Plates, m.p. 87° (Seelig, Ann. 1887, 237, 163).

2:3:4-Trichloro-o-toluidine (?); by reduction of 2:3:4-trichloronitrotoluene (?) with stannous chloride and hydrochloric acid. Small needles, m.p. 105° (Seelig, Ann. 1887, 237, 142).

3:4:6-Trichloro-o-toluidine (?); by reduction of trichloronitrotoluene with tin and hydrochloric acid (Schultz, Ann. 1877, 187, 278). Needles, m.p. 91° (Schultz) or 94°–95° (Seelig, Ann. 1887, 237, 141; Ber. 1885, 18, 423). Becomes rose-coloured on keeping.

Acetyl-derivative; m.p. 191°.

Benzoyl-derivative; m.p. 213° (Schultz).

3-Bromo-o-toluidine; by reduction of 3-bromo-2-nitrotoluene (Neville and Winther, Ber. 1880, 13, 1945; Chem. Soc. Trans. 1890, 37, 630; cf. Wynne, *ibid.* 1892, 61, 1036, note). Oil. With bromine water it yields 3:5-dibromo-o-toluidine.

4-Bromo-o-toluidine; by reduction of 4-bromo-2-nitrotoluene (Körner, Zeit. f. Chem. 1869, (2) 5, 636; Hübner and Wallach, Ann. 1870, 154, 298; Hübner and Roos, Ber. 1873, 6, 799; Wroblewsky, Ann. 1873, 168, 77; Neville and Winther, Chem. Soc. Trans. 1890, 37, 442); from dinitrotoluene by conversion into 2-nitro-p-toluidine, replacement of the amino-group by bromine and reduction of the nitro-group (Heinemann, Ann. 1871, 158, 340). Plates, m.p. 32° (H. and R.), b.p. 253°–257° with partial decomposition. B'HCl, six-sided rhombic plates (H. and R.); B'HNO₃, long rhombic tables (W.; H.); B'H₂SO₄, plates.

5-Bromo-o-toluidine; by successive bromination and hydrolysis of aceto-o-toluidide (Wroblewsky, Ann. 1873, 168, 162); by reduction of 5-bromo-2-nitrotoluene (Greve, Ann. 1874, 177, 249; Ber. 1875, 8, 865). Rhombic plates, m.p. 59°–5° (Alt, Ann. 1882, 252, 321) or 56° (Wroblewsky; Niemannowaki, Ber. 1892, 25, 869; Cohen and Dutt, Chem. Soc. Trans. 1915, 19, 847, 848; cf. Neville and Winther, l.c.) b.p. 240°. B'HCl, needles; B'ED, prisms, plates, needles, etc.

m.p. 183°; $B_2H_5SO_4 + 2H_2O$ (Alt); *oxalate*, needles, (G.).

Acetyl-derivative; by bromination of aceto-*o*-toluidine (W.; A.; N.); quantitatively by treating 5-iodoaceto-*o*-toluidine with bromine in chloroform solution (Malleis and Meyer, J. Amer. Chem. Soc. 1913, 35, 970); by the action of hydrobromic and nitric acids on aceto-*o*-toluidine (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20). Long needles, m.p. 156°–157° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 511). For compounds with sodium and potassium hydroxides, see Cohen and Brittain (*ibid.* 1898, 73, 161). *N*-Bromo-*derivative*; yellow rectangular plates, m.p. 91°. On heating with water at 100° it yields 3:5-dibromo-aceto-*o*-toluidine (Chattaway and Orton, *ibid.* 1900, 77, 794).

6-Bromo-*o*-toluidine; by reduction of 6-bromo-2-nitrotoluene with tin, stannous chloride, and hydrochloric acid (Friedländer, Bruckner and Deutsch, Ann. 1912, 388, 23). Yellow oil, b.p. 253°–255° (Nölting, Ber. 1904, 37, 1015).

Sulphate; m.p. 256° (N.).

Acetyl-derivative; white needles, m.p. 158° (N.), or 159°–161° (Cohen and Dutt, *l.c.*; Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627) or 163° (F., B. and D.). It is oxidised by potassium permanganate at 80° in the presence of magnesium sulphate to bromoacetyl-anthranilic acid, m.p. 224°.

3:5-Dibromo-*o*-toluidine; by passing bromine vapour into a solution of *o*-toluidine hydrochloride (Wroblewsky, Ann. 1873, 168, 187); by boiling bromoacetodibromo-*o*-toluidine with excess of alcoholic potassium hydroxide (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 288); by dibromination of *o*-toluidine and by the action of bromine on *o*-toluidine 5-sulphonic acid (Neville and Winther, Chem. Soc. Trans. 1880, 37, 429, 629; cf. Wynne, *ibid.* 1892, 61, 1038). Needles, m.p. 45°–46° (N. and W.; Cohen and Dutt), 50° (W.); Möhlau and Öhmichen, J. pr. Chem. 1881, (2) 24, 478, volatile with steam. It forms unstable compounds with strong acids.

Compounds with mercuric chloride, with zinc chloride, and with the chloride and bromide of cadmium are described by Hann and Spencer (J. Washington Acad. Sci. 1925, 15, 163).

($BHCl$), $PtCl_4$, yellow needles (A. and W.), $+1\frac{1}{2}H_2O$ (Claus and Immel, Ann. 1891, 265, 70).

Acetyl-derivative; needles, m.p. 205° (Chattaway and Orton, Ber. 1900, 33, 2399).

N-Bromo-*derivative*; plates, m.p. 120° (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 794).

Bromoacetyl-derivative; slender needles, m.p. 207° (A. and W.).

Diacyl-derivative; slender needles, m.p. 88° (A. and W.).

4:5-Dibromo-*o*-toluidine; by reduction of 4:5-dibromo-2-nitrotoluene. It melts at 96°–98° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 439; Cohen and Dutt, *ibid.* 1914, 105, 515; cf. Wroblewsky, Ann. 1873, 168, 184).

5:6-Dibromo-*o*-toluidine; by bromination of 6-bromoaceto-*o*-toluidine, followed by hydrolysis. It melts at 58°.

Acetyl-derivative; m.p. 165°–166° (Cohen and Dutt, *l.c.*).

*Tribromo-*o*-toluidine*; m.p. 105°–106°, is described by Gerver (Ann. 1873, 169, 379) as

being obtained by the action of 3 mols. of bromine on *o*-toluidine, and he states further that 1 mol. of bromine and a dilute alcoholic solution of *o*-toluidine yields a mixture of di- and tribromotoluidines, m.p. 85°–89°. Neville and Winther (Chem. Soc. Trans. 1880, 37, 438) could not prepare any higher derivative than a dibromotoluidine, however, and state that Gerver's *o*-toluidine possibly contained aniline.

3:5:6-Tribromo-*o*-toluidine; by reduction of 3:5:6-tribromo-2-nitrotoluene with iron powder and acetic acid; by bromination of 6-bromo-*o*-toluidine (Blanksma, Chem. Weekblad, 1914, 11, 185). Colourless crystals, m.p. 87°.

Acetyl-derivative; colourless crystals, m.p. 218° (B.).

Tribromotoluidine; from *p*-bromotoluene *o*-sulphonic acid by nitration, reduction, and bromination (Schäfer, Ann. 1874, 174, 362; Ber. 1874, 7, 1355). M.p. 72°.

4-Iodo-*o*-toluidine; by reduction of 4-iodo-2-nitrotoluene (Heinemann, Ann. 1871, 158, 338). Needles, m.p. 48°–49°, b.p. 273° (decomp.). $BHNO_3$, leaflets.

5-Iodo-*o*-toluidine; reduction of 3-iodo-6-nitrotoluene with ferrous sulphate and ammonia in aqueous solution at 66°–70° (Artmann, Monatsh. 1905, 26, 1091); by the action of iodine chloride on aceto-*o*-toluidine followed by hydrolysis (Fichter and Phillip, J. pr. Chem. 1906, (2) 74, 297); by the action of iodine on *o*-toluidine (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 498); and by trituration of *o*-toluidine hydrochloride with iodine and calcium carbonate, the yield being 98 p.c. (Hann and Berliner, J. Amer. Chem. Soc. 1925, 47, 1709). Long white needles, m.p. 91°–92° (A.), or short, colourless crystals, m.p. 88° (F. and P.), or 87°–2° (H. and B.).

$BHCl$, short white needles, m.p. 214°; $BHNO_3$, slender tetragonal scales. The salts are dissociated by water. B_2HgCl_4 , m.p. 134°–5°.

Acetyl-derivative; slender matted needles, m.p. 162°–163° (A.), 168° (F. and P.), 169° (W. and L.), or 176° (Malleis and Meyer, J. Amer. Chem. Soc. 1913, 35, 970). Oxidised by potassium permanganate to 5-iodo-*o*-acetylaminobenzoic acid, m.p. 235° (decomp.) (W. and L.).

Benzoyl-derivative; colourless needles, m.p. 184° (W. and L.).

6-Iodo-*o*-toluidine; obtained by reducing 2-iodo-6-nitrotoluene, is a liquid. $BHCl$, plates (Cohen and Miller, Chem. Soc. Trans. 1904, 85, 1627), m.p. 254° (decomp.) (Nölting, Ber. 1904, 37, 1015).

Acetyl-derivative; white needles, m.p. 166° (N.).

3:6-Di-iodo-*o*-toluidine; by reduction of 2:5-di-iodo-6-nitrotoluene. Colourless needles, m.p. 86° (Wheeler and Brautlecht, Amer. Chem. J. 1910, 44, 126).

4:5-Di-iodo-*o*-toluidine; by the action of iodine chloride on *p*-iodo-*o*-toluidine. Stout needles or long prisms (Wheeler and Brautlecht, *ibid.* 1910, 44, 493).

3:5-Dibromo-4-iodo-*o*-toluidine; by reduction of dibromo-iodonitrotoluene (m.p. 69°) (Wroblewsky, Ann. 1878, 192, 210). Needles, m.p. 84°. On treatment with sodium amalgam it yields *o*-toluidine.

Acetyl-derivative; small needles, m.p. 121° (W.).

5-Nitroso-o-toluidine; by heating a mixture of 1 part of 5-nitroso-o-cresol, 5 parts of ammonium chloride, and 15 parts of dry ammonium acetate at 100° (Mehne, Ber. 1888, 21, 731). Small green needles with a bluish lustre, m.p. 115°-116° with slight detonation. On heating with sodium hydroxide it yields nitrosocresol and ammonia, and with hydroxylamine it is transformed into toluquinonedioxime.

3-Nitro-o-toluidine; together with the 5-nitro-isomeride by nitration of aceto-o-toluidide, followed by hydrolysis (Beilstein and Kuhlberg, Ann. 1871, 158, 345; Lellmann and Wurthner, *ibid.* 1885, 228, 240; Reverdin and Crépieux, Ber. 1900, 33, 2498; 1902, 35, 1439; Meisenheimer and Hesse, *ibid.* 1919, 52, 1161; Gabriel and Thieme, *ibid.* 1079; Cohen and Dakin, Chem. Soc. Trans. 1901, 79, 1127). Also by heating oxalo-o-toluidide on the water-bath with concentrated sulphuric acid until water-soluble, cooling to 50° and nitrating slowly with a mixture of nitric acid (D 1.52) and sulphuric acid, keeping the temperature below 50°. The product, after keeping for some hours and diluting with water, is heated at 140° until solution is complete, and finally at 150° for 50 minutes. This is then considerably diluted and steam distilled (Hadfield and Kenner, Chem. Soc. Proc. 1914, 30, 253). By treating 2:3-dinitrotoluene with 2.5N methyl alcoholic ammonia under pressure at 150°-160° for 15 hours (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 856); from 3-nitro-o-toluidine 5-sulphonic acid by eliminating the sulphonic group (Gnehm and Blumer, Ann. 1898, 304, 105; Nietzki and Pollini, Ber. 1890, 23, 138); together with the 5-nitro-isomeride by the transformation of o-toluene-nitroamine (Bamberger and Stingelin, Ber. 1897, 30, 1259).

Orange-yellow prisms, m.p. 97° (K. and P.; Zincke and Schwarz, Ann. 1899, 307, 44) or 95° (Wibaut, Rec. trav. chim. 1913, 32, 244; R. and C.).

Acetyl-derivative; large shining plates or prisms, m.p. 158° (L. and W.; Körner and Contardi, Atti R. Accad. Lincei, 1915, (v.) 24, i. 888).

4-Nitro-o-toluidine; together with the 6-nitro-derivative by nitration of phthalyl-o-toluidide, followed by hydrolysis (Städel, Ann. 1884, 225, 385); together with 2-nitro-p-toluidine by treating 2:4-dinitrotoluene with warm alcoholic ammonium sulphide (Graeff, Ann. 1885, 229, 343) or alone by reduction with stannous chloride and alcoholic hydrochloric acid (Anschütz, and Heussler, Ber. 1886, 19, 2161); by warming 2:4-toluylenediamine with an aqueous solution of sodium peroxide (O. Fischer and Trost, Ber. 1893, 26, 3085); by a modification of the method of Green and Lawson (Chem. Soc. Trans. 1891, 59, 1013) by adding powdered potassium nitrate to a solution of o-toluidine in concentrated sulphuric acid cooled to -5°, a small amount of the 6-nitro-isomeride being formed simultaneously (Cohen and Dakin, *ibid.* 1902, 81, 1333); by heating 4-nitro-6-amino-m-toluid acid or its acetyl-derivative with concentrated sulphuric acid (Errera and Maltese, Gazz. chim. ital. 1905, 35, ii. 870); in 75 p.c. yield, together with 2-5 p.c. of 4-nitro-o-toluidine, by nitrating o-tolu-

idine in concentrated sulphuric acid (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1539) with mixed acids (Brady and Williams, *ibid.* 1920, 117, 1138). The latter method is much simpler than that of Nölting and Collin (Ber. 1884, 17, 265). Monoclinic prisms, m.p. 107° (N. and C.), 109° (S.), 104°-105° (A. and H.); cf. Jäger, Z. Krist. 1903, 89, and Willgerodt and Kok, Ber. 1908, 41, 2077.

B'HCl, white needles, m.p. 230° (Willgerodt and Kok); B'HB, small lustrous pale red crystals (Staden, J. pr. Chem. 1902, (2) 65, 249); B₂H₂SO₄, plates, decomposed by water.

Nitrous acid yields 4-nitro-o-cresol and nitro-indazole, whilst with sodium amalgam it yields azoxytoluidine.

Formyl-derivative, small yellow prisms, m.p. 178°-179° (Geigy & Co., U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

Acetyl-derivative; yellowish-white needles, m.p. 150°-151° (Nölting and Collin, *l.c.* 269).

5-Nitro-o-toluidine; by nitration of toluene p-sulphonyl-o-toluidide (Reverdin and Crépieux, Bull. Soc. chim. 1902, 27, 742); by nitration of aceto-o-toluidide, followed by hydrolysis (see the 3-nitro-derivative); as a by-product of the action of nitric anhydride on o-toluidine (Bamberger and Hoff, Ann. 1900, 311, 95); in low yield by heating 2:5-dinitrotoluene with alcoholic ammonia at 150° for 15 hours (Kenner and Parkin, Chem. Soc. Trans. 1920, 117, 859). Small citron-yellow needles, m.p. 127° (K. and P.) or 130° (Wibaut, Rec. trav. chim. 1913, 32, 244; Jäger, *l.c.*; Reverdin and Crépieux, Ber. 1900, 33, 2498).

Acetyl-derivative; short white needles, m.p. 201.6° (Körner and Contardi, Atti R. Accad. Lincei, 1915, (v.) 24, i. 888).

6-Nitro-o-toluidine; obtained in 80 p.c. yield by the gradual addition of a 15 p.c. ammonium sulphide solution to 2:6-dinitrotoluene in boiling alcohol, followed by complete extraction of the product with dilute hydrochloric acid (Cohen and Marshall, Chem. Soc. Trans. 1904, 85, 527; Ullmann, Ber. 1884, 17, 1957; Bernthsen, Ber. 1882, 15, 3018; Cunerth, Ann. 1874, 172, 223); in small quantities together with the 4-nitro-isomeride by nitrating o-toluidine in presence of an excess of sulphuric acid (Green and Lawson, Chem. Soc. Trans. 1891, 59, 1014). For separation from 2-nitro-p-toluidine, see Bernthsen (*l.c.*). Thin rhombic leaflets (Jäger, Z. Kristall. 1903, 38, 89) or long yellow needles, m.p. 91.5° (U.). B'HCl, long flat prisms; B'HB, yellowish leaflets or long thin needles, decomposed by water; B'HI, rhombohedra or flat prisms (Tatschloff, J. pr. Chem. 1902, (2) 65, 259).

Acetyl-derivative; prisms, m.p. 157.5°-158° (U.), m.p. 160° (Cohen and Hodman, Chem. Soc. Trans. 1907, 91, 975), or colourless needles, m.p. 163°; *benzyl-derivative*, m.p. 167°-167.5° (U.), or 145°-146° (C.).

3:4-Dinitro-o-toluidine; as main product, together with 4:5-dinitro-o-toluidine, by adding a sulphuric acid solution of 4-nitroaceto-o-toluidide to nitric acid (D. 1.5) cooled in ice, followed by hydrolysis by heating for 4-5 hours on the water-bath with dilute sulphuric acid (1 part acid; 2 parts water) (Brady and Williams, Chem. Soc. Trans. 1920, 117, 1138; Morgan and Glover, *ibid.* 1921, 119, 1702). Lustrous, yellowish-brown needles, m.p. 131°-131.5°

Acetyl-derivative; yellowish-white needles, m.p. 186° (M. and G.).

3:5-Dinitro-*o*-toluidine; in small quantity by nitrating toluene *p*-sulphonyl-*o*-toluidide (Reverdin and Crépieux, Bull. Soc. chim. 1902, (3) 27, 742); by heating dinitro-*o*-cresol and its ethers with alcoholic ammonia (Städel, Ann. 1883, 217, 183, 203; Ber. 1881, 14, 900; van Romburgh, Rec. trav. chim. 1884, 3, 398; Barr, Ber. 1888, 21, 1543); by transformation of 5-nitro-*o*-toluene nitroamine (Bamberger and Seitz, Ber. 1897, 30, 1255; Bamberger and Hoff, Ann. 1900, 311, 111); in upwards of 95 p.c. yield by the action of liquid ammonia, methyl or ethyl alcoholic ammonia on 2-chloro-3:5-dinitrotoluene (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 790).

Yellow columns or long tables, m.p. 208° or 209°-210° (H.), 211° (B. and S.), 213° (M. and D.).

Acetyl-derivative; slender white needles, m.p. 205-2° (Körner and Contardi, Atti R. Accad. Lincei, 1915, [v.] 24, 1. 888. See also Reverdin and Crépieux, Ber. 1902, 35, 1439).

3:6-Dinitro-*o*-toluidine (see 5:6-dinitro-*o*-toluidine). Brilliant orange-yellow prisms, m.p. 151°.

Acetyl-derivative; pale yellow microscopic prisms, m.p. 209° (Brady and Taylor; cf. Körner and Contardi).

4:5-Dinitro-*o*-toluidine (see 3:4-dinitro-*o*-toluidine). Yellow needles, m.p. 191°-191.5°.

Acetyl-derivative; colourless needles, m.p. 180° (Morgan and Glover; Brady and Williams).

4:6-Dinitro-*o*-toluidine; together with 2:6-dinitro-*p*-toluidine by reducing 2:4:6-trinitrotoluene with ammonium hydrosulphide (Holleman and Boeseken, Rec. trav. chim. 1897, 16, 426) or by reducing in hydrochloric acid solution in presence of cupric chloride at a copper cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487); together with 2:6-dinitrotolyl-*p*-hydroxylamine by reducing 2:4:6-trinitrotoluene in cold alcoholic ammoniacal solution with hydrogen sulphide (Anechütz and Zimmermann, Ber. 1915, 48, 152). It melts at 155° (H. and B.; A. and Z.) or 135° (B. and E.). On diazotisation it is converted into 2:4-dinitrotoluene and 2:4-dinitroindazole (B. and E.).

Acetyl-derivative; white needles, m.p. 224° (B. and E.).

5:6-Dinitro-*o*-toluidine; formed together with 3:6-dinitro-*o*-toluidine by adding 6-nitro-aceto-*o*-toluidide to a mixture of sulphuric acid and nitric acid (D 1.5) at 4°-7°, and allowing the temperature to rise to 12°, followed by hydrolysis with concentrated sulphuric acid at 100°. The bases are separated by conversion into the acetyl-derivatives or by crystallisation from glacial acetic acid and sieving the crystals (Brady and Taylor, Chem. Soc. Trans. 1920, 117, 876). Deep yellow needles, m.p. 216° (B. and T.).

Acetyl-derivative; large white crystals, m.p. 180° (B. and T.).

3-Chloro-5-nitro-*o*-toluidine; by chlorination of 5-nitro-*o*-toluidine. It melts at 168° (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151).

3-Chloro-6-nitro-*o*-toluidine; apparently formed together with 5-chloro-6-nitro-*o*-toluidine by heating 6-nitrotolyl-*o*-hydroxylamine with concentrated hydrochloric acid (Brand and Zeller, Ber. 1907, 40, 3324).

5-Chloro-3-nitro-*o*-toluidine; in poor yield together with 5-chloro-4-nitro-*o*-toluidine by dissolving 1 part of 5-chloro-2-toluidine nitrate in 25 parts of nitric acid (66 p.c.) and keeping for 6 hours. On pouring into water only the 4-nitro-derivative separates (Claus and Stapelberg, Ann. 1893, 274, 295). Yellow plates, m.p. 118°-119° (C. and S.), or long orange-yellow needles, m.p. 129°-130° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330).

Acetyl-derivative; in excellent yield by nitrating 5-chloro-aceto-*o*-toluidide in glacial acetic acid at 15°-20° (C. and D.). Glistening needles, m.p. 187° (C. and S.), or prismatic needles, m.p. 197°-198° (C. and D.).

5-Chloro-4-nitro-*o*-toluidine; see 5-chloro-3-nitro-*o*-toluidine (cf. Reverdin and Crépieux, Ber. 1900, 33, 2505). Yellow columns, m.p. 128° (C. and S.), or 124° (Wibaut, Rec. trav. chim. 1913, 32, 244), 129°-130° (C. and D.).

5-Chloro-6-nitro-*o*-toluidine; by heating 6-nitrotolyl-*o*-hydroxylamine (Brand and Zöller, l.c.); by chlorination of 6-nitroaceto-*o*-toluidide in glacial acetic acid, followed by hydrolysis with hydrochloric acid in a sealed tube (Cohen and Hodsman, Chem. Soc. Trans. 1907, 91, 975). Yellow needles, m.p. 95°-96°.

Acetyl-derivative; m.p. 158°-160° (B. and Z.), or 153° (C. and H.); *benzoyl-derivative*; m.p. 212°-213° (C. and H.).

6-Chloro-3-nitro-*o*-toluidine; obtained quantitatively by the action of liquefied ammonia, or saturated alcoholic ammonia, on 2-chloro-5:6-dinitrotoluene. Pale amber refractive prisms with pyramidal ends, m.p. 151.5° (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 787).

3(?) : 5-Dichloro-6-nitro-*o*-toluidine; by chlorination of 6-nitroaceto-*o*-toluidide in glacial acetic acid for 5 hours at 100°. It melts at 195°-197° (Cohen and Hodsman, l.c.).

(a) **Trichloronitrotoluidine**; by the action of alcoholic ammonia on trichlorodinitrotoluene (m.p. 227°). Orange-yellow needles, m.p. 191° (Seelig, Ber. 1885, 18, 423; Ann. 1887, 237, 140).

(β) **Trichloronitrotoluidine**; in a similar manner to the α-compound from trichlorodinitrotoluene (m.p. 141°). Orange-red needles, m.p. 192° (Seelig).

3-Bromo-5-nitro-*o*-toluidine; by bromination of 5-nitro-*o*-toluidine (Neville and Winther, Ber. 1880, 13, 964; Chem. Soc. Trans. 1880, 37, 431; Cohen and Dutt, Chem. Soc. Trans. 1914, 108, 572). It melts at 180.3°-181.3°.

5-Bromo-3-nitro-*o*-toluidine; by successive bromination, nitration, and hydrolysis of aceto-*o*-toluidide (Wroblewsky, Ann. 1878, 192, 206; Neville and Winther, Ber. 1880, 13, 969; Chem. Soc. Trans. 1880, 37, 436, 448). Orange prisms, m.p. 139° (W.), or 143° (N. and W.).

Acetyl-derivative; by treating 5-bromo-aceto-*o*-toluidide with 4 parts of nitric acid (D 1.48) below 25°. Needles, m.p. 205° (Niementowski, Ber. 1892, 25, 869; Claus and Beck, Ann. 1892, 269, 219).

5-Bromo-4-nitro-*o*-toluidine; by nitration of 5-bromo-*o*-toluidine in sulphuric acid with nitric acid (D 1.42) and sulphuric acid below 3°. Yellow crystals, m.p. 118° (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 949).

6-Bromo-3-nitro-*o*-toluidine; by nitration and hydrolysis of 6-bromoaceto-*o*-toluidide

(Blanksma, Chem. Weekblad, 1912, 9, 968). Orange-yellow crystals, m.p. 144° (B.).

Acetyl-derivative; yellow crystals, m.p. 190° (B.).

3:5-Dibromo-4-nitro-o-toluidine; by bromination of 4-nitro-o-toluidine. Yellow crystals, m.p. 104°.

Acetyl-derivative; colourless crystals, m.p. 201°; *diacetyl-derivative*; m.p. 159° (Blanksma, Chem. Weekblad, 1909, 6, 717; Morgan and Clayton, l.c. 951). It shows a remarkable stability to diazotising agents, which leave it practically unaffected.

3:5-Dibromo-6-nitro-o-toluidine; by bromination of 6-nitro-o-toluidine. It melts at 105° (Blanksma, Chem. Weekblad, 1914, 11, 185).

6-Bromo-3:5-dinitro-o-toluidine; by heating 2:6-dibromo-3:5-dinitrotoluene with alcoholic ammonia at 100°. Yellow crystals, m.p. 200°.

Acetyl-derivative; colourless crystals, m.p. above 300° (Blanksma, *ibid.* 1912, 9, 968).

5-Bromo-3:6(?)-dinitro-o-toluidine; *acetyl-derivative*; by treating 1 part of 5-bromo-aceto-o-toluidide with a mixture of 1 part of sodium nitrate and 20 parts of sulphuric acid. Pale yellow hair-like needles, m.p. 244° (decomp.) (Niementowski, Ber. 1892, 25, 870).

3:5-Dibromo-4:6-dinitro-o-toluidine; *acetyl-derivative*; by the action of nitric acid (D 1.52) and sulphuric acid on 3:5-dibromo-4-nitro-aceto-o-toluidide. White crystals, m.p. 280° (Blanksma, Chem. Weekblad, 1909, 6, 717).

3:5:6-Tribromo-4-nitro-o-toluidine; by nitration and hydrolysis of 3:5:6-tribromoaceto-o-toluidide. Light brown crystals, m.p. 203°.

Acetyl-derivative; colourless crystals, m.p. 275° (Blanksma, Chem. Weekblad, 1914, 11, 185).

3-Iodo-5-nitro-o-toluidine; by the action of iodine chloride on 5-nitro-o-toluidine in glacial acetic acid. Long brown prisms, m.p. 173° (Wheeler, Brautlecht and Hoffman, Amer. Chem. J. 1910, 44, 493).

5-Iodo-3-nitro-o-toluidine; by the action of iodine chloride on 3-nitro-o-toluidine in glacial acetic acid. Orange needles, m.p. 135° (Wheeler, &c.).

5-Iodo-4-nitro-o-toluidine; similarly from 4-nitro-o-toluidine. Bright yellow prisms, m.p. 109° (Wheeler, &c.).

5-Iodo-6-nitro-o-toluidine; by warming equal weights of 6-nitro-o-toluidine and iodine for several hours with ether, water, and calcium carbonate. Yellow prisms, m.p. 85° (Wheeler, &c.).

Methyl-o-toluidine; by reduction of nitroso-methyl-o-toluidine with tin and hydrochloric acid (Monnet, Reverdin and Nötling, Ber. 1878, 11, 2279); by heating o-tolylglycine at 200°-210° (Abenius and Widman, J. pr. Chem. 1888, (2) 38, 303); in a yield of 46 p.c. by methylation of o-toluidine hydrobromide or hydroiodide with methyl alcohol at 150° (Reinhardt and Staedel, Ber. 1883, 16, 29) or with dimethyl sulphate (Ullmann, Ann. 1903, 327, 104; Gnehm and Blumer). Colourless oil, b.p. 207°-208°; D_{20}^{20} 0.973; $B^{\circ}H, PCl_5$ (A. and W.); $B^{\circ}HCl$, prisms (Gnehm and Blumer, Ann. 1899, 304, 96); $B^{\circ}O, H_2O$, leaflets (G. and B.); *picrate*, prisms (G. and B.).

For the manufacture of safranine and azine dyes from methyl-o-toluidine, see Bayer & Co.,

Eng. Pat. 6176 of 1895; Fr. Pat. 245841; D. R. P. 90256 of 1895; and M. L. B., D. R. P. 80768 of 1894; Weinberg, Ber. 1893, 26, 307; Bernthsen, *ibid.* 992.

Acetyl-derivative; m.p. 55°-56°, b.p. 260° (M., R. and N.), or 250°-251° (R. and S.).

Nitrosoamine; oil. Transformed by alcoholic hydrochloric acid into 5-nitroso-methyl-o-toluidine, green plates, m.p. 151°. With boiling aqueous sodium hydroxide it yields nitroso-o-cresol and methylamine. It is oxidised by potassium permanganate to *nitromethyltoluidine*, greenish-yellow needles, m.p. 134° (Kock, Ann. 1888, 243, 308).

4-Chloromethyl-o-toluidine; by methylating 4-chloro-o-toluidine (Störmer and Hoffmann, Ber. 1898, 31, 2532). Liquid, b.p. 248.5°-249.5°/760 mm., D_{20}^{20} 1.138.

Nitrosoamine; oil. D_{20}^{20} 1.226 (S. and H.).

5-Chloromethyl-o-toluidine; oil, b.p. 245°-246°/740 mm. (Geigy & Co., D. R. P. 105103 of 1898).

Dichloromethyl-o-toluidine; by heating dichloro-o-tolylglycine above its melting-point (Hentschel, J. pr. Chem. 1899, (2) 60, 83). Oil, b.p. 258°-259°; $B^{\circ}H, PCl_5$, slender yellow needles (H.).

3-Nitromethyl-o-toluidine; together with 5-nitromethyl-o-toluidine by the transformation of the N-methylester of toluene o-nitroamine (Bamberger and Stingelin, Ber. 1897, 30, 1259). Yellowish-red oil. According to Gnehm and Blumer (Ann. 1899, 304, 103) when methyl-o-toluidine is nitrated a mixture of 4-nitromethyl-o-toluidine and a product, m.p. 48°, is obtained. This latter is stated to be possibly the 3-nitro-derivative.

4-Nitromethyl-o-toluidine; by boiling its acetyl-derivative with concentrated hydrochloric acid (Gnehm and Blumer, l.c.); by nitration of methyl-o-toluidine; by methylation of 4-nitro-o-toluidine. Red leaflets or yellow prisms, m.p. 107.5°.

$B^{\circ}HCl$, leaflets decomposed by water; *picrate*, compact red prisms; *nitrosoamine*, pale yellow needles, m.p. 95°.

Acetyl-derivative; m.p. 119°.

5-Nitromethyl-o-toluidine; by oxidation of a dilute solution of 5-nitrosomethyl-o-toluidine with potassium permanganate (Kock, Ann. 1888, 243, 309); together with 5-nitrodimethyl-o-toluidine by methylating 5-nitro-o-toluidine. The products are separated by acetylation and distillation with steam (Bernthsen, Ber. 1892, 25, 3131); together with the 3-nitro-isomeric by the method of Bamberger and Stingelin (l.c.). Yellow tables, m.p. 137° (B.). It does not form a sulphate with sulphuric acid.

Nitrosoamine; oil which crystallises on keeping, m.p. 65° (B.).

Acetyl-derivative; rhombohedra-like crystals, m.p. 97° (B.).

6-Chloro-3-nitromethyl-o-toluidine; by the action of methylamine on 2-chloro-5:6-dinitro-toluene in alcoholic solution; by heating 6-chloro-3-nitro-o-toluidine with 1 part of methyl sulphate and 2 parts of toluene for 2 hours at 110° (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 149). Orange-coloured molecular prisms, m.p. 84°-87°.

Nitrosoamine; pale yellow prismatic needles, m.p. 86°-87° (M. and J.).

4:7-Nitro-4-chloromethyl-o-toluidine; by the

action of concentrated hydrochloric acid on its nitrosoamine (Störmer and Hoffmann, Ber. 1898, 31, 2533). Bright yellow needles, m.p. 185°-186°; nitrosoamine; yellowish-white plates, m.p. 80.5°-81.5° (S. and H.).

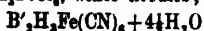
4-Nitrobromomethyl-o-toluidine; by bromination of 4-nitromethyl-o-toluidine in glacial acetic acid with cooling. Yellowish-brown needles, m.p. 133° (Gnehm and Blumer, Ann. 1899, 304, 103).

3:5-Dinitromethyl-o-toluidine; by the transformation of the N-methyl ester of 5-nitro-o-toluene nitroamine (Bamberger and Seitz, Ber. 1897, 30, 1255). M.p. 128°.

Nitrosoamine; yellowish rhombohedra, m.p. 94°-95° (S. and H.).

3:5-Dinitrotolyl-o-methylnitroamine; by boiling dimethyl-o-toluidine with nitric acid (D 1.48-1.5). Pale yellow crystals, m.p. 119°-120°. Decomposed by heating with 5 p.c. potassium hydroxide into methylamine and 3:5-dinitro-o-cresol, and on reduction with tin and hydrochloric acid it yields the corresponding monomethyl-triamine (Romburgh, Rec. trav. chim. 1884, 3, 396).

Dimethyl-o-toluidine; by heating o-toluidine with methyl iodide (Clarke, Amer. Chem. J. 1905, 33, 496); by distilling trimethyl-o-toluidine hydrate (Thomsen, Ber. 1877, 10, 1586; Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279); in 93 p.c. yield by methylating o-toluidine hydrobromide or hydriodide with a little more than 2 equivalents of methyl alcohol for 8 hours at 150° (Reinhardt and Stadel, Ber. 1883, 16, 29). Liquid, b.p. 184.8°, D_4^{20} 0.9286 (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 623), or b.p. 185.5°; D_4^{20} 0.9417, D_{15}^{15} 0.9333, D_{25}^{25} 0.9268 (Perkin, Chem. Soc. Trans. 1896, 69, 1211); magnetic rotatory power at 15.3° 18.61 (P.); refractive power, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218). It does not condense with formaldehyde in presence of hydrochloric acid (Cohn, Chem. Zeit. 1900, 24, 564). $B_2H_2PtCl_6$, white needles;



yellow unstable crystals (Wurster and Roser, Ber. 1879, 12, 1826); oxide, $CH_3C_6H_4N(CH_3)_2O$, is formed together with other products by prolonged action of hydrogen peroxide on dimethyl-o-toluidine. The oxide forms a *picrate*, long greenish-yellow needles, m.p. 145.5°-146.5° (Bamberger and Tschirner, Ber. 1890, 32, 354).

Bromodimethyl-o-toluidine; by brominating dimethyl-o-toluidine in acetic acid; by heating bromo-o-toluidine with methyl alcohol and hydrochloric acid at 180°-200° (Michler and Sampaio, Ber. 1881, 14, 2172). Liquid, b.p. 244°-245°, volatile with steam.

4-Nitrodimehyl-o-toluidine; nitration of dimethyl-o-toluidine with mixed acids at 0° (Gnehm and Blumer, Ann. 1899, 304, 107; Rohde, Zeitsch. f. Elektrochem. 1901, 7, 329); by methylation of 4-nitro-o-toluidine (G. and B.; Staden, J. pr. Chem. 1902, (2) 65, 249). Golden leaflets or rods, m.p. 14° (S.), formerly described as a yellow oil, b.p. 280° (decomp.). B^*HCl , yellow leaflets, m.p. 192°.

5-Nitrodimehyl-o-toluidine; together with 5-nitromethyl-o-toluidine by methylating 5-nitro-o-toluidine (Bernthsen, Ber. 1892, 25, 3133; cf. Haibach, J. pr. Chem. 1902, (2) 65,

242). Dark red flat rhombic pyramids, m.p. 48°-50° (H.), or small tables or needles, m.p. 47.5° (B.).

6-Nitrodimehyl-o-toluidine; by heating 6-nitro-o-toluidine hydrobromide with methyl alcohol for 6-10 hours at 100°-110°. Transparent golden crystals, m.p. 25°-25.5°, b.p. 191°-192°/9.5-10 mm. (von Tatschloff, J. pr. Chem. 1902, (2) 65, 239). B^*HBr , greyish-brown leaflets (T.).

Ethyl-o-toluidine; in 54 p.c. yield by heating o-toluidine hydrobromide or hydriodide with 5 p.c. excess of ethyl alcohol at 150° for 8 hours (Reinhardt and Stadel, Ber. 1883, 16, 31); by electrolytic reduction of aceto-o-toluidine in sulphuric acid solution (Baillie and Tafel, Ber. 1899, 32, 73; Vorländer, *ibid.* 1901, 34, 1462). Liquid, b.p. 213°-214° (R. and S.), or 204°-206° (Norton, Amer. Chem. J. 1885, 7, 118), or 214°-216°/737 mm. (B. and T.); D_{15}^{15} 0.9534 (N.).

Acetyl-derivative; b.p. 254°-256° (R. and S.); nitrosoamine; oil, volatile with steam (N.).

5-Chloroethyl-o-toluidine; oil, b.p. 252°-253°/760 mm. (Geigy & Co., D. R. P. 105103 of 1898).

5-Nitroethyl-o-toluidine; by keeping a mixture of ethyltolyl-o-nitrosoamine and absolute alcoholic hydrochloric acid (O. Fischer and Hepp, Ber. 1886, 19, 2994); by the action of sodium nitrite upon a solution of ethyl-o-toluidine in hydrochloric acid (O. Fischer, Ann. 1895, 286, 163; Weinberg, Ber. 1892, 25, 1610). Green leaflets with a blue shimmer, m.p. 140°.

4-Nitroethyl-o-toluidine; by nitration of ethyl-o-toluidine with mixed acids at a low temperature (MacCullum, Chem. Soc. Trans. 1895, 67, 247). Light red needles, m.p. 81°-82°.

Nitrosoamine; m.p. 56°. When treated with zinc chloride or sulphuric acid the ethyl-amino-compound is regenerated (M.).

Acetyl-derivative; tables, m.p. 90° (M.).

5-Nitroethyl-o-toluidine; together with a little of the diethyl-derivative by heating 5-nitro-o-toluidine with ethyl iodide, alcohol and sodium hydroxide. The two bases are separated by crystallisation from a little hot alcohol and acetylation. Large dark yellow plates, m.p. 96° (Bernthsen, Ber. 1892, 25, 3137).

Acetyl-derivative; tables or prisms, m.p. 96°-97° (B.).

4-Nitrobromoethyl-o-toluidine; by brominating 4-nitroethyl-o-toluidine in acetic acid. Needles, m.p. 114°; B^*HBr , m.p. 194°-195° (decomp.) (MacCullum, *l.c.*).

Diethyl-o-toluidine; in 70 p.c. yield by ethylating ethyl-o-toluidine with ethyl iodide at 100° (Norton, Amer. Chem. J. 1885, 7, 119), or in 90 p.c. yield by ethylating o-toluidine hydrobromide or hydriodide with ethyl alcohol at 150° for 8 hours (Reinhardt and Stadel, Ber. 1883, 16, 29). Oil, b.p. 206°-200°/755 mm. (R. and S.), or 210°/738 mm. (van Romburgh, Rec. trav. chim. 1884, 3, 402). $B^*HI + H_2O$, prisms, m.p. 72°-73° (N.).

When warmed with fuming nitric acid it yields a dinitrotolyl-o-ethylnitroamine, crystals, m.p. 71°-72° (v. R.), and when treated in acid solution with iodine and potassium iodide, it yields a hydrogen iodide peroxide, $C_{10}H_9NH_2$, steel-blue crystalline precipitate or dark brown

prisms, m.p. 109° (Santleben, Ber. 1898, 31, 1145).

5-Nitrodiethyl-o-toluidine; see 5-nitroethyl-o-toluidine. Oil, readily soluble in dilute sulphuric acid (Bernthsen, Ber. 1892, 25, 3137).

Phenyl-o-toluidine; together with diphenylamine and ditolylamine, by heating o-toluidine with aniline hydrochloride at 280° (Girard and Willm, Bull. Soc. chim. 1876, (1) 25, 248) or by heating a mixture of 1 part of bromobenzene with 3 parts of o-toluidine and 8 parts of soda lime for 8 hours at 390° (Merz and Paschkowetzky, J. pr. Chem. 1893, (2) 48, 461). M.p. 41°, b.p. 305°/727.5 mm. (Graebe, Ann. 1887, 238, 363). It forms a violet-blue coloration with nitric acid.

6-Chloro-3-nitrophenyl-o-toluidine; by heating 2-chloro-5:6-dinitrotoluene with alcoholic aniline for several weeks; in 75 p.c. yield by heating 2-chloro-5-nitro-o-toluidine for 10 hours under a reflux with bromobenzene in presence of nitrobenzene, potassium carbonate, and cuprous iodide. Rhomboidal plates, m.p. 108°-109°.

Nitrosoamine, yellow prisms, m.p. 91° (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190).

2:4-Dinitrophenyl-o-toluidine; from chloro-2:4-dinitrobenzene and o-toluidine. M.p. 101°-102° (Leymann, Ber. 1882, 15, 1236), or 123° (M. L. B., Eng. Pat. 17639 of 1895; Fr. Pat. 250460; D. E. P. 85388 of 1895), or 120° (Reitzenstein, J. pr. Chem. 1903, (2) 68, 251).

3:5-Dinitrophenyl-o-toluidine; from 2-chloro-3:5-dinitrotoluene and aniline. Red leaflets, m.p. 169° (Nietzki and Rehe, Ber. 1892, 25, 3007).

Di-o-tolylamine (see phenyl-o-toluidine, Girard and Willm); by heating o-cresol, ammonium-zinc chloride, and ammonium chloride at 330°-340° (Merz and Müller, Ber. 1887, 20, 547). Liquid, b.p. 312°/727.5 mm. (Graebe).

Anhydroformaldehyde-o-toluidine; from formaldehyde and o-toluidine. Oil (Wellington and Tollens, Ber. 1885, 18, 3307), or lustrous plates, m.p. about 100° (Eberhardt and Welter, Ber. 1894, 27, 1808).

Methylene-di-o-tolyl-diimide; by heating a mixture of o-toluidine, formaldehyde, potassium hydroxide, and alcohol at 100° (Eberhardt and Welter, l.c.); or by the action of formaldehyde on an aqueous solution of o-toluidine (Eibner, Ann. 1898, 302, 349).

Prismatic needles, m.p. 52° (E. and W.). On heating with aniline hydrochloride it yields diaminoditolylmethane, and by boiling with alcohol it yields anhydroformaldehyde-o-toluidine (E. and W.).

The condensation of formaldehyde with o-toluidine in presence of concentrated sulphuric and acetic acids (cf. J. Russ. Phys. Chem. Soc. 1904, 36, 1126) yields as sole product 6-amino-5-methylbenzo-cyclo-butadiene (Nastukoff and Kroneberg, *ibid.* 1912, 44, 1200; cf. Kroneberg, *ibid.* 1914, 46, 305).

It is also stated that when 4 mols. of o-toluidine and 1 mol. of methylene chloride are heated for 7 hours at 110°-115°, two methylenedi-o-toluidines are formed.

The liquid compound is a thick oil, b.p. above 360° (decomp.); B.E. PtCl₃ is amorphous.

The solid compound forms small trimetric crystals, m.p. 124°, yielding a crystalline di-

hydrochloride, dihydrobromide, sulphate, and dioxalate (Grünhagen, Ann. 1890, 256, 303).

Tolyl-o-hydroxylamine; by reducing o-nitrotoluene with zinc dust and 66 p.c. alcohol in the presence of calcium chloride and sufficient ether to keep the temperature at about 65° (Bretschneider, J. pr. Chem. 1897, (2) 55, 293); by electrolytic reduction of o-nitrotoluene in dilute acetic acid (Haber, Zeitsch. Elektrochem. 1898, 5, 77); by oxidising o-toluidine with a persulphate in presence of ether and in contact with ice (Bamberger and Tschirner, Ber. 1899, 32, 1677). It solidifies to a resin in a mixture of solid carbon dioxide and ether and is readily oxidised to o-nitrosotoluene. On mixing with thionyl-aniline in benzene solution it yields o-toluidine phenyl sulphonomate, m.p. 206°, and azo-o-toluene (Michaelis and Petou, Ber. 1898, 31, 984). The action of methyl alcohol, ethyl alcohol and sulphuric acid, dilute sulphuric acid, dilute and concentrated hydrochloric acid on o-, m-, and p-tolylhydroxylamine under various conditions is described by Bamberg (Ann. 1921, 424, 233, 297).

6-Nitrotolyl-o-hydroxylamine; obtained in 50-60 p.c. yield when 2:6-dinitrotoluene is reduced electrolytically in presence of sodium acetate, acetic acid and alcohol (Brand and Zöller, Ber. 1907, 40, 3324). It exists in three modifications, two stable and one unstable, which are interconvertible by inoculation of their solutions in benzene. The stable yellow form has m.p. 117°-117.5°, the stable colourless form becomes yellow at 105° and melts at 117°-117.5° (Brand, Ber. 1911, 44, 2045).

With aqueous sodium hydroxide it yields mainly 2:2'-dinitro-6:6'-azoxytoluene, and when heated dinitroazotoluene is formed. When oxidised with ferric chloride and sodium acetate in aqueous solution 2-nitro-6-nitrosotoluene, colourless needles, m.p. 117°, is obtained, whilst with concentrated sulphuric acid it yields 2-nitro-6-amino-3-hydroxytoluene, and when heated with concentrated hydrochloric acid 3-chloro-2-nitro-6-aminotoluene, together with a small amount of the isomeric 5-chloro-2-nitro-6-aminotoluene, is produced (Brand and Zöller, l.c.).

4:6-Dinitrotolyl-o-hydroxylamine; together with 2:6-dinitrotolyl-p-hydroxylamine by reducing 2:4:6-trinitrotoluene in almost neutral solution at a silver cathode. Light yellow crystals, m.p. 109° (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; Ber. 1916, 49, 673).

m-Toluidine; by reduction of m-nitrotoluene (Beilstein and Kuhlberg, Ann. 1870, 155, ¶; 1870, 156, 66); from p-toluidine by successive acetylation, nitration, hydrolysis, elimination of the amino-group, and reduction (Lorenz, Ber. 1874, 7, 448); by heating m-cresol with ammonium-zinc bromide and ammonium bromide at 330°-340° (Merz and Müller, Ber. 1887, 20, 548); by reducing m-nitrobenzylidene chloride with zinc in presence of alcohol and hydrochloric acid below 12° (Karlrich, Ber. 1883, 16, 2011; Widman, *ibid.* 1890, 13, 677; Harn, *ibid.* 1895, 18, 3398; Steiner and Vienna, Bull. Soc. chim. 1881, (2) 35, 429; Widman, *ibid.* 1881, (2) 36, 216); from m-nitrotoluene by passing its vapour mixed with hydrogen over heated reduced copper or nickel (Graham and Saunders, Chem. rep. 1901, 124, 321).

Colourless oil, b.p. 203.3° (Kahlbaum, *Zeitsch. physikal. Chem.* 1898, 26, 621, 648), 202°-205° (M. and M.; Lorenz, *Ann.* 1874, 172, 180), 199°-202° (Buckha and Schachtebeck, *Ber.* 1889, 22, 840), 199°-199.5° (Schraube and Romig, *ibid.* 1893, 26, 579); D_4^{20} 0.98912 (Kahlbaum), D_4^{15} 1.0041, D_{15}^{15} 0.9981, D_{25}^{25} 0.990 (Perkin, *Chem. Soc. Trans.* 1896, 69, 1245; cf. Neubeck, *Zeitsch. physikal. Chem.* 1897, 1, 658); magnetic rotatory power at 15° 16.21 (P.); refractive power, see Brühl (*Zeitsch. physikal. Chem.* 1895, 16, 216); molecular heat of combustion at constant volume, 964.6 Cal.; at constant pressure, 965.6 Cal. (Petit, *Ann. Chim.* 1889, [6] 18, 154).

Its solution in diluted sulphuric acid is coloured yellow-brown by chromic acid and sulphuric acid, and dark red by nitric acid. When *m*-toluidine is dissolved in ether and an equal volume of water is added, followed by a few drops of calcium hypochlorite solution, the aqueous layer is coloured brownish-yellow, and the ethereal layer reddish (Lorenz, *Ann.* 1874, 172, 180).

It resembles the *o*-compound in many of its properties, but may be distinguished from the latter by its acetyl-derivative, m.p. 65.5° (aceto-*o*-toluidide melts at 110°). It may be detected and also estimated by conversion into the dimethyl-derivative, which, unlike the corresponding *o*- and *p*-compounds, readily yields a nitroso-derivative as a yellow crystalline precipitate when treated with nitrous acid (Wurster and Riedel, *Ber.* 1879, 12, 1796).

When hydrogenated in the presence of reduced nickel it yields *m*-methyl cyclohexylamine, together with the corresponding secondary and tertiary bases (Sabatier and Senderens, *Bull. Soc. chim.* 1904, (3) 31, 709). It reacts with diphenylthiocarbamide in presence of lead hydroxide to yield diphenyl-*m*-tolyl-guanidine (Alway and Viele, *Amer. Chem. J.* 1902, 28, 294); with benzylidene-acetyl-acetone to yield β -toluidinebenzyl-acetyl-acetone (Ruhemann and Watson, *Chem. Soc. Trans.* 1904, 85, 1170); with methylene di-iodide to yield di-*m*-tolyl-methylene-diamine (Senier and Goodwin, *ibid.* 1902, 81, 280); with chloroacetylurethane to yield β -*m*-tolylhydantoin (Frerichs and Breustedt, *J. pr. Chem.* 1902, (2) 66, 231), and with benzaldehyde cyanhydrin to yield *m*-tolylamino-benzyl cyanide (Sachs and Goldmann, *Ber.* 1902, 35, 3319). Coupling with diazo-compounds has been studied by Mehner (*J. pr. Chem.* 1902, (2) 66, 401). The action of dichloroacetic acid on *m*-toluidine has been studied by Heller (*Ann.* 1908, 358, 349).

It is only employed to a limited extent technically in the production of dyestuffs (M. L. B., *Eng. Pat.* 5119 of 1897; *Fr. Pat.* 264579; *D. R. P.* 93499 of 1896; *Eng. Pat.* 14937 of 1906; *U.S. Pat.* 913940; *D. R. P.* 219210 of 1907; Monnet, Reverdin and Nölting, *Ber.* 1879, 12, 445; Rosenstiehl and Gerber, *Compt. rend.* 1882, 94, 1319; 95, 238).

For a new sensitive indicator from *m*-toluidine see Träger and Hille (*J. pr. Chem.* 1903, (2) 68, 297).

Salts (see Lorenz); $BHCl$, leaflets, m.p. 228°, b.p. 247.5°/728 mm. or 249.8°/760 mm. (Ullmann, *Ber.* 1898, 31, 1699); $BHNO_2$, large

rhombic tables; $B_2H_4SO_4$, needles; $B_2C_2H_4O_4$, unstable leaflets; $B_2(C_2H_4O_4)_2$; $B_2C_2H_4O_4$ (Eisenberg, *Ann.* 1880, 205, 270); $B_2H_4PtCl_6$, yellow slender needles (Widman); $BHIBl$ (Kraut, *Ann.* 1881, 210, 323); $B_2H_4ZnCl_4$, needles (Base, *Amer. Chem. J.* 1898, 20, 654); $B_2H_4ZnCl_4$, needles (B.); $BHCl_2HgCl_2$, tables (Swan, *Amer. Chem. J.* 1898, 20, 624); $BHCl_2HgCl_2$, tables (Swan); $(B_2H_4Cl)_2HgCl_2$, leaflets (Swan); $BHSnCl_4 + 4H_2O$, silver leaflets (Slagle, *Amer. Chem. J.* 1898, 20, 642); $B_2H_4SnCl_4 + H_2O$, monoclinic tables (Slagle); $B_2H_4SbCl_4 + H_2O$ (Higbee, *Amer. Chem. J.* 1900, 23, 150); $B_2H_4SbCl_4$, rhombic tables (H.); $B_2H_4ZnBr_4 + 4H_2O$ prisms (B.); $B_2H_4ZnBr_4$, needles and prisms (B.); $B_2H_4SbBr_4 + H_2O$ (H.); $B_2H_4SbI_4$ (H.); $B_2H_4SnCl_4$, pearly white plates, m.p. 76° (Druce, *Chem. News*, 1919, 119, 272); $B_2H_4SnCl_4$, pale pink, nacreous plates, m.p. 284° (D.); *picrate*, striated monoclinic crystals, decomposing when heated above 180° (Jerusalem, *Chem. Soc. Trans.* 1909, 95, 1284).

Formyl-derivative; liquid at -18°, b.p. 278°/724 mm. (Niementowski, *Ber.* 1887, 20, 1892). Decomposes on long boiling, forming methane ditolylamidine, $CH(NC_2H_5)_2NHC_2H_5$, needles or plates, m.p. 123°.

Acetyl-derivative; long needles, m.p. 65.5°, b.p. 203° (Beilstein and Kuhlberg; Morgan and Micklethwait, *Chem. Soc. Trans.* 1913, 103, 1400); **benzoyl-derivative**; m.p. 125° (Just, *Ber.* 1886, 19, 983).

Chloroacetyl-derivative; m.p. 141°. On fusion with potassium hydroxide it is converted into 5:5'-dimethylindigotin (Kuhara and Chikashigé, *Amer. Chem. J.* 1902, 27, 1).

Dichloroacetyl-derivative; plates which sublime, m.p. 98°-100° (Rugheimer and Hoffmann, *Ber.* 1885, 18, 2988).

2-Chloro-*m*-toluidine; by reducing 2-chloro-3-nitrotoluene (Wynne and Greeves, *Chem. Soc. Proc.* 1895, 11, 151; *Chem. Soc. Trans.* 1895, 67, 1548; cf. Cohen and Dakin, *ibid.* 1901, 79, 1128); by the action of hydrochloric acid on *m*-tolylhydroxylamine (Bamberger, *Ber.* 1902, 35, 3697). M.p. 6.6° (Wibaut, *Rec. trav. chim.* 1913, 32, 244), b.p. 228°-229° (W. and G.), and is volatile with steam.

Acetyl-derivative; needles, m.p. 132°-133° (W. and G.; W.), or 133°-134° (Bamberger, Ter-Sarkisjan and de Werra, *Ber.* 1906, 35, 3697, 3711), or 126°-128° (Cohen and Dakin, *l.c.* 1321); **benzoyl-derivative**; needles, m.p. 125° (W.).

4-Chloro-*m*-toluidine; by the action of hydrochloric acid on *m*-tolylhydroxylamine (Bamberger); reduction of 4-chloro-3-nitrotoluene (Goldschmidt and Hönig, *Ber.* 1886, 19, 2442; Gattermann and Kaiser, *Ber.* 1885, 18, 2601; cf. Engelbrecht, *ibid.* 1874, 7, 797; Claus, *J. pr. Chem.* 1892, (2) 46, 29). Thin very volatile colourless leaflets, m.p. 29°-30° or 32°, b.p. 230°/758 mm. (G. and K.; C.).

$BHCl$, needles, partially dissociated in water (G. and K.).

Acetyl-derivative; long silky needles, m.p. 96°-97° (G. and K.; G. and H.; E.), or 124° (C.).

5-Chloro-*m*-toluidine; by reduction of 2-chloro-3-nitrotoluene (Hönig, *Ber.* 1887, 20, 2419). Liquid, b.p. 242°/730 mm., volatile with steam.

B'HCl , small needles; B'HNO_3 , m.p. 198° (decomp.) (H.).

Acetyl-derivative; needles, m.p. 146° (H.) or 151° (W. and G.).

6-Chloro-m-toluidine; by the action of hydrochloric acid on m-tolylhydroxylamine (Bamberger); by the method of Chattaway and Orton (Chem. Soc. Trans. 1901, 79, 461); by reducing 6-chloro-3-nitrotoluene (Henry and Radziszewski, Ber. 1869, 2, 308, 599; Wroblewsky, Ann. 1873, 168, 206; Goldschmidt and Hönig, Ber. 1886, 19, 2443; 1887, 20, 199; Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1544); by reducing m-nitrotoluene with zinc and hydrochloric acid (Kock, Ber. 1887, 20, 1567). Tables, m.p. 83.5° – 84.1° (Bamberger, Ter-Sarkisjanz and de Werra; Reverdin and Crépieux, Ber. 1900, 33, 2503; Chattaway and Orton).

B'HCl , long slender needles; B'HNO_3 , long broad needles, m.p. 164° ; $\text{B}_2\text{H}_4\text{SO}_4$.

Acetyl-derivative; colourless plates, m.p. 89° (G. and H.), 91.2° – 91.7° (B., T.-S. and de W.), 92° (M. and C.).

2:5-Dichloro-m-toluidine; by reduction of 2:5-dichloro-3-nitrotoluene (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1330). It melts at 69° – 70° .

2:6-Dichloro-m-toluidine; by chlorination of 2-chloro-aceto-m-toluidide followed by hydrolysis with hydrochloric acid at 130° (Cohen and Dakin), or by reduction of 2:6-dichloro-3-nitrotoluene, followed by distillation with steam (C. and D., l.c. 1346). Colourless needles, m.p. 59° – 60° .

Acetyl-derivative; long needles, m.p. 120° – 122° (C. and D.); *benzenesulphonyl-derivative*, m.p. 114° (Raper, Cohen and Thomson, *ibid.* 1904, 85, 371).

4:5-Dichloro-m-toluidine; by reducing 3-nitro-4:5-dichlorotoluene; *acetyl-derivative*, needles, m.p. 158° – 159° (Cohen and Dakin, l.c. 1338).

4:6-Dichloro-m-toluidine; by chlorination of aceto-m-toluidide in glacial acetic acid with sodium chlorate and hydrochloric acid, followed by hydrolysis (Reverdin and Crépieux, l.c.); by reduction of 2:4-dichloro-5-nitrotoluene (Cohen and Dakin, l.c.). Crystals, m.p. 85° , volatile with steam (cf. Seelig, Ann. 1887, 237, 163).

Acetyl-derivative; as above (R. and C.); by the action of bleaching powder on aceto-m-toluidide in glacial acetic acid (C. and D., l.c. 1332). Colourless needles, m.p. 156° – 157° (R. and C.; C. and D.).

5:6-Dichloro-m-toluidine; by reducing 2:3-dichloro-5-nitrotoluene. Needles, m.p. 88° , b.p. 292° (Wynne and Greeves, l.c.).

Acetyl-derivative, m.p. 187° (W. and S.).

2:4:6-Trichloro-m-toluidine; by chlorination of aceto-m-toluidide in acetic and hydrochloric acids with sodium chlorate at 15° – 25° , followed by hydrolysis of the acetyl-derivative with 50 p.c. sulphuric acid (Cohen and Dakin, l.c. 1335; Reverdin and Crépieux). Glistening white needles, volatile with steam, m.p. 77° – 78° (C. and D.).

Acetyl-derivative; m.p. 181° (R. and C.).

2:5:6-Trichloro-m-toluidine; by nitration and reduction of 2:5:6-trichlorotoluene. It melts at 55° – 57° (Cohen and Dakin, Chem. Soc. Trans. 1904, 85, 1281).

4-Bromo-m-toluidine; by reduction of 4-bromo-3-nitrotoluene (Neville and Winther, Chem. Soc. Trans. 1880, 37, 442; Ber. 1880, 13, 972; Claus, J. pr. Chem. 1892, (2) 46, 25; Wroblewsky, Ann. 1873, 168, 77; Hübner and Roos, Ber. 1873, 6, 800). Prisms, m.p. 20.6° – 22° (N. and W.), 35° (C.), 67° (W.), 75° (H. and R.). The higher melting-point compounds are impure.

Acetyl-derivative; m.p. 113.7° – 114.6° (N. and W.), 164° (C.).

5-Bromo-m-toluidine; by reducing 5-bromo-3-nitrotoluene (Wroblewsky, Ann. 1878, 192, 203). It crystallises with difficulty, m.p. 35.6° – 36° , b.p. 255° – 260° ; D_{15}^{20} 1.442 (W.; Neville and Winther, Ber. 1880, 13, 964; Chem. Soc. Trans. 1880, 37, 429). B'HCl , tables; B'HNO_3 , long needles; $\text{B}_2\text{H}_4\text{SO}_4$, tables.

Acetyl-derivative; m.p. 167° – 168° (N. and W.).

6-Bromo-m-toluidine; by brominating aceto-m-toluidide, followed by hydrolysis of the product with alcoholic potash (Wroblewsky, Ann. 1873, 168, 172); by reducing 6-bromo-3-nitrotoluene (Neville and Winther, l.c.). Crystals, m.p. 78.4° – 78.8° , b.p. 240° (N. and W.). B'HNO_3 , prisms.

It is probable that the product, described as a liquid and obtained by Hübner and Roos (Ber. 1873, 6, 801) by the reduction of nitrated o-bromotoluene is identical with this amine. B'HCl , small rhombic tables; B'HNO_3 , small rhombic tables; $\text{B}_2\text{H}_4\text{SO}_4$, very slightly soluble in water.

2:5-Dibromo-m-toluidine; by reduction of 2:5-dibromo-3-nitrotoluene. M.p. 72.4° – 73.1° (Neville and Winther, l.c.).

Acetyl-derivative; m.p. 144° – 145° (N. and W.).

2:6-Dibromo-m-toluidine; this compound is stated by Wroblewsky to be formed by the action of 2 mols. of bromine on aceto-m-toluidide, followed by hydrolysis, and is described as melting at 92.5° . Neville and Winther (Chem. Soc. Trans. 1880, 37, 439) found that under these conditions a mixture of a monobromotoluidine, m.p. 76° – 77° , 4:6-dibromo-m-toluidine, 2:6-dibromo-m-toluidine, m.p. 33° – 35° , and 2:4:6-tribromo-m-toluidine is formed.

4:5-Dibromo-m-toluidine; by reducing the corresponding dibromonitrotoluene (Neville and Winther, l.c.; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 510). Long needles or flat prisms, m.p. 58° – 59° (N. and W.).

Acetyl-derivative; m.p. 163.5° – 164° (C. and D.).

4:6-Dibromo-m-toluidine; together with 2:6-dibromo-m-toluidine by brominating aceto-m-toluidide, separation being effected by crystallisation from alcohol in which the 2:6-derivative is more soluble; by brominating 4-bromo-aceto-m-toluidide, followed by hydrolysis (Neville and Winther, l.c.); by bromination of 6-bromoaceto-m-toluidide (Cohen and Dutt, l.c., 515); by reduction of 4:6-dibromo-3-nitrotoluene with tin and hydrochloric acid (Davies, Chem. Soc. Trans. 1901, 81, 872). Dull greyish radiating prisms, m.p. 74.5° – 75° (D.).

Acetyl-derivative; white prisms or needles, m.p. 168° – 168.5° (N. and W.), 168° – 169° (C. and D.).

5:6-Dibromo-m-toluidine; by successive bromination and hydrolysis of 4-bromoaceto-

toluidide; by reduction of 5:6-dibromo-3-nitrotoluene (Neville and Winther, l.c.). It melts at 86-4° (N. and W.) or 83°-85° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 512).

Acetyl-derivative; m.p. 204°-205° (N. and W.).

2:4:6-Tribromo-*m*-toluidine; by the action of bromine vapour on *m*-toluidine hydrochloride; by bromination of aceto-*m*-toluidide, followed by hydrolysis (Wroblewsky, Ann. 1873, 168, 195; Neville and Winther, Chem. Soc. Trans. 1880, 37, 440, 448).

Monooacetyl-derivative; colourless crystals, m.p. 205°.

Diacetyl-derivative; colourless crystals, m.p. 103° (Blanksma, Chem. Weekblad, 1909, 6, 717).

2:5:6-Tribromo-*m*-toluidine; by brominating 2:5-dibromoaceto-*m*-toluidide, followed by hydrolysis (Neville and Winther). It melts at 93°-94°.

Acetyl-derivative; m.p. 179°-181° (N. and W.).

4:5:6-Tribromo-*m*-toluidine; by successive bromination and hydrolysis of 4:5-dibromoaceto-*m*-toluidide (N. and W.). It melts at 96°-96.8°.

Acetyl-derivative; m.p. 171°-173° (N. and W.).

Tribromo-toluidine; from *o*-bromotoluene *m*-sulphonic acid, by nitration, reduction and bromination (Schäfer, Ann. 1874, 174, 362; Ber. 1874, 7, 1355). M.p. 82°.

Tetra-bromo-m-toluidine; by brominating 5-bromo-*m*-toluidine (Neville and Winther, Ber. 1880, 13, 975; Chem. Soc. Trans. 1880, 37, 449); or 4:5-dibromo-*m*-toluidine (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 510). White needles, m.p. 223°-224° (N. and W.).

6-Chloro-2:4-di-bromo-*m*-toluidine; by brominating an aqueous solution of 6-chloro-*m*-toluidine 4-sulphonic acid (Davies, Chem. Soc. Trans. 1921, 119, 866). Long colourless needles, m.p. 99.5°, which on keeping become bright red. Insoluble in dilute hydrochloric acid and only slightly soluble in hot fuming hydrochloric acid.

2-Iodo-*m*-toluidine; by reducing 2-iodo-3-nitrotoluene with ferrous sulphate and ammonia (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441). Long flat prisms, m.p. 41°-42°.

Acetyl-derivative; m.p. 135°. On oxidation with potassium permanganate it yields 2-iodo-3-acetylaminobenzoic acid, m.p. 119° (Wh. and L.).

4-Iodo-*m*-toluidine; similarly from 4-iodo-3-nitrotoluene. It melts at 38°-38.5° (Wheeler and co-workers, *ibid.* 1910, 44, 126, 493), and not at 48° as stated by Willgerodt and Simonis (Ber. 1906, 39, 269). B'HCl, pale yellow needles; B'HNO₃, red needles; B'H₂SO₄ (Wi. and S.).

Acetyl-derivative; m.p. 151° (W.), 145°-146° (Wi. and S.). On treatment with iodine chloride it yields 4:6-di-iodoaceto-*m*-toluidide.

Formyl-derivative; slender colourless needles, m.p. 129° (Wi. and S.).

5-Iodo-*m*-toluidine; by reducing 5-iodo-3-nitrotoluene (W.). Long colourless needles, m.p. 78°-78.5°.

Acetyl-derivative; m.p. 183° (W.).

An *o*-toluidine; needles or leaflets, m.p. 188°-189° described by Hübner and Glassner (Ber. 1875, 8, 562), and is obtained from nitrated

p-iodotoluene. It forms a *hydrochloride*, needles; a *nitrate*, plates; and a *sulphate*, needles.

6-Iodo-*m*-toluidine; by reducing 6-iodo-3-nitrotoluene (Artmann, Monatsh. 1905, 26, 1091; Holleman, Rec. trav. chim. 1912, 31, 267). Colourless leaflets which decompose slowly on exposure to air, m.p. 98°-99° (A.), or m.p. 37°-39° (Wheeler, &c.), or m.p. 42° (H.). B'HCl, short needles; B'HNO₃, aggregates of slender needles (A.).

Acetyl-derivative; white needles, m.p. 132° (A.).

2:5-Di-iodo-*m*-toluidine; by reduction of 2:5-di-iodo-3-nitrotoluene (Wheeler, &c.). Pale brown prisms, m.p. 82°.

Acetyl-derivative; long colourless needles, m.p. 198°-199° (W.).

2:6-Di-iodo-*m*-toluidine; by the action of iodine chloride on 2-iodoaceto-*m*-toluidide, followed by hydrolysis (Wheeler, &c.). Colourless prisms, m.p. 88°.

Acetyl-derivative; colourless prisms, m.p. 171° (W.).

4:5-Di-iodo-*m*-toluidine; by reducing 4:5-di-iodo-3-nitrotoluene (Wheeler, &c., l.c.). Colourless slender needles, m.p. 66°-67°.

Acetyl-derivative; m.p. 183°-184° (W.).

4:6-Di-iodo-*m*-toluidine; by the action of iodine on 4-iodo-*m*-toluidine (Wheeler, &c.). Stout colourless needles, m.p. 73°-74°.

Acetyl-derivative; long colourless needles, m.p. 213° (W.).

5:6-Di-iodo-*m*-toluidine; by the action of ferrous sulphate and ammonia on 2:3-di-iodo-5-nitrotoluene (W.). Colourless crystals, volatile with steam, m.p. 106°.

Acetyl-derivative; m.p. 208° (W.).

2:4:6-Tri-iodo-*m*-toluidine; pale brown hair-like needles, m.p. 135°.

Acetyl-derivative; m.p. 265° (W.).

2:4:6-Tri-iodo-*m*-toluidine; together with 2:4:5:6-tetraiodo-*m*-toluidine by warming a mixture of 2:5-di-iodo-*m*-toluidine with iodine, water, ether and calcium carbonate for 18 hours. Colourless needles, m.p. 119°-120° (W.).

4:5:6-Tri-iodo-*m*-toluidine; by warming a mixture of 5:6-di-iodo-*m*-toluidine, iodine, water, ether and calcium carbonate for several hours. Small needles, m.p. 122°.

Acetyl-derivative; colourless needles, m.p. 265° (decomp.) (W.).

2:4:5:6-Tetraiodo-*m*-toluidine; together with other products by iodination of 2:5- or 5:6-di-iodo-*m*-toluidine under similar conditions (W.). Small needles, m.p. 205° (W.).

6-Chloro-4-iodo-*m*-toluidine; by successive chlorination and hydrolysis of 4-iodoaceto-*m*-toluidide (Willgerodt and Simonis, Ber. 1906, 39, 269). Thin colourless plates, m.p. 65°; *oxalate*; large plates, m.p. 165°.

Acetyl-derivative; aggregates of small colourless needles, m.p. 196°-197° (Wi. and S.).

6-Nitroso-*m*-toluidine; by heating 1 part of nitroso-*m*-cresol with 15 parts of dry ammonium acetate and 5 parts of ammonium chloride for 1 hour at 100° (Mehne, Ber. 1888, 21, 730). Steel-blue needles, m.p. 178°.

2-Nitro-*m*-toluidine; see also Limpricht, Ber. 1885, 18, 1402; Städel and Kolb, Ann. 1890, 259, 216; Nölting and Stoecklin, Ber. 1891, 24, 564; together with small quantities

of 3-nitro-*o*-toluidine and 2:3-toluylenediamine by reduction of 2:3-dinitrotoluene suspended in alcoholic hydrochloric acid, with stannous chloride and absolute alcohol at 7° and keeping the mixture for 12 hours. It forms deep red prisms, m.p. 107°-108° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052), and was formerly erroneously regarded as a dinitro-*o*-toluene (Kenner and Parkin, *ibid.* 1920, 117, 857). When 2:3-dinitrotoluene is reduced with hydrogen sulphide in alcoholic ammoniacal solution, Kenner and Parkin (*l.c.*) obtained a dinitroditolyl sulphide (most probably the 2:2':6:6'-compound) and a substance, m.p. 54°. 2-Nitro-*m*-toluidine is obtained also by heating 3-chloro-2-nitrotoluene with concentrated ammonia solution (D 0-880) at 200° for 8 hours.

Acetyl-derivative; transparent prisms, m.p. 126° (B. and K.) or 136° (L.).

4-Nitro-*m*-toluidine; from 4-nitro-*m*-tolyl-ethyl ether and ammonia (Städel and Kolb, Ann. 1890, 259, 224; Green and Rowe, Chem. Soc. Trans. 1913, 103, 898; Morgan and Scharff, Chem. Soc. Trans. 1914, 105, 121); by hydrolysis of the acetyl-derivative, obtained together with 6-nitroaceto-*m*-toluidide by nitrating aceto-*m*-toluidide with fuming nitric acid in glacial acetic acid (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333); from 4-nitro-2:5-toluylenediamine by the diazo-reaction (Morgan and Micklethwait, *ibid.* 1913, 103, 1399; Morgan and Scharff, *l.c.*); by heating 3:4-dinitrotoluene with 2:5/*N*-methyl alcoholic ammonia at 150° for 6 hours (Kenner and Parkin, *ibid.* 1920, 117, 858). Golden-yellow plates, or orange-yellow spicules, m.p. 109° (S. and K.), 110°-110.5° (C. and D.), or 112° (M. and M.).

Acetyl-derivative; yellow needles, m.p. 88°-89° (M. and M.) or 86°-87° (C. and D.); *benzoyl-derivative*; long yellow needles, melting indefinitely at 83° (M. and M.); *benzenesulphonyl-derivative*; prisms, m.p. 137°-138° (M. and S.).

5-Nitro-*m*-toluidine; in 80 p.c. yield by reducing 3:5-dinitrotoluene with alcoholic ammonium sulphide (Städel, Ann. 1883, 217, 199; Neville and Winther, Ber. 1882, 15, 2985; Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 529). Yellow or brownish-red needles, m.p. 98°-98.4° (N. and W.; Haibach). B'HBr, thin leaflets (Haibach, J. pr. Chem. 1902, (2) 65, 242).

Acetyl-derivative; white microcrystalline powder, m.p. 187° (B., D. and R.). If a solution of the acetyl-derivative in concentrated sulphuric acid is added to nitric acid, or if the solid compound be added to a mixture of nitric and sulphuric acids, 5:6-dinitroaceto-*m*-toluidide is the main product, but if the acetyl-compound is added directly to fuming nitric acid 4:5-dinitroaceto-*m*-toluidide preponderates (B., D. and R.).

6-Nitro-*m*-toluidine; by successive nitration and hydrolysis of aceto-*m*-toluidide (Beilstein and Kuhlberg, Ann. 1871, 158, 348), or together with the 4-nitro-isomeride when the nitration is effected in glacial acetic acid solution (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333; Cook and Brady, *ibid.* 1920, 117, 752); by heating 6-nitro-3-amino-*p*-toluidic acid with hydrochloric acid at 150° (Filioli and Orosi, Gazz. chim. Ital. 1899, 18, 394); by heating 6-nitro-3-cresol

ethyl ether with concentrated ammonia (D 0-9) at 140°-150° for 8 hours (Städel and Kolb, Ann. 1890, 259, 214); as chief product, together with the 4-nitro-isomeride, by nitrating *m*-toluidine dissolved in glacial acetic acid and sulphuric acid with nitric acid (63 p.c.) and sulphuric acid at 0°, the isomerides being separated by distilling with a current of steam (Nöling and Stoecklin, Ber. 1893, 26, 564; cf. Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1397; Kenner and Parkin, *ibid.* 1920, 117, 858). Long, slender, saffron-yellow needles, m.p. 138° (N. and S.), 138°-140° (M. and M.), 133°-134° (C. and D.), or 135°-138° (Cohen and Hodsman, *ibid.* 1907, 91, 976).

Acetyl-derivative; small rhombic cubes, m.p. 101°-102° (B. and K.), or massive red prisms, m.p. 103°-104° (C. and D.), or m.p. 109° (M. and M.). It is separated from 4-nitroaceto-*m*-toluidide by mechanical means, followed by crystallisation from alcohol (C. and D.), or by pouring the reaction product into water when the 6-nitro-isomeride separates, whilst the filtrate on keeping deposits 4-nitroaceto-*m*-toluidide (C. and B.).

2:4-Dinitro-*m*-toluidine; *acetyl-derivative*; colourless needles, m.p. 211°-212° (C. and B.).

2:6-Dinitro-*m*-toluidine; in 10-15 p.c. yield by the action of hydroxylamine hydrochloride on 2:6-dinitrotoluene in methyl alcoholic potassium hydroxide solution at 30°, and addition of much water to the resulting solution (Meisenheimer and Patzig, Ber. 1906, 39, 2533); by the action of 10 p.c. alcoholic ammonia on 3-bromo-2:6-dinitrotoluene (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339). Pale yellow prisms or needles, m.p. 133.8° (K. and C.) or 132.5° (M. and P.).

Acetyl-derivative; colourless plates or large prisms, m.p. 166° (K. and C.; C. and B.).

4:5-Dinitro-*m*-toluidine; see 5-nitro-*m*-toluidine. Large brownish-yellow needles, m.p. 131°.

Acetyl-derivative; fine white needles, m.p. 177° (B., D. and R.).

4:6-Dinitro-*m*-toluidine; by keeping a mixture of 3:4:6-trinitrotoluene and alcoholic ammonia for 1 day (Hepp, Ann. 1883, 215, 368); by heating *m*-bromo-4:6-dinitrotoluene with alcoholic ammonia (Bentley and Warren, Amer. Chem. J. 1890, 12, 2); by heating 4:6-dinitro-*m*-cresyl ethyl-ether with concentrated aqueous ammonia at 100° (Städel and Kolb, Ann. 1890, 259, 220); as the main product, together with a small quantity of 2:6-dinitro-*m*-toluidine, and very little, if any, 2:4-dinitro-*m*-toluidine, by gradual addition of aceto-*m*-toluidide to 10 times its weight of nitric acid (D 1.5) with thorough agitation, keeping the temperature below 25°, followed by hydrolysis. Occasionally 2:4:6-trinitro-*m*-toluidine is formed also (Cook and Brady, Chem. Soc. Trans. 1920, 117, 750); together with the 2:6-dinitro-isomeride by gradual addition of 6-nitroaceto-*m*-toluidide to an excess of nitric acid (D 1.5) below 25°, followed by hydrolysis (C. and B.). Small golden-yellow crystals, m.p. 192°-193° (H.) or 195° (S. and K.).

Acetyl-derivative; pale yellow needles, m.p. 103° (C. and B.).

5:6-Dinitro-*m*-toluidine; see 5-nitro-*m*-toluidine. Orange-yellow plates, m.p. 145°.

Acetyl-derivative: faintly yellow sandy powder, m.p. 172° (Brady, Day and Rolt).

2:4:6-*Trinitro-m-toluidine*: by the action of concentrated alcoholic ammonia on the ethyl-ether of 2:4:6-trinitro-*m*-cresol (Nölting and Salis, Ber. 1882, 15, 1864; Ann. Chim. 1885, (6) 4, 128; Stadel and Kolb, Ann. 1890, 259, 222), or on *m*-bromo-trinitrotoluene (Bentley and Warren, Amer. Chem. J. 1890, 12, 5), or on 3-chloro-2:4:6-trinitrotoluene (Reverdin, Dresel and Deletra, Bull. Soc. chim. 1904, (3) 31, 631). Small crystals, m.p. 136° (S. and K.) or 126° (N. and S.).

Acetyl-derivative, microscopic white silky needles, m.p. 249° (decomp.) (Cook and Brady, Chem. Soc. Trans. 1920, 117, 752).

2-Chloro-4-nitro-*m-toluidine*: by keeping a solution of 2-chloro-3:4-dinitrotoluene in about 60 parts of absolute alcohol saturated with ammonia for 14 days (Morgan and Glover, Chem. Soc. Trans. 1921, 119, 1704). Golden-yellow needles, m.p. 105°. It yields a deep red coloration with alcoholic sodium hydroxide.

6-Chloro-4-nitro-*m-toluidine*: obtained together with 6-chloro-2-nitro-*m-toluidine* by successive nitration and hydrolysis of 6-chloro-aceto-*m-toluidide* (B. A. S. F., D. R. P. 226772 of 1908; Morgan and Challenor, Chem. Soc. Trans. 1921, 117, 1544), or together with 27 p.c. 6-chloro-3-nitro-*p-toluidine*, by the action of alcoholic ammonia on 2-chloro-4:5-dinitrotoluene. The latter mixture melts at 144°, and is not separated by repeated crystallisation from alcohol, petroleum or glacial acetic acid (Morgan and Drew, *ibid.* 1920, 117, 789; Morgan and Challenor, *l.c.*). Yellowish-brown prisms, m.p. 158°-159°.

2:4:5-*Trichloro-6-nitro-m-toluidine*: the *acetyl-derivative*, which does not melt below 200°, is obtained together with a *dichloro-6-nitroaceto-m-toluidide*, colourless needles, m.p. 181°-183°, by treating 6-nitroaceto-*m-toluidide* with aqueous sodium chlorate in presence of glacial acetic and concentrated hydrochloric acids (Cohen and Dakin, Chem. Soc. Trans. 1903, 83, 333).

4:5:6-*Trichloro-2-nitro-m-toluidine*: by treating 4:5:6-trichlorodinitrotoluene with alcoholic ammonia at 80°-100°. It melts at 192° (Seelig, Ber. 1885, 18, 420).

6-Bromo-2-nitro-*m-toluidine*: see 6-bromo-4-nitro-*m-toluidine*. It melts at 102°-103° (Neville and Winther, Ber. 1880, 13, 972; Chem. Soc. Trans. 1880, 37, 444; Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 513).

6-Bromo-4-nitro-*m-toluidine*: as main product together with the 2-nitro-isomeride by nitrating 4-bromoaceto-*m-toluidide* with sulphuric and nitric acids (N. and W.), or in presence of glacial acetic acid (C. and D.), followed by hydrolysis. Dark yellow or brown needles, m.p. 179°-181°.

Acetyl-derivative: m.p. 125°-125.5° (C. and D.).

5-Bromo-6-nitro-*m-toluidine*: by successive nitration and hydrolysis of 5-bromoaceto-*m-toluidide* (Neville and Winther, Ber. 1880, 13, 1945; Chem. Soc. Trans. 1880, 37, 630). It melts at 87°-88°.

2:6-Dibromo-4-nitro-*m-toluidine*: by bromination of 6-bromo-4-nitro-*m-toluidine* (N. and W.). Yellow needles, m.p. 139°-133° (C. and D.) or 124°-130° (N. and W.).

2:4:6-Tribromo-5-nitroaceto-*m-toluidide*: by nitrating 2:4:6-tribromoaceto-*m-toluidide* with nitric acid (D 1-52), followed by hydrolysis with concentrated sulphuric acid at 110° (Blankama, Chem. Weekblad, 1909, 6, 717). Pale yellow needles, m.p. 184°.

Acetyl-derivative: colourless needles, m.p. 261°; *diacetyl-derivative*: colourless crystals, m.p. 188° (B.).

Methyl-m-toluidine: by the action of dimethyl sulphate (Ullmann, Ann. 1903, 327, 104) or methyl iodide on *m-toluidine*. The product is freed from *m-toluidine* by treating the ethereal solution with dilute sulphuric acid and from the dimethyl-derivative by subsequent treatment with acetic anhydride (Monnet, Reverdin and Nölting, Ber. 1878, 11, 2279). Liquid, b.p. 206°-207°.

Acetyl-derivative: m.p. 66°, b.p. about 250°.

4-Nitromethyl-*m-toluidine*: by the action of methylamine on the methyl-ether of 4-nitro-*m*-cresol. Brownish-yellow flat prisms, m.p. 83° (O. Fischer and Rigeud, Ber. 1902, 35, 1258).

6-Nitromethyl-*m-toluidine*: by the action of concentrated nitric acid on the nitrosoamine (Störmer and Hoffmann, Ber. 1898, 31, 2535). Yellowish-brown plates with a blue sheen, m.p. 92°-93°.

Nitrosoamine; yellowish plates, m.p. 73°-74°.

6-Chloro-4-nitromethyl-*m-toluidine*: by the action of dry methylamine on an absolute alcoholic solution of 6-chloro-4:5-dinitrotoluene; by heating 6-chloro-4-nitro-*m-toluidine* with methyl sulphate in toluene at 100° for 4 hours (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190). Long red acicular prisms, m.p. 126°-127°.

Nitrosoamine; yellow plates, m.p. 70°.

2:4:6-Trinitromethyl-*m-toluidine*: by the action of methylamine on the methyl-ether of 2:4:6-trinitro-*m*-cresol. It melts at 138° (Blankama, Rec. trav. chim. 1902, 21, 327).

Dimethyl-*m-toluidine*: by the action of methyl iodide on *m-toluidine* or by distilling toluene trimethylammonium hydroxide (Monnet, Reverdin and Nölting). B.p. 215° (Wurster and Riedel, Ber. 1879, 12, 1797), 208° (Reinhardt and Stadel, *ibid.* 1883, 16, 31). $B'_2H_4Fe(CN)_6 + 2H_2O$, white needles; $B'_2H_4Fe(CN)_6 + 1\frac{1}{2}H_2O$ (Wurster and Roser, *ibid.* 1879, 12, 1826).

Nitroso-derivative; green leaflets or long needles, m.p. 92°. Does not give Liebermann's nitroso-reaction. With aniline, *o*-toluidine, &c., it yields steel-blue double compounds. $B'HCl$, yellow or greenish-yellow needles; $B'_2H_4Fe(CN)_6 + H_2O$; $B'_2H_4Fe(CN)_6 + H_2O$ (Wurster and Roser).

Nitrodimethyl-*m-toluidine*: by oxidising the above nitroso-compound with potassium permanganate (Wurster and Riedel). Long yellow needles, m.p. 84°.

5-Nitrodimethyl-*m-toluidine*: blood-red, glistering rhombic tables or double pyramids, m.p. 52° (Jäger, Z. Kristall. 1903, 38, 89), or 48°-50° (Haibach, J. pr. Chem. 1902, (2) 65, 242).

Dinitrodimethyl-*m-toluidine*: by nitrating an acetic acid solution of dimethyl-*m-toluidine* (Wurster and Riedel). Yellow needles, m.p. 107°. When the nitration is carried out with nitric acid alone or in presence of sulphuric acid this compound is accompanied by an isomeride, small yellow crystals, m.p. 168°, which is less

soluble in alcohol than the former (Wurster and Riedel).

Bromodimethyl-m-toluidine; by brominating dimethyl-m-toluidine hydrochloride (Wurster and Riedel, Ber. 1879, 12, 1800). White leaflets, m.p. 98°, b.p. 276°. $B_3H_7Fe(CN)_6 + 4H_2O$; $B_3H_7Fe(CN)_6 + 4\frac{1}{2}H_2O$ (Wurster and Roser, l.c., 1825).

4-Nitroethyl-m-toluidine; by treating the ethyl-ether of 4-nitro-m-cresol with ethylamine at 165°-170°. It melts at 60° (Fischer and Rigaud, Ber. 1901, 34, 4202).

2:4:6-Trinitroethyl-m-toluidine; in a similar manner from 2:4:6-trinitro-m-cresol. It melts at 98°, and the nitroamine at 79° (Blanksma).

Diethyl-m-toluidine; b.p. 227°-228° (Reinhardt and Stadel, Ber. 1883, 16, 31).

Phenyl-m-toluidine; by strongly heating a mixture of 5-phenylamino-m-cresol with zinc dust (Zega and Buch, J. pr. Chem. 1886, (2) 33, 542). Reddish oil, b.p. 300°-305°. Its solution in sulphuric acid is coloured an intense green by nitric acid.

4-Nitrophenyl-m-toluidine; by heating 5-phenylamino-4-nitrotoluene 2-sulphonic acid with sulphuric acid (25 p.c.) at 145° for 4 hours (Schräube and Romig, Ber. 1893, 26, 581). Yellowish-red plates from alcohol or six-sided tables from ligroin, m.p. 110°.

Diphenyl-m-toluidine; by the interaction of m-chlorotoluene and potassium diphenylamine (Haessermann, Ber. 1901, 34, 38). It melts at 69°-70°.

6-Chloro-4-nitrophenyl-m-toluidine; by boiling 2-chloro-4:5-dinitrotoluene with aniline in alcoholic solution for 36 hours; in a yield of 50 p.c. from 6-chloro-4-nitro-m-toluidine by heating under a reflux with bromobenzene, potassium carbonate and cuprous iodide (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 190). Rectangular pyramids, m.p. 95°-96°.

Nitrosoamine; yellow prisms, m.p. 95°-96°.

2-Chloro-4-nitrophenyl-m-toluidine; in a similar manner to the 6:4-isomeride from 2-chloro-3:4-dinitrotoluene and 2-chloro-4-nitro-m-toluidine, respectively (M. and J.). Orange-red needles, m.p. 95°.

Di-m-tolylamine; by heating m-toluidine with its hydrochloride at 210°-240° (Cosack, Ber. 1880, 13, 1091); by heating m-cresol with ammonia, zinc chloride and ammonium chloride at 330°-340° (Merz and Müller, Ber. 1887, 20, 90). Liquid, b.p. 319°-320°, volatile with steam.

Acetyl-derivative; tables, m.p. 43° (C.).

Tolyl-m-hydroxylamine; plates, m.p. 68° (Bamberger, Ber. 1895, 28, 248). On oxidation yields m-oxxytoluene and m-nitrosotoluene.

Nitroso-derivative, $(CH_3)_2C_6H_4N(NO)OH$, as glistening needles, m.p. 54°-54.5° (B.). **Di-m-hydroxylamine** when treated in the same manner with formaldehyde or when acted upon by methanone yields **methylene-N-N-di-tolyl-hydroxylamine**, $CH_3[N(OH)C_6H_4CH_3]_2$, needles, m.p. 118° (Bamberger and Tschirner, Ber. 1900, 33, 951, 958), and when added in a dry-divided condition to concentrated hydrochloric acid saturated at -8° to -10° with hydrogen chloride and the mixture allowed to remain in an ice chest for 7 days, the product consists of m-oxxytoluene, 3-amino-6-cresol, 4-chloro-m-toluidine, 2-chloro-m-toluidine, and

4-chloro-m-toluidine (Bamberger, Ter-Sarkissian and de Werra, Ber. 1902, 35, 3697; cf. Bamberger and de Werra, *ibid.* 3711). It reacts with thionyl aniline yielding m-toluidine phenylsulphonamide and benzene-azo-m-toluidine (Michaelis and Petou, Ber. 1898, 31, 984).

p-Toluidine; see o-toluidine; by reduction of p-nitrotoluene (Muspratt and Hofmann, Ann. 1845, 54, 1; 1848, 66, 144; Noad, *ibid.* 1847, 63, 305; Miller, Zeit. f. Chem. 1864, 161; Sell, Chem. Soc. Trans. 1863, 16, 186); together with ditolyl oxide by heating p-cresol with ammoniacal zinc chloride at 300° (Buch, Ber. 1884, 17, 2037; Merz and Müller, *ibid.* 1887, 20, 545); by reduction of p-nitrobenzyl chloride with zinc dust (Rudolf, Jahresbericht, 1885, 2082; D. R. P. 34234 of 1885); by treating p-aminobenzyl alcohol with a solution of stannous chloride at 100° for $\frac{1}{2}$ hour (Thiele and Dimroth, Ann. 1899, 305, 121); by reduction of polymerised anhydro-p-aminobenzyl alcohol with zinc dust and hydrochloric acid (Kalle & Co., Eng. Pat. 1963 of 1895; Fr. Pat. 246918; D. R. P. 83544 of 1894); by the action of heat on the salts of methylaniline (Hofmann, Ber. 1872, 5, 720).

The conversion of methylaniline into p-toluidine hydrochloride has been studied by Beckmann and Correns (Ber. 1922, 55, 852), who showed that the main factor governing the change is the temperature, the addition of such salts as zinc chloride or aluminium chloride having little effect. p-Toluidine is also formed by the action of hydroxylamine on toluene in presence of aluminium or ferric chloride (Graebe, Ber. 1901, 34, 1778), and by heating hydrazo-p-toluene with alcohol at 120°-130° (Biehringer and Busch, Ber. 1903, 36, 339).

Commercial p-nitrotoluene usually contains some nitrobenzene and o-nitrotoluene, consequently the crude reduction product contains aniline and o-toluidine. The crude product may be first purified by distillation, freezing the fraction, b.p. 195°-205°, followed by crystallising the solid product from ligroin.

p-Toluidine crystallises from aqueous alcohol in leaflets, m.p. 45° (Städeler, J. pr. Chem. 1864, 425), or 42.77° (Mills, Phil. Mag. 1883, (5) 14, 27), 42.8° (Perkin, Chem. Soc. Trans. 1896, 68, 1245), b.p. 198° (Muspratt and Hofmann), or 200.4° (Hulett, Zeitsch. physikal. Chem. 1899, 28, 651, 657; Kahlbaum, *ibid.* 1898, 26, 621; cf. Neuback, *ibid.* 1887, 1, 659), or 200.3° (P.); D_{50}^{20} 0.973, D_{70}^{20} 0.967 (P.), 1.046 (Räddorf, Ber. 1879, 12, 252); magnetic rotatory power at 50° 15.87 (P.); dissociation constant, $K = 20.6 \times 10^{-10}$ (Löwenherz, Zeitsch. physikal. Chem. 1898, 25, 394); refractive power, see Brühl (*ibid.* 1895, 16, 216), Eykman (Rec. trav. chim. 1893, 12, 278); cryoscopic behaviour, see Auwers (*ibid.* 1897, 23, 451), Ampola and Rinatoni (Gazz. chim. ital. 1897, 27, 1, 43); heat of combustion at constant pressure 958.8 Cal., heat of combustion at constant volume, 957.86 Cal. (Petit, Compt. rend. 1898, 107, 206; Ann. Chim. 1899, (6) 18, 152).

p-Toluidine may be separated from aniline by means of the oxalate (Brinmeyer, Zeit. f. Chem. 1865, (2) 1, 513), or by acetylation (Wald and Merz, Ber. 1895, 2, 453), or by means of formaldehyde (D. R. P. 37615 of 1895). 4-nitro-

of *o*- and *p*-toluidine may be separated in a similar manner (Rosenstiehl). This method has been used quantitatively for the separation of *o*- and *p*-toluidine (Rosenstiehl, Ann. Chim. 1872, (4) 26, 249; Lorenz, Ann. 1874, 172, 190; cf. Raabe, Zeitsch. anal. Chem. 1890, 30, 720). A method of estimating *p*-toluidine in admixture with *o*-toluidine which depends upon the solidifying point of the acetylated product is given by Holleman (Proc. K. Akad. Wetensch. Amsterdam, 1904, 7, 395).

Salts: $B'HCl$, scales (Rosenstiehl, Bull. Soc. chim. 1868, (2) 10, 199), needles, m.p. 238°–240° (Bischoff and Walden, Ann. 1894, 279, 134), 236° (Krafft, Ber. 1899, 32, 1601), 243°; b.p. 255.5°/728 mm. or 257.5°/760 mm. (Ullmann, *ibid.* 1898, 31, 1699); $B'HB$, plates (Stadel, *ibid.* 1883, 16, 28); $B'HI$, plates (S.); $B'HNO_3$, long rhombic tables; $B'_2H_2SO_4$, scales (Beilstein and Kuhlberg), $B'_2H_2SO_4$ (Wellington and Tollens, Ber. 1885, 18, 3311), $+H_2O$ (Hitzel, Bull. Soc. chim. 1894, [3] 11, 1054); *chlorate*, long white crystals, exploding at 125° (Datta and Choudhury, J. Amer. Chem. Soc. 1916, 38, 1079); $B'_2H_2PO_4$, large glistening plates (Lewy, Ber. 1886, 19, 1717), $B'_2H_2ClO_4$, needles, m.p. 101°–102° (Baralis, Jahresbericht, 1884, 698) or 97.5° (Suchin, Ber. 1888, 21, 1259); $B'_2H_2Cl_2O_4$, needles, m.p. 135°–136° (Duisberg, Ber. 1885, 18, 194) or 140°–141° (Baralis); $B'_2H_2Cl_2O_4$, m.p. 137° (Baralis); $B'_2H_2Cl_2O_4$, prisms, m.p. 135° (Baralis); $B'_2H_2O_4 + \frac{1}{2}H_2O$ (Bornemann, Ber. 1899, 22, 2710; Rosenstiehl, Bull. Soc. chim. 1871, (2) 17, 4); $B'HB$, glistening leaflets (Kraut, Ann. 1881, 210, 324); $(B'_2H_2SO_4) \cdot HI \cdot I_2$ (Jørgensen, J. pr. Chem. 1876, (2) 14, 386); $B'_2Si_2F_8$ (Corney and Jackson, Amer. Chem. J. 1888, 10, 173); $B'_2ZnCl_2 + 3H_2O$, crystalline precipitate (Lachowicz, Monatsh. 1889, 9, 513); $B'_2H_2ZnCl_4$ (Grafinghoff, Zeit. f. Chem. 1865, (2) 1, 599), tables (Base, Amer. Chem. J. 1898, 20, 656); $B'_2H_2ZnCl_4$, triclinic crystals (B.); $B'_2 + 2ZnSO_4$ (L.); B'_2MgCl_2 (Tombeck, Ann. Chim. 1900, (7) 21, 397); $2B'CdCl_2$ (L., *i.e.* 698; T.); $B'HClHgCl_2$, needles (Swan, Amer. Chem. J. 1898, 20, 626); B'_2HgCl_2 , thick needles, m.p. 123°–125° (Klein, Ber. 1878, 11, 744); $2B'HgBr_2$, large plates, m.p. 120°–121° (Klein, *ibid.* 1880, 13, 835); $2B'HgI_2$, m.p. 81° (K.); $B'_2Cu_2H_4(SO_4)_2$; $B'HgH_4(SO_4)_2 + H_2O$ (Denigès, Compt. rend. 1891, 112, 870); $B'HSCN \cdot Cr(NH_3)_4(SCN)_4$ (Christensen, J. pr. Chem. 1892, (2) 45, 362); $B'_2H_2Co(CN)_6 + 2H_2O$; $(B'HCN) \cdot (B'HCN)Co(CN)_6 + 11H_2O$ (Weselsky, Jahresbericht, 1869, 314); B'_2CoCl_2 (Lippmann and Vortmann, Ber. 1879, 12, 81); $2B'_2NiCl_2 + 2C_2H_5OH$ (L. and V.); $4B' + Ag_2SO_4 + 2H_2O$, hair-like needles (Mixer, Amer. Chem. J. 1880–1, 1, 240); $B'_2H_2CuCl_2$ (Pomey, Compt. rend. 1887, 104, 300); $B'HSCl_2 + \frac{1}{2}H_2O$, yellow crystals (Slagle, Amer. Chem. J. 1898, 20, 644); $B'_2H_2SnCl_4$; $B'_2H_2SnCl_4$, monoclinic crystals (Hjortdahl, Jahresbericht, 1882, 535); $B'_2H_2SnCl_4$, yellow crystals (St.); $(B'HCi)_2SbF_6$ (Redetz, Archiv. der Pharmacie, 236, 273); $(B'HCi)_2SbF_6$, plates, m.p. 232° (R.); $B'_2H_2SbCl_4 + \frac{1}{2}H_2O$ (Higbee, Amer. Chem. J. 1900, 23, 150); $B'_2H_2SbCl_4 + H_2O$ (H.); $B'_2H_2BiCl_4$ (Hauser and Vanno, Ber. 1900, 33, 2271); B'_2ZnBr_2 (Tombeck, Ann. Chim. 1900, (7) 21, 438); $B'_2H_2ZnBr_2$, leaflets decomposed by water (Base, Amer. Chem. J. 1898, 20, 659; Tom-

beck); B'_2CdBr_2 (T.); $B'_2H_2SbBr_2 + H_2O$ (H.); $B'_2H_2SbBr_2$ (H.); $B'_2H_2SbBr_2$ (H.); $B'_2H_2OCl_2$ (T.); $B'HsBi$ (H.); B'_2AgNO_3 , m.p. 101° (T.); Mixer); B'_2MgSO_4 (T.); B'_2CdSO_4 (T.); $B'_2Zn(C_2H_5O_2)_2$ (T.); B'_2AuCl_4 ; $B'_2H_2PtCl_4$ (M.; H.; de Coninck, Bull. Soc. chim. 1886, (2) 45, 131); B'_2PtCl_4 (Gordon, Ber. 1870, 3, 177; Cochlin, Bull. Soc. chim. 1879, (2) 31, 499); $B'_2PtCl_4P(OC_2H_5)_3$ (Saillard, Bull. Soc. chim. 1872, (2) 18, 111); $B'_2PtCl_4P(OCH_3)_3$; $B'_2PtCl_4P(OC_2H_5)_3$ (Cochlin, Jahresbericht, 1878, 315); $B'_2H_2Pt(CN)_6$, monoclinic crystals (Scholz, Monatsh. 1880, 1, 905); $B'_2Cu(NO_3)_2$ (Lachowicz, Monatsh. 1889, 10, 896); B'_2ZnBr_2 ; B'_2ZnI_2 ; B'_2CdBr_2 ; B'_2CdI_2 ; $B'_2Cd(NO_3)_2$; B'_2HgCl_2 ; $B'_2Hg(NO_3)_2$; $B'_2Hg(CN)_2$; $B'_2UO_2Cl_2$; B'_2MnCl_2 (Leeds, Jahresbericht, 1882, 503); *muicate*, $B'_2C_6H_5O_4$, yellow crystals; *picrate*, $B'_2C_6H_5N_3O_4$, flat yellow prisms, m.p. 169° (decomp.) (Smolka, Monatsh. 1885, 6, 923); *phenate*, needles (Dyson, Chem. Soc. Trans. 1883, 43, 468); *compound with picramide*, $B'_2C_6H_5(NO_2)_2NH_2$, black needles with a brown reflex (Mertens, Ber. 1878, 11, 843); *toluene p-sulphonic acid salt*, needles, m.p. 140° (Hälsig, J. pr. Chem. 1897, (2) 55, 217).

Sodium salt: from *p*-toluidine and sodamide, amorphous (Titherley, Chem. Soc. Trans. 1897, 71, 465). *p*-Toluidine monohydrate, see Walker and Beveridge, *ibid.* 1907, 91, 1797; Lewy, Ber. 1886, 19, 2728.

A solution of *p*-toluidine in ether or water is not coloured by calcium hypochlorite, and a blue colour indicates the presence of *o*-toluidine. A solution in diluted sulphuric acid is coloured red by chromic acid, and blue, changing to red and finally to brown by nitric acid (Rosenstiehl, Bull. Soc. chim. 1868, (2) 10, 200). A solution in acetic acid, diluted with water or alcohol, is coloured bright red by lead peroxide (Lauth, Compt. rend. 1890, 111, 975).

When a few drops of ferric chloride solution are added to a slightly acid solution of *p*-toluidine in hydrochloric acid and boiled, a bordeaux-red colour is produced. If aniline or *o*-toluidine is present, a bluish-green precipitate is formed and the filtrate is red. This reaction is so sensitive that traces of *p*-toluidine may be detected in 'pure' specimens of aniline and *o*-toluidine (Biehringer and Busch, Chem. Zeit. 1902, 26, 1128).

p-Toluidine acts as a very weak base (Walker, Zeitsch. physikal. Chem. 1890, 5, 195; Bredig, *ibid.* 1894, 13, 323; Lowenherz, *ibid.* 1908, 25, 394).

By the action of potassium dichromate on *p*-toluidine sulphate, Perkin (Chem. Soc. Trans. 1880, 37, 646) obtained two oxidation products, $C_{12}H_{11}N_3$ and $C_{12}H_{11}N_3$. Oxidation with lead peroxide leads to one or other of these products depending upon the conditions (Börnstein, Ber. 1901, 34, 1274). Oxidation with ozone yields *p*:*p*-azotoluene (Otto, Ann. Chim. 1898, (7) 13, 143). When treated in sulphuric acid solution with potassium permanganate, *p*-toluidine yields nitrosotoluene (Bamberger and Tschirner, Ber. 1898, 31, 1524), whilst with chloroform and calcium chloride, azotoluene is formed (Meigen and Normann, *ibid.* 1900, 33, 2711); the latter is formed also when *p*-toluidine is oxidized with ozone, hydrogen peroxide, or potassium dichromate under certain conditions (Bamberger

and Tschirner, *ibid.* 1899, 32, 1877; Otto, Ann. Chim. 1898, (7) 13, 142). When heated with aqua regia *p*-toluidine yields chlorotoluene; with hydrogen iodide toluene is produced; and when heated with a meta-derivative of nitrobenzene in the presence of hydrochloric acid, dyestuffs of the chrysaniline series are formed (D. R. PP. 65985 of 1892; 78377, 79263, 79585, 79877, 81048 of 1894).

p-Toluidine heated with sulphur gives rise to the primuline bases (Green, Ber. 1889, 22, 968; Jacobson, *ibid.* 330; Gattermann, *ibid.* 422; Gattermann and Pfizinger, *ibid.* 1063; Hunter, J. Soc. Chem. Ind. 1923, 42, 302 T). Heated with ethyl alcohol and zinc chloride *p*-toluidine forms 4-amino-1-methyl-3-ethylbenzene (Willgerodt and Brandt, J. pr. Chem. 1904, (2) 69, 433).

p-Toluidine condenses with bromo- and sulphonated methylaminoanthraquinones, &c., forming bluish-green dyes (Fr. Bayer & Co., D. R. P. 159129 of 1901; Wacker, Ber. 1902, 35, 2593; Friedländer and Schick, Zeitsch. Farb. Text. Ind. 1904, 3, 218; see also M. L. B., Eng. Pat. 8905 of 1903; U.S. Pat. 748375; D. R. P. 149780; Bayer & Co., D. R. P. 148767, 153517 of 1903; M. L. B., D. R. P. 174131 of 1905).

p-Toluidine also condenses with diazo-compounds (Mehner, J. pr. Chem. 1902, (2) 65, 401); with phenylurethane (Dixon, Chem. Soc. Trans. 1901, 79, 102); with methylene iodide (Senier and Goodwin, *ibid.* 1902, 81, 280); with acetylene tetrabromide (Sabaneff and Rakovsky, J. Russ. Phys. Chem. Soc. 1902, 34, 408); with phenyl isocyanate (Walther and Stenz, Bull. Soc. chim. 1901, (3) 26, 395); with epichlorhydrin (Cohn and Friedländer, Ber. 1904, 37, 3034); and with trinitrotoluene, *p*-toluidine forms an additive compound, dark red crystals, m.p. 68° (Jackson and Clarke, Chem. Soc. Proc. 1906, 22, 84). *p*-Toluidine reacts with phenylazoisimide at 140° to form a substance, $C_{11}H_{11}N_3$, colourless needles, m.p. 116°, converted into a brown viscous mass on benzoylation, from which benzo-*p*-toluidide is obtained by treatment with alcoholic hydrochloric acid (Wolff and Kolasius, Ann. 1912, 394, 59).

As in the case of *o*-toluidine, the *p*-isomeride when diazotised in sulphuric acid solution, then saturated with sulphur dioxide, treated with copper, filtered, washed with ammonia and the filtered filtrate treated with ferric chloride, the ferric toluene sulphinat, $Fe(C_6H_4(CH_3)SO_3)_3$, is formed (Thomas, Chem. Soc. Trans. 1909, 95, 53).

p-Toluidine condenses with aromatic aldehydes in the presence of its hydrochloride forming acridines (Ullmann, Ber. 1903, 35, 107). Other condensation products of *p*-toluidine with aldehydes, see Eibner and Amann (Ann. 1903, 329, 211); Friedländer (Ber. 1892, 25, 149); Eibner and Parucker (*ibid.* 1900, 33, 321); Hantzsch and Schwab (*ibid.* 1901, 34, 2, 841); Cohn and Friedländer (*ibid.* 1902, 35, 1266); Cohn and Blau (Monatsh. 1904, 25, 3), &c. On hydrogenation in presence of fused nickel, *p*-toluidine yields *p*-methylbenzylamine, together with the corresponding secondary and tertiary bases (Sabatier and Deriva, Bull. Soc. chim. 1904, (3) 31, 709). When treated with ethyl alcohol in presence of

zinc chloride it yields aminomethylstyrene (Willgerodt and Brandt, J. pr. Chem. 1904, (2) 69, 433). With dichloroacetic acid it yields *p*-tolylamino-*p*-methyl-oxindole (Keller, Ann. 1904, 332, 247).

On exhaustive chlorination in acetic acid with moist chlorine *p*-toluidine yields heptachloromethylcyclohexanone. When *p*-toluidine is chlorinated in 97 p.c. sulphuric acid it is converted mainly into 3-chloro- and partly into 2-chloro-derivatives. The same products, together with 3:5-dichloro-*p*-toluidine, are obtained if 40 p.c. sulphuric acid is used. 3-Chloro-, 3:5-dichloro-, and higher chlorinated products are obtained by chlorinating aceto-*p*-toluidide (Hafner, Ber. 1889, 22, 2535; Wroblewsky, Ann. 1873, 168, 196; Lellmann and Klotz, *ibid.* 1885, 231, 308; Zincke, Ber. 1895, 28, 3121). Chlorinated products are obtained also when *p*-toluidine is electrolysed in an excess of hydrochloric acid (Eils and Brunschweiler, J. pr. Chem. 1895, (2) 52, 559).

Formyl-derivative; together with the oxalyl-derivative by heating *p*-toluidine oxalate (Hübner, Ann. 1881, 209, 372); by boiling *p*-toluidine with formic acid (Tobias, Ber. 1892, 15, 2446). Very long needles, m.p. 52° (T.) or 53° (Bamberger and Wulz, *ibid.* 1891, 24, 2080). $NaC_6H_4NO + H_2O$ (T.); AgC_6H_4NO , needles (Cornstock and Clapp, Amer. Chem. J. 1891, 13, 527); $Hg(C_6H_4ON)_2$, needles (Wheeler and MacFarland, *ibid.* 1896, 18, 545); $HgCl_2 \cdot C_6H_4ON$, needles, (W. and M.); $(C_6H_4ON)_2 \cdot HgBr_2$, colourless prisms (Cornstock, *ibid.* 1898, 20, 79). For crystalline and liquid modifications of formyl-*p*-toluidide, see Orloff (J. Russ. Phys. Chem. Soc. 1905, 37, 439).

Acetyl-derivative; when *p*-toluidine is boiled for $\frac{1}{2}$ hour with an excess of acetic anhydride a mixture of 32 p.c. of the monoacetyl-derivative and 60 p.c. of the diacetyl-derivative is formed (Sudborough, Chem. Soc. Trans. 1901, 79, 537). Dimorphous, crystallising in monoclinic forms (Pancbianco, Gazz. chim. ital. 1879, 9, 362; Riche and Berard, Ann. 1864, 129, 77), m.p. 147° (Hübner and Wallach, Ann. 1870, 154, 302; Kelbe, Chem. Soc. Abstr. 1883, 44, 915), 145°-149° (S.), or 153° (Feitler, Zeitsch. physikal. Chem. 1889, 4, 76), b.p. 307° (Boilestein and Kuhlberg, Ann. 1870, 156, 74). On oxidation with potassium permanganate it yields acetyl-*p*-aminobenzoic acid, and on treatment with phosphorus pentachloride the iminochloride $CH_2Cl \cdot N(C_6H_4 \cdot CH_3)$ is formed (Wallach, Ann. 1882, 214, 203). The *nitrocamine* is obtained by the action of nitrous acid on an acetic acid solution of aceto-*p*-toluidide (O. Fischer, Ber. 1877, 10, 959), or by treating a strongly alkaline solution of toluene-*p*-diazonium chloride at -5° with acetic anhydride (Pechmann and Frobenius, Ber. 1894, 27, 653). It forms needles, m.p. 90° (decomp.), and regenerates aceto-*p*-toluidide on reduction.

Aceto-*p*-toluidide forms compounds with sodium methoxide and ethoxide (Cohen and Archdeacon, Chem. Soc. Trans. 1896, 69, 93), and yields an *N*-chloro-derivative, four-sided prisms, m.p. 81°-82°, and an *N*-bromo-derivative, yellow four-sided prisms, m.p. 94°-95° (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 791).

For the halogen derivatives of aceto-*p*-

toluolide containing the halogen in the acetyl-group, *see* Tommasi (Bull. Soc. chim. 1873, (2) 19, 400); Eckenroth and Donner (Ber. 1890, 23, 3287); Bischoff and Walden (Ann. 1894, 279, 65); Grothe (Archiv. der Pharmacie. 238, 589); Cech (Ber. 1877, 10, 879); Rugheimer and Hoffmann (*ibid.* 1885, 18, 2980); Judson (*ibid.* 1870, 3, 784); Cloëz (Ann. Chim. 1886, (6) 9, 216); Abenius (J. pr. Chem. 1889, (2) 40, 433); Meyer (Ber. 1875, 8, 1154); Keller (Ann. 1904, 332, 247).

Diacetyl-derivative; colourless crystals, m.p. 48° (Sudborough, Chem. Soc. Trans. 1901, 79, 537; *cf.* Clayton, Ber. 1898, 28, 1665), b.p. 153.5°-154.5°/11 mm., 177.5°-178.5°/30 mm., 211.5°-212°/100 mm. (Kay, Ber. 1893, 26, 2852). B'HCl, m.p. 120° (Dehn, J. Amer. Chem. Soc. 1912, 34, 1399).

Benzoyl-derivative; from *p*-toluidine and benzoyl chloride (Jaillard, Zeit. f. Chem. 1865, (2) 1, 440; Kelbe, Ber. 1875, 8, 875; Hübner, Ann. 1881, 208, 310; Wallach, Ann. 1882, 214, 217; Gudeman, Ber. 1888, 21, 2553; Müller, Ber. 1889, 22, 2404). Needles, m.p. 158°, b.p. 232°.

p-Nitro-derivative, yellow needles, m.p. 197° (Gattermann, Ber. 1892, 25, 1082).

Phthalyl-derivative; m.p. 204° (Fröhlich, Ber. 1884, 17, 2679).

2-Chloro-p-toluidine; by reducing 2-chloro-4-nitrotoluene or 2-chloro-4-nitrobenzyl bromide with tin and hydrochloric acid (Witt, Ber. 1892, 25, 86; Lellmann, Ber. 1884, 17, 535); together with other products by reducing 2-chloro-4-nitrotoluene with sodium disulphide (Blanksma, Chem. Weekblad, 1909, 6, 899), or with iron powder in the presence of a small quantity of sulphuric acid (Wibaut, Rec. trav. chim. 1913, 32, 244), or almost quantitatively with iron filings and hydrochloric acid (Davies, Chem. Soc. Trans. 1921, 119, 868); by boiling acetyl-*p*-toluidine-2-diazopiperidine with concentrated hydrochloric acid (Wallach, Ann. 1886, 235, 253). Colourless crystalline solid, m.p. 26° (D.) or 23.1° (W.), b.p. 237°-238.5°, or 242°-244°/760 mm. (D.), or 245° (Wynne and Greeves, Chem. Soc. Proc. 1895, 11, 151). B'HCl, very large needles; B'₂H₄SO₄, small leaflets; B'₂H₄PtCl₆.

Acetyl-derivative; m.p. (+1H₂O) 86° (W. and G.), 104°-105° (anhydrous) (Blanksma, *l.c.*; Kunkell and Lillig, J. pr. Chem. 1912, (2) 86, 517; Wibaut, *l.c.*); *benzoyl-derivative*; needles, m.p. 122° (Wibaut).

3-Chloro-p-toluidine; in poor yield by successive chlorination and hydrolysis of aceto-*p*-toluolide (Wroblewski, Ann. 1873, 168, 196; Lellmann and Klotz, Ann. 1885, 231, 309; Lellmann, Ber. 1894, 24, 4111); as the chief product by passing a rapid stream of chlorine through a boiling solution of aceto-*p*-toluolide in its own weight of acetic acid, followed by hydrolysis, a dichloro-derivative being simultaneously formed (Erdmann, Ber. 1891, 24, 2768); by chlorination of *p*-toluidine hydrochloride in 15 times its weight of 40 p.c. hydrochloric acid (Hafner, Ber. 1889, 22, 2536); together with 3:5-dichloro-*p*-toluidine and higher chlorinated products by the action of sulphuryl chloride on a suspension of aceto-*p*-toluolide in carbon disulphide, followed by hydrolysis (Wynne, Chem. Soc. Trans. 1892, 61, 1053); together with other products by the action of hydrochloric acid on *p*-nitrotoluene

(Bamberger, Büsdorf and Szolayaki, Ber. 1899, 32, 218); by treating aceto-*p*-toluolide in acetic acid with aqueous sodium chlorate followed by hydrolysis (Reverdin and Crépiaux, Ber. 1900, 33, 2500); by reduction of 3-chloro-4-nitrotoluene (Reverdin and Crépiaux, Ber. 1900, 33, 2505); in a yield of 50 p.c. by chlorination of aceto-*p*-toluolide by means of bleaching powder, followed by hydrolysis with alcohol and sulphuric acid (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 792). Oil, which solidifies at 0°, m.p. 7°, b.p. 218°-219°/732 mm. (L. and K.; Lellmann, Ber. 1891, 24, 4111), or 223°-224° (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1337); D₂₀ 1.151 (W.). B'HCl; B'HNO₃; B'₂H₄SO₄; B'₂C₄H₄O₄.

Acetyl-derivative; Anorthic crystals (Pope, Chem. Soc. Trans. 1892, 61, 1057), m.p. 118° (L.), 115° (L. and K.), 111°-112° (E.), 113°-113.5° (Wynne; C. and D.); *N*-chloro-derivative; short prisms, m.p. 48° (C. and O.); *benzoyl-derivative*; m.p. 137°-139° (C. and D.).

2:3-Dichloro-p-toluidine; by reducing 2:3-dichloro-4-nitrotoluene with tin and hydrochloric acid (Cohen and Dakin). It is volatile with steam and melts at 40°-42°.

Acetyl-derivative; needles, m.p. 128°-129° (C. and D.).

2:5-Dichloro-p-toluidine; by reducing 2:5-dichloro-4-nitrotoluene (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 789; *cf.* Cohen and Dakin, *ibid.* 1901, 79, 1130; 1902, 81, 1347). It melts at 91°-92°.

2:6-Dichloro-p-toluidine; by reduction of 2:6-dichloro-4-nitrotoluene with iron filings and dilute hydrochloric acid (Davies, *ibid.* 1922, 121, 813). Colourless needles, m.p. 56°-57°. B'HCl, long colourless needles.

Acetyl-derivative; colourless slender needles, m.p. 220° (D.).

3:5-Dichloro-p-toluidine (*see* 3-chloro-*p*-toluidine); by successive chlorination and hydrolysis of aceto-*p*-toluolide and of 3-chloroaceto-*p*-toluolide (Lellmann and Klotz, Ann. 1885, 231, 322; *cf.* Cohen and Dakin); by other methods (Bamberger, Büsdorf and Szolayaki; Wynne; Chattaway and Orton; Cohen and Dakin). Needles, scarcely volatile with steam, m.p. 60°. Sublimes.

Acetyl-derivative; crystals which sublime in long needles, m.p. 201° (L. and K.) or 199° (C. and D.). It is hydrolysed by heating with concentrated hydrochloric acid at 120°. *N*-chloro-derivative; slender four-sided prisms, m.p. 72° (C. and O.).

2:3:5-Trichloro-p-toluidine; *acetyl-derivative*, formed by the action of sodium chlorate on a solution of 3:5-dichloroaceto-*p*-toluolide in presence of acetic acid and hydrochloric acid (Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1337); by the action of a mixture of hydrochloric and nitric acids on aceto-*p*-toluolide (Mannino and Donato, Gazz. chim. ital. 1908, 38, ii. 20). Colourless needles, m.p. 170°.

2-Bromo-p-toluidine; by reduction of 2-bromo-4-nitrotoluene (Neville and Winther, Ber. 1881, 14, 418; Chem. Soc. Trans. 1881, 89, 85); by boiling acetyl-*p*-toluidine-2-diazopiperidine with concentrated hydrobromic acid (Wallach, Ann. 1886, 235, 255); together with 3-bromo-*p*-toluidine by keeping a mixture of *p*-toluidine sulphate and bromine in the presence of sul-

phuric acid for 10 days (Hafner, Ber. 1889, 22, 2903); together with 2-bromo-4-aminobenzaldehyde by reduction of 2-bromo-4-nitrotoluene with sodium disulphide in presence of alcohol (Blanksma, Chem. Weekblad, 1909, 6, 899). It melts at 25°-26° (N. and W.), and boils at 254°-257° (H.). B'HCl, needles; B'HB'r (W.).

Acetyl-derivative; m.p. 113° (B.). On boiling with potassium permanganate solution it yields 2-bromo-4-acetylamino benzoic acid.

3-Bromo-*p*-toluidine; by successive bromination and hydrolysis of aceto-*p*-toluidide (Wroblewsky, Ann. 1873, 168, 153; Neville and Winther); together with other products by the action of hydrobromic acid on *p*-nitrosotoluene (Bamberger, Büsdorf and Szolayski, Ber. 1899, 32, 219); by bromination of *p*-toluidine hydrochloride (Klages and Liecke, J. pr. Chem. 1900, (2) 61, 326). Large plates, m.p. 26° (Claus and Steinberg, Ber. 1883, 16, 914), b.p. 240°; D₄²⁰ 1.510 (W.), 1.498 (Hand, Ann. 1886, 234, 156). B'HCl, softens at 210° and melts at 221° (decomp.). B'HNO₃, plates, m.p. 182°; B'₂H₄SO₄ + 2H₂O. The bromotoluidine obtained by Fechmann (Ann. 1874, 173, 210) by distilling brominated *p*-aminotoluene *m*-sulphonic acid with potassium hydroxide is probably identical with the above.

Acetyl-derivative; needles, m.p. 117.5° (W.). *N*-bromo-*derivative*; yellow four-sided plates, m.p. 87°. On heating at 110° it yields 3:5-dibromoaceto-*p*-toluidide (Chattaway and Orton, Chem. Soc. Trans. 1900, 77, 795).

Diacetyl-derivative; thick prisms, m.p. 75°-75.5° (Ulffers and Janson, Ber. 1894, 27, 98).

Benzoyl-derivative; m.p. 148.5° (Pinnow, Ber. 1891, 24, 4170).

2:5-Dibromo-*p*-toluidine; by reduction of the corresponding nitro-*derivative* (Wroblewsky, Ann. 1873, 168, 185; Neville and Winther, Ber. 1890, 13, 962; Chem. Soc. Trans. 1890, 37, 445). Prisms, m.p. 83° (W.), leaflets, m.p. 84.6°-85° (N. and W.).

2:6-Dibromo-*p*-toluidine; by reduction of the corresponding nitro-*derivative* (Neville and Winther). It melts at 88°-89°.

3:5-Dibromo-*p*-toluidine; by the action of hydrobromic acid on *p*-nitrosotoluene (Bamberger, Büsdorf and Szolayski); from *p*-toluidine and bromine (Wroblewsky, Ann. 1873, 168, 188; Neville and Winther; Klages and Liecke, J. pr. Chem. 1900, (2) 61, 326); together with 3-bromo-*p*-toluidine 5-sulphonic acid by the action of bromine on *p*-toluidine 3-sulphonic acid (N. and W.; cf. Fechmann, Ann. 1874, 173, 216). Long monoclinic needles, m.p. 73° (Jäger, Z. Kristall. 903, 38, 89), or 73.5°-74.5° (Bamberger, Ber. 1899, 32, 221). Does not combine with acids.

Acetyl-derivative; long needles, m.p. 183° (Claus and Herabny, Ann. 1891, 265, 3777), or prisms, 199°-200° (Ulffers and Janson, Ber. 1894, 27, 99; cf. Kunckell, *ibid.* 1908, 41, 4111); *isocetyl-derivative*; thick tables and prisms, m.p. 191°-191.5° (U. and J.).

2:4-Dibromo-*p*-toluidine; by reducing the corresponding nitro-compound (N. and W.; Wroblewsky). M.p. 98° (N. and W.), or 85° (V.).

2:3:5-Tribromo-*p*-toluidine; by brominating 2-bromo-*p*-toluidine hydrochloride (Neville and Winther, *ibid.* Ber. 1891, 14, 418). Needles, m.p. 82.4°-82°.

2:3:6-Tribromo-*p*-toluidine; by reducing the corresponding nitro-*derivative* with iron and acetic acid (N. and W.). Needles, m.p. 118°-119° (Cohen and Dutt, Chem. Soc. Trans. 1914, 105, 514).

Fechmann (Ann. 1874, 173, 217) obtained a *tribromotoluidine*, long needles, m.p. 113°, by the action of bromine on *p*-aminotoluene *m*-sulphonic acid.

Tetrabromo-*p*-toluidine; by brominating 2:6-dibromo-*p*-toluidine hydrochloride (N. and W.); together with dibromonitrotoluene by heating *p*-nitrotoluene with bromine and a little iron bromide at 90° (Scheufelen, Ann. 1885, 231, 179). Slender needles, m.p. 226°-227°.

3-Chloro-5-bromo-*p*-toluidine; by brominating 3-chloro-*p*-toluidine in glacial acetic acid and boiling until most of the hydrogen bromide is removed (Orton and Reed, Chem. Soc. Trans. 1907, 91, 1570); from aceto-*p*-toluidide by successive bromination and chlorination with hydrochloric acid and sodium chlorate in glacial acetic acid, followed by hydrolysis (Cohen and Murray, *ibid.* 1915, 107, 847). Colourless needles, m.p. 65° (O. and R.) or 63.5° (C. and M.).

Acetyl-derivative; prisms, m.p. 189° (O. and R.), or 199° (C. and M.); *diacetyl-derivative*; m.p. 82° (C. and M.).

2-Iodo-*p*-toluidine; by reducing 2-iodo-4-nitrotoluene with ferrous sulphate in ammoniacal solution (Willgerodt and Gartner, Ber. 1908, 41, 2813); or together with 2-iodo-4-aminobenzaldehyde by reducing with sodium disulphide (Blanksma, Chem. Weekblad, 1909, 6, 899). Large white needles, m.p. 37°-38°. B'HCl, long dark needles; B'₂H₄SO₄, leaflets; B'HNO₃, rhombs; B'C₂H₃O₄, small rhombs.

Acetyl-derivative; white needles, m.p. 130°; *iodochloride*, yellow needles, decomposing at 110° (W. and G.).

3-Iodo-*p*-toluidine; by the interaction of iodine and *p*-toluidine (Wheeler and Liddle, Amer. Chem. J. 1909, 42, 441). Colourless needles, m.p. 40°. B'HCl, m.p. 188° (decomp.); B'C₂H₃O₄, m.p. 119°-120° (decomp.).

Acetyl-derivative; long colourless needles, m.p. 133°; *benzoyl-derivative*; colourless needles, m.p. 161° (W. and L.). The acetyl-*derivative* when boiled with concentrated hydrochloric acid yields 3:5-di-iodo-*p*-toluidine.

2:5-Di-iodo-*p*-toluidine; by reducing 2:5-di-iodo-4-nitrotoluene with ferrous sulphate and ammonia. Buff-coloured prisms, m.p. 109° (Wheeler, &c., Amer. Chem. J. 1910, 44, 493).

3:5-Di-iodo-*p*-toluidine; by the action of iodine chloride on *p*-toluidine hydrochlorides (Michael and Norton, Ber. 1878, 11, 116); by boiling 3-iodoaceto-*p*-toluidide with concentrated hydrochloric acid (Wheeler and Liddle) or by the action of 2 mols. of iodine on *p*-toluidine in presence of water and calcium carbonate (Wheeler and Liddle). Long slender needles, m.p. 124.5° (M. and N.).

Acetyl-derivative; stout colourless prisms, m.p. 226° (W. and L.).

2-Nitro-*p*-toluidine; together with 4-nitro-*p*-toluidine by partial reduction of 2:4-dinitrotoluene with alcoholic ammonium sulphide (Graeff, Ann. 1885, 229, 343; Anschütz and Henseler, Ber. 1886, 19, 2161; Bollstein and Kuhlberg, Ann. 1870, 155, 14); together with a little 3-nitro-*p*-toluidine by treating a solution

of *p*-toluidine in sulphuric acid with nitric acid, but when a large amount of sulphuric acid is used only the 2-nitro-isomeride is obtained (Hübner, Ber. 1877, 10, 1716; Nölting and Collin, *ibid.* 1884, 17, 263; Foth, Ann. 1885, 230, 399). Yellow glistening broad needles, m.p. 81.5° (Haibach, J. pr. Chem. 1902, (2) 65, 246). $BHCl$, m.p. 220° (decomp.); $BHNO_2$, m.p. 186°; $B_2H_2SO_4 + 2H_2O$, stellate needles; $4C_6H_4N_2O_2 + AgNO_3$, greenish-yellow crystals, m.p. 131°–132° (Mixer, Amer. Chem. J. 1880, 1, 241).

Formyl-derivative; white voluminous needles (Geigy & Co., U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

Acetyl-derivative; needles, m.p. 160° (Cunert, Ann. 1874, 172, 229) or 144.5° (Wallach, *ibid.* 1886, 234, 354).

Benzoyl-derivative; pale yellow prisms, m.p. 172° (Bell, Chem. News, 1874, 30, 202).

3-Nitro-*p*-toluidine; by successive nitration and hydrolysis of benzoyl-*p*-toluidine, aceto-*p*-toluidide, or toluene *p*-sulphonyl-*p*-toluidide (Beilstein and Kuhlberg, Ann. 1870, 155, 23; Lorenz, *ibid.* 1874, 172, 77; Hübner, *ibid.* 1881, 208, 313; Lellmann, *ibid.* 1883, 221, 7; Cosack, Ber. 1880, 13, 1088; Ehrlich, *ibid.* 1882, 15, 2009; Gattermann, *ibid.* 1885, 18, 1483; Nölting and Collin, *ibid.* 1884, 17, 263; Reverdin and Crépeux, *ibid.* 1902, 35, 1439; Bull. Soc. chim. 1902, (3) 27, 743; Noyes, Amer. Chem. J. 1888, 10, 475); by heating 3-nitro-*p*-cresol with 35 p.c. ammonia for 16 hours at 170°–180° (Barr, Ber. 1888, 21, 1543); by the transformation of *p*-toluene nitroamine (Bamberger and Hoff, Ber. 1897, 30, 1258; Ann. 1900, 311, 93); or, together with other products by the action of nitric anhydride on *p*-toluidine (B. and H.). Red monoclinic prisms (Pancbianco, Gazz. chim. ital. 1879, 9, 358; Jäger, Z. Kristall, 1903, 38, 89), m.p. 114° (B. and K.; R. and C.), 116°–117° (Schraube and Romig, Ber. 1893, 26, 579), or 117°–118° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1401). Volatile with steam. $BHCl$, yellow prisms immediately decomposed by water; $BHNO_2$, six-sided yellow tables or slender needles (Hübner); $BHBr$, large laminae (Haibach, J. pr. Chem. 1902, (2) 65, 249).

Acetyl-derivative; slender yellow needles from water or concentrated alcoholic solution, long colourless needles from dilute alcoholic solution, m.p. 94°–95° (Gattermann). For the relation and properties of the two forms of 3-nitro-aceto-*p*-toluidide, see Schaum, Ann. 1898, 300, 224; Ber. 1898, 31, 129; Schenck, Zeitsch. physikal. Chem. 1900, 33, 450; Auwers, *ibid.* 1897, 23, 460.

Diacetyl-derivative; citron-yellow prisms, m.p. 78° (Ullfers and Janson, Ber. 1894, 27, 101).

Benzoyl-derivative; yellow needles, m.p. 146°–148° (M. and M.) or 143° (Hübner).

The electrolytic reduction of 3-nitro-*p*-toluidine yields a mixture of *p*-diamino-*o*-azoxy-toluene and *p*-diamino-*o*-azotoluene (Elbs and Schwarz, J. pr. Chem. 1901, (2) 63, 562).

2:3-Dinitro-*p*-toluidine; by hydrolysis of the acetyl-derivative which is obtained as the sole product by nitrating 2-nitroaceto-*p*-toluidide with nitric acid alone; or together with 2:5-dinitroaceto-*p*-toluidide when the nitration is effected in presence of sulphuric acid by means

of potassium nitrate (Scott and Robinson, Chem. Soc. Trans. 1922, 121, 844). Orange-yellow needles, m.p. 124°. Weak base.

Acetyl-derivative; colourless silky needles, m.p. 174.5°.

2:5-Dinitro-*p*-toluidine (see above). Deep orange-red needles, m.p. 189°. Feeble base.

Acetyl-derivative; aggregates of colourless slender needles, m.p. 132.5° (S. and R.).

2:6-Dinitro-*p*-toluidine; by reduction of 2:4:6-trinitrotoluene with ammonium sulphide (Tiemann, Ber. 1870, 3, 218; Beilstein, *ibid.* 1880, 13, 243; Stadel, Ann. 1884, 225, 384; Holleman and Boesken, Rec. trav. chim. 1897, 16, 425); by reduction of 2:6-dinitro-*p*-tolyl-hydroxylamine with copper powder and hydrochloric acid; or together with 4:6-dinitro-*o*-toluidine by reducing 2:4:6-trinitrotoluene in hydrochloric acid solution in presence of cuprid chloride at a copper cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 27; Cohen and McCandlish, *ibid.* 1905, 87, 1265). Yellow hair-like needles, m.p. 166.5°–168° (T.; B.), 171° (H. and B.), 168°–169° (C. and D.; Anschütz and Zimmermann, Ber. 1915, 48, 152). It exists in four distinct crystalline phases (Artini, Atti R. Accad. Lincei, 1917 [v.] 26, i. 392).

Acetyl-derivative; slender white needles, m.p. 223° (Körner and Contardi, *ibid.* 1916, [v.] 25, ii. 339).

3:5-Dinitro-*p*-toluidine; by successive nitration and hydrolysis of the acetyl- or benzoyl-derivative of *p*-toluidine (Beilstein and Kuhlberg, Ann. 1871, 158, 341; Jackson and Itner, Amer. Chem. J. 1897, 19, 6; Hübner, Ann. 1881, 208, 278; 1884, 222, 73; Brady, Day and Rolt, Chem. Soc. Trans. 1922, 121, 527); from 3:5-dinitro-*p*-cresol alkyl ether and alcoholic ammonia in the cold (Stadel, Ann. 1883, 217, 185); by transformation of 3-nitro-*p*-toluene nitroamine (Bamberger and Voss, Ber. 1897, 30, 1257; Bamberger and Hoff, Ann. 1900, 311, 112). Yellow needles, m.p. 166° (B. and K.), 168° (Hübner; B. and V.; Niementowski, Ber. 1886, 19, 717).

Acetyl-derivative; long yellow needles, m.p. 190.5° (B. and K.), or 195° (Friederici, Ber. 1878, 11, 1975).

Diacetyl-derivative; thick citron-yellow tables, m.p. 129.5° (Ullfers and Janson, Ber. 1894, 27, 101).

Benzoyl-derivative; needles, m.p. 186° (Hübner).

(β)-Dinitro-*p*-toluidine; by treating 2:3:4-trinitrotoluene with alcoholic ammonia at 100° (Hepp, Ann. 1882, 215, 371). Short golden-yellow needles, m.p. 94°.

3-Chloro-2-nitro-*p*-toluidine; by heating 2-nitrotolyl-*p*-hydroxylamine with hydrochloric acid (Brand and Zoller, Ber. 1907, 40, 3324). Pale yellow needles, m.p. 63° (B. and Z.) or 67°–68° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052).

Acetyl-derivative; m.p. 123°–124° (B. and Z.).

5-Chloro-2-nitro-*p*-toluidine; by treating dry 3-chloro-*p*-toluidine nitrate with 5 parts of sulphuric acid at –12° to –15° (Claus and Davidson, Ann. 1891, 265, 244; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 1323); as a by-product of the action of hydrochloric acid

on 2-nitrotolyl-*p*-hydroxylamine (Brand and Zoller). Orange-red plates, m.p. 129-5° (Claus and Davidsen), 131° (B. and Z.).

Acetyl-derivative, m.p. 143° (Cl. and D.).

2-Chloro-5-nitro-*p*-toluidine; by successive nitration and hydrolysis of 2-chloroaceto-*p*-toluidide (Claus and Böcher, Ann. 1891, 265, 354; Davies, Chem. Soc. Trans. 1921, 119, 868); by adding 2-chloro-*p*-toluidine nitrate to well-cooled sulphuric acid (Cohen and Dakin, *l.c.*); together with 6-chloro-4-nitro-*m*-toluidine by the action of alcoholic ammonia on 2-chloro-4:5-dinitrotoluene; or from *o*-toluidine by nitration, replacement of the amino-group by chlorine, reduction, acetylation, nitration and hydrolysis (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1538, 1545). Golden-yellow plates, m.p. 165°.

Acetyl-derivative; pale yellow crystals, m.p. 112° (Blanksma, Rec. trav. chim. 1910, 29, 410), 113° (C. and B.).

3-Chloro-5-nitro-*p*-toluidine; by nitration of 3-chloroaceto-*p*-toluidide (Claus and Davidsen) in presence of glacial acetic acid at 20°, followed by hydrolysis with hydrochloric acid (Cohen and Dakin). Orange-red needles, m.p. 72-73°, slowly volatile with steam (C. and D.) or orange-red plates, m.p. 70-5° (Cl. and D.).

Acetyl-derivative; m.p. 196° (Cl. and D.).

2:6-Dichloro-3-nitro-*p*-toluidine; by the gradual addition of 2:6-dichloroaceto-*p*-toluidide to nitric acid (D 149) cooled in ice-water, followed by hydrolysis with alcoholic sodium hydroxide (Davies, Chem. Soc. Trans. 1922, 121, 813). Minute orange needles, m.p. 130°-131°. B'HCl, clusters of colourless needles, immediately hydrolysed by cold water.

Acetyl-derivative; colourless needles, m.p. 180° (D.).

2-Chloro-3:5-dinitro-*p*-toluidine; by the gradual addition of 2-chloroaceto-*p*-toluidide to well-cooled nitric acid (D 15), keeping for 6 hours, followed by hydrolysis with cold sulphuric acid (Davies, *ibid.* 1921, 119, 868). Thin golden-yellow needles, m.p. 137°.

Acetyl-derivative; colourless leaflets, m.p. 238° (D.).

2-Bromo-5-nitro-*p*-toluidine; by nitration and hydrolysis of 2-bromoaceto-*p*-toluidide (Blanksma, Chem. Weekblad, 1912, 9, 968). Orange-red needles, m.p. 165°.

Acetyl-derivative; pale yellow needles, m.p. 20° (B.).

3-Bromo-5-nitro-*p*-toluidine; by nitration and hydrolysis of 3-bromoaceto-*p*-toluidide (Problewsky, Ann. 1878, 192, 202); by bromination and nitration (or *vice versa*) of aceto-*p*-toluidine, followed by hydrolysis (Neville and Linther, Ber. 1880, 13, 968; Chem. Soc. Trans. 1900, 37, 429). Orange-red needles, m.p. 64-65° (Cohen and Dutt, Chem. Soc. Trans. 1914, 45, 510).

Acetyl-derivative; m.p. 210° (C. and D.); *acetyl-derivative*; large greenish-yellow tables, m.p. 79° (Ulfers and Jansson, Ber. 1894, 27, 30).

4-Bromo-5-nitro-*p*-toluidine; by dissolving parts of dry 2-bromo-*p*-toluidine nitrate in parts of sulphuric acid at -10° and keeping 2-3 days (Claus and Herbay, Ann. 1891, 45, 367). Pale yellow needles, m.p. 121° (C. and D.).

Acetyl-derivative; Morgan and Clayton, Chem.

Soc. Trans. 1905, 87, 948), or 118°-119° (Cohen and Dutt, *ibid.* 1914, 105, 515).

3:5-Dibromo-2-nitro-*p*-toluidine; by bromination of 2-nitro-*p*-toluidine (Blanksma, Chem. Weekblad, 1909, 6, 717). Yellow crystals, m.p. 82°.

Acetyl-derivative; by nitrating 3:5-dibromoaceto-*p*-toluidide with fuming nitric acid (Kunckell, Ber. 1908, 41, 4111); by acetylating 3:5-dibromo-2-nitro-*p*-toluidine with acetic anhydride and a drop of sulphuric acid (B.). M.p. 238°.

3-Bromo-2:6-dinitro-*p*-toluidine; together with a little 3:5-dibromo-2:6-dinitro-*p*-toluidine by the action of bromine on 2:6-dinitro-*p*-toluidine in presence of sodium acetate and acetic acid (Körner and Contardi, Atti R. Accad. Lincei, 1916, [v.] 25, ii. 339). Pale yellow prisms or short needles, m.p. 174°.

Acetyl-derivative; almost colourless plates, m.p. 151° (K. and C.).

3:5-Dibromo-2:6-dinitro-*p*-toluidine; by further bromination of the 3-bromo-*p*-toluidine (K. and C.). Pale yellow prisms, m.p. 177°.

Acetyl-derivative; m.p. 265°-267°, by nitrating 3:5-dibromoaceto-*p*-toluidide with fuming nitric acid in presence of sulphuric acid (Kunckell, Ber. 1908, 41, 4111).

5-Iodo-3-nitro-*p*-toluidine; by warming 3-nitro-*p*-toluidine with iodine chloride in glacial acetic acid (Wheeler and Scholes, Amer. Chem. J. 1910, 44, 126). Golden needles, m.p. 98°.

Acetyl-derivative; by acetylating the above (W. and S.) or by nitration of 5-iodoaceto-*p*-toluidide (Wheeler and Liddle, *ibid.* 1909, 42, 441). Prisms, m.p. 202°-203°.

Methyl-*p*-toluidine; by methylation with dimethyl sulphate (Ullmann, Ann. 1903, 327, 104); together with dimethyl-*p*-toluidine by the action of methyl chloride on boiling *p*-toluidine. The product is extracted with ether and the unchanged *p*-toluidine precipitated by sulphuric acid. The remainder of the product is acetylated, fractionally distilled, and the acetyl-derivative hydrolysed with dilute hydrochloric acid or sodium hydroxide (Thomsen, Ber. 1877, 10, 1582); by the reduction of nitrosomethyl-*p*-toluidine with tin and hydrochloric acid (Nöling, Ber. 1878, 11, 2279); from *p*-toluidine and diazomethane (von Pechmann, *ibid.* 1895, 28, 858). Liquid, b.p. 208° (T.). B'HCl, m.p. 119-5° (Bamberger and Wulz, *ibid.* 1891, 24, 2081); B'H₂PtCl₆.

Acetyl-derivative; large plates, m.p. 83°, b.p. 283°. It yields trinitromethyl-*p*-toluidine on boiling with nitric acid.

Nitrosoamine; large prisms, m.p. 54° (T.), or 52°-53° (B. and W.).

2-Nitromethyl-*p*-toluidine; by nitration of methyl-*p*-toluidine in presence of sulphuric acid below 0° (Pinnow, Ber. 1895, 28, 3040); by methylation of 2-nitro-*p*-toluidine (Jaubert, Bull. Soc. chim. 1899, (3) 21, 19). Yellow crystals, m.p. 45° (J.), or slender red needles or thick prisms, m.p. 57° (P.).

Acetyl-derivative; slender yellow needles, m.p. 128°-128.5° (P.).

Nitrosamines; slender yellow needles or thick prisms, m.p. 55° (P.).

3-Nitromethyl-*p*-toluidine; from 3-nitro-*p*-toluidine, methyl iodide, and methyl alcohol (Gattermann, Ber. 1885, 18, 1487); by the action

of nitric acid on *p*-tolymethyl nitroamine in presence of acetic acid (Pinnow, Ber. 1897, 30, 835); by oxidation of 3-nitrodimethyl-*p*-toluidine with chromic acid in acetic acid (Pinnow, *l.c.* 3121; J. pr. Chem. 1900, (2) 62, 514). Red prisms, m.p. 84°-85° (G.).

Acetyl-derivative; small plates, m.p. 64°; *picrate*, yellow crystalline precipitate, m.p. 210°-212° (decomp.) (Niemetowski, Ber. 1887, 20, 1876).

(γ) 2:3-Dinitromethyl-*p*-toluidine; see below (Pinnow). Long orange-yellow plates, with a bluish shimmer, m.p. 158°-159.5°. On treatment with nitric acid (D 1.52) it yields trinitrotolyl-*p*-methyl nitroamine; with alcoholic ammonium sulphide, γ -nitroaminomethyl-*p*-toluidine; with tin and hydrochloric acid 2:3-diaminomethyl-*p*-toluidine (Pinnow, J. pr. Chem. 1900, (2) 62, 507).

Acetyl-derivative; bright yellow needles, m.p. 90.5°; *benzoyl-derivative*; m.p. 110.5°.

Nitrosoamine; yellow needles, m.p. 128°-128.5° (Pinnow, Ber. 1897, 30, 840).

(β) 2:5-Dinitromethyl-*p*-toluidine; the nitration of dimethyl-*p*-toluidine in concentrated sulphuric acid and further treatment of the product with nitric acid in the presence of sodium nitrite yields dinitrotolymethyl nitroamine. The latter on boiling with phenol and sulphuric acid in the presence of amyl alcohol yields a mixture of 2:5- and 2:3-dinitromethyl-*p*-toluidine (Pinnow, Ber. 1895, 28, 3040; 1897, 30, 836, 840; J. pr. Chem. 1900, (2) 62, 507). Also formed by the oxidation of dinitrodimethyl-*p*-toluidine (m.p. 103.5°-104°) with chromic acid and acetic acid (van Romburgh, Rec. trav. chim. 1889, 8, 248). Bright red prisms with a greenish reflex, m.p. 184.5°-185.5°. On reduction with alcoholic ammonium sulphide 2-amino-5-nitromethyl-*p*-toluidine is formed; with tin and hydrochloric acid at low temperatures it yields 2:5-diaminomethyl-*p*-toluidine, and at higher temperatures methyldiaminocresol (Pinnow, J. pr. Chem. 1900, (2) 62, 507).

Acetyl-derivative; bright yellow needles, m.p. 151° (P.).

Nitrosoamine; m.p. 123°-124° (P.).

(α) 3:5-Dinitromethyl-*p*-toluidine; by nitration of methyl-*p*-toluidine (Thomsen, Ber. 1877, 10, 1582; Gattermann, Ber. 1885, 18, 1487); by boiling 3:5-dinitrotolyl-*p*-methyl nitroamine with a little phenol (van Romburgh, Ber. 1896, 29, 1015); by the transformation of the *N*-methyl ester of 3-nitro-*p*-toluene nitroamine with acids (Bamberger and Voss, Ber. 1897, 30, 1258); by the prolonged action of nitrous acid on methyl-*p*-toluidine (Störmer and Hoffmann, Ber. 1898, 31, 2535); by the transformation of an alcoholic solution of 3:5-dinitro-4-nitromethylamino-toluene in presence of sunlight (Reverdin, Bull. Soc. chim. 1913, [4] 13, 485; J. pr. Chem. 1913, (2) 88, 90). Light red needles, m.p. 129° (G.).

Nitrosoamine; yellow needles, m.p. 125° (Gattermann), or 128°-128.5° (van Romburgh; Pinnow, Ber. 1897, 30, 840).

3:5-Dinitrotolyl-*p*-methyl nitroamine; by the action of nitric acid (D 1.48) on dimethyl-*p*-toluidine (van Romburgh, Rec. trav. chim. 1884, 3, 404; Gattermann, Ber. 1885, 18, 1488; cf. Pinnow, Ber. 1897, 30, 842); by boiling methyl-aceto-*p*-toluidide for 1-2 hours with 10 p.c.

nitric acid (Norton and Livermore, Ber. 1887, 20, 2269); by the action of fuming nitric acid on 3:5-dinitrodimethyl-*p*-toluidine (Pinnow and Matcovich, Ber. 1898, 31, 2518); by the gradual addition of 50 c.c. nitric acid (D 1.48) to a solution of 5 c.c. of dimethyl-*p*-toluidine in 5 c.c. of glacial acetic acid (van Romburgh, Ber. 1896, 29, 1015); by the action of nitrous acid on a solution of 3-nitrodimethyl-*p*-toluidine in 40 p.c. nitric acid (Pinnow, Ber. 1895, 28, 3044); by dissolving methyl-*p*-tolymethyl nitroamine in a mixture of acetic acid and nitric acid (D 1.4) with cooling (Pinnow). Yellow serrated needles, m.p. 126° (P.), or 138° (van R.).

2:3:5-Trinitromethyl-*p*-toluidine; by boiling a mixture of 2:3:5-trinitro-*p*-tolymethyl nitroamine, phenol, sulphuric acid, and amyl alcohol (Pinnow, Ber. 1897, 30, 838); by nitration of mono- or dinitromethyl-*p*-toluidine (Gattermann, Ber. 1885, 18, 1488). Orange-red needles, m.p. 129.5°-130° (P.), or yellow needles or large prisms, m.p. 137°-138° (G.).

Nitrosoamine; yellow plates, m.p. 108°-109° (P.). The nitroamine is obtained by heating 2-nitro-*p*-tolymethyl nitroamine with nitric acid (D 1.52) at 100°. It melts at 156.5°-157° (P.).

*Dimethyl-*p*-toluidine*; together with isomerides and homologues by heating the trimethylammonium iodide, $C_6H_4N(CH_3)_3I$, at 220°-230° (Hofmann, Ber. 1872, 5, 707); from *p*-toluidine, methyl iodide or methyl chloride (Thomsen, Ber. 1877, 10, 1586; Clarke, Amer. Chem. J. 1905, 33, 496); by heating its trimethylammonium iodide with water and lead oxide and distilling the product (Hübner, Töle and Athenstädt, Ann. 1884, 224, 337); together with dimethyleneditoluidine by the electrolytic reduction of *p*-nitrotoluene in presence of alcohol, hydrochloric acid and 40 p.c. formaldehyde (Löb, Zeit. Elektrochem. 1898, 4, 428). Liquid, b.p. 209.5°/760 mm. (Kahlbaum, Zeitsch. physikal. Chem. 1898, 26, 623, 646), or 211.2° (Perkin, Chem. Soc. Trans. 1896, 60, 1245), D_4^{20} 0.92870 (K.), L_4^{20} 0.9502, D_{15}^{15} 0.9424, D_{25}^{25} 0.9364 (P.); magnetic rotatory power at 15.4° 22.84 (P.). Refractive power, see Brühl (Zeitsch. physikal. Chem. 1895, 16, 218).

*Dimethyl-*p*-toluidine oxide*; by the action of hydrogen peroxide on dimethyl-*p*-toluidine at 60°-70° (Bamberger and Tschirner, Ber. 1899, 32, 353). *Picrate*; sulphur-yellow needles or prisms, m.p. 106°-107°.

2-Nitrodimethyl-*p*-toluidine; by nitration of dimethyl-*p*-toluidine (M. L. E., D. R. P. 69188 of 1891; cf. Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 947); by methylation of 2-nitro-*p*-toluidine (Haibach, J. pr. Chem. 1902, (2) 65, 246). Orange-red prisms, m.p. 35° (H.), or 37° (M. and C.).

3-Nitrodimethyl-*p*-toluidine; by the action of a concentrated aqueous solution of sodium nitrite on a solution of dimethyl-*p*-toluidine in hydrochloric acid (D 1.06) (Pinnow, Ber. 1895, 28, 3041; 1897, 30, 3119). Six-sided columns, m.p. 24.5°-25°. On reduction with tin and hydrochloric acid a mixture of dimethyltoluenediamine, dimethylbenzimidazole and a compound containing chlorine is obtained.

3-Bromo-6-nitrodimethyl-*p*-toluidine; by heating the hydrobromide of 3-bromo-5-nitro-

toluidine with methyl alcohol for 8 hours at 140°-180°. The resultant mixture is treated with acetic anhydride to remove any unaltered base or secondary amine (Morgan and Clayton, *l.c.*). Yellow needles, m.p. 38°.

3:5-Dinitrodimethyl-*p*-toluidine; by the action of 30 p.c. nitric acid on a solution of dimethyl-*p*-toluidine dissolved in dilute sulphuric acid (Pinnow and Mateovich, *Ber.* 1898, 31, 2518). Bright red needles or four-sided prisms, m.p. 95°. With fuming nitric acid it yields 3:5-dinitrotolyl-*p*-methyl nitroamine, m.p. 138°-139°.

2:5-Dinitrodimethyl-*p*-toluidine; together with other products by the action of sodium nitrite on 2-nitrodimethyl-*p*-toluidine dissolved in hydrochloric acid (Pinnow, *Ber.* 1895, 28, 3041); together with 2-nitrodimethyl-*p*-toluidine by nitrating dimethyl-*p*-toluidine and pouring the product into water so that the temperature rises to 30°-40° (M. and C.). Glistening red plates, m.p. 103.5°-104° (P.), dark red needles, or scarlet scales, m.p. 103° (M. and C.).

Ethyl-*p*-toluidine; from *p*-toluidine by heating with hydriodic acid or hydrobromic acid and ethyl alcohol (N. and L.); from *p*-toluidine and ethyl iodide by heating for 2 days at 100° (Morley and Abel, *Ann.* 1854, 93, 313). Liquid, b.p. 217°. D_{15}^{20} 0.9391. $B^{\circ}H_2SO_4$; $B^{\circ}C_2H_5O_4$; $B^{\circ}H_2PtCl_6$, pale yellow crystals.

Acetyl-derivative; liquid, b.p. 258° (Norton and Livermore, *Ber.* 1887, 20, 2271).

2-Nitroethyl-*p*-toluidine; by nitrating a solution of *p*-ethyltoluidine in 20 parts of sulphuric acid (Nölting and Stricker, *Ber.* 1886, 19, 549); by ethylation of 2-nitro-*p*-toluidine (Jaubert, *Bull. Soc. chim.* 1899, (3) 21, 20). Long flat red prisms, m.p. 47°-48° (N. and S.), or yellow needles, m.p. 50° (J.).

3-Nitroethyl-*p*-toluidine; by ethylating 3-nitro-*p*-toluidine (Gattermann, *Ber.* 1885, 18, 1483); by successive nitration and hydrolysis of ethylaceto-*p*-toluidine in presence of sulphuric acid (Nölting and Abt, *Ber.* 1887, 20, 3000). Large bright red crystals, m.p. 58°-59°.

3:5-Dinitroethyl-*p*-toluidine; by nitration of 3-nitroethyl-*p*-toluidine at about 30° (Gattermann, *l.c.*, 1485). Long orange-yellow needles, m.p. 126°-126.5°.

Nitrosoamine; large yellow rhombic crystals, m.p. 77°-78° (G.).

3:5-Dinitrotolyl-*p*-ethyl nitroamine; by adding diethyl-*p*-toluidine to nitric acid (D_{15}^{20} 1.48-1.5) and boiling the solution until it becomes yellow (Van Bomburgh, *Rec. trav. chim.* 1884, 3, 409; Gattermann); by boiling ethylaceto-*p*-toluidine with 10 p.c. nitric acid (Norton and Livermore, *Ber.* 1887, 20, 2271). Long straw-yellow needles, m.p. 116°. On boiling with 4 p.c. sodium hydroxide it yields dinitro-*p*-cresol, m.p. 83°.

Diethyl-*p*-toluidine; by heating potassium *p*-toluidine *m*-sulphonate with ethyl bromide and absolute alcohol at 150° (Schmidt, *J. pr. Chem.* 1893, (2) 48, 46); from ethyl-*p*-toluidine and ethyl iodide (Morley and Abel, *l.c.*); in 95 p.c. yield by heating *p*-toluidine hydrobromide or hydroiodide with 5 p.c. excess of ethyl alcohol for 8 hours at 150° (Reinhardt and Stadel, *Ber.* 1893, 16, 29). Liquid, b.p. 227°-228°. D_{15}^{20} 0.9242. $B^{\circ}HCl$, m.p. 177° (Schmidt); $B^{\circ}H_2PtCl_6$, rhombohedra (Söfiling, *Beiblätter zu den Annalen der Physik und Chemie*, 8, 190);

$B^{\circ}HBr$, monoclinic crystals; $B^{\circ}HNO_3$, monoclinic crystals; $B^{\circ}HI$, crystals; $B^{\circ}HCH_2Cl$, $+\frac{1}{2}H_2O$, triclinic crystals. The salts are described by Söfiling (*Jahresbericht*, 1884, 463).

Phenyl-*p*-toluidine; by distilling tritolylrosaniline acetate (Hofmann, *Ann.* 1884, 132, 291); together with diphenylamine and ditolylamine by heating *p*-toluidine and aniline hydrochloride at 210°-240° (Girard, de Laire and Chapoteaut, *Ann.* 1886, 140, 347; *Bull. Soc. chim.* 1867, (2) 7, 360); by heating phenol with *p*-toluidine and zinc chloride, or *p*-cresol with aniline and zinc chloride at 260°-300°, or with antimony trichloride (Buch, *Ber.* 1884, 17, 2634); by heating *p*-toluidine with bromobenzene and soda lime at 360°-390°, or *p*-bromotoluene, aniline, and soda lime in a similar manner (Merz and Paschkowesky, *J. pr. Chem.* 1893, (2) 48, 455; see also Merz and Weith, *Ber.* 1881, 14, 2345). Crystals, m.p. 87°, b.p. 334.5° (H.), or 317°-318°/727.5 mm. (Graebe, *Ann.* 1887, 238, 363). Dissolves in nitric acid with a blue colour. $B^{\circ}HCl$, leaflets.

Acetyl-derivative; m.p. 51° (Bonna).

Nitrosoamine; slender yellow needles, m.p. 82° (Bonna, *Ann.* 1887, 239, 56), or 45° (Reichold, *Ann.* 1889, 255, 163).

***p*-Nitroso-derivative**; blue prisms or tables from alcohol, or green leaflets from benzene, m.p. 163° (Reichold).

For condensation with nitrochlorobenzenes, see Schöpf (Ber. 1890, 23, 1843); Jacobson and Lischke (*Ann.* 1898, 303, 377); Engelhardt and Latschinow (*Zeit. f. Chem.* 1870, (2) 6, 233); Willgerodt (*Ber.* 1876, 9, 980); Hepp (*Ann.* 1882, 215, 369); Jackson and Littner (*Amer. Chem. J.* 1897, 19, 10, 199, 205; *Ber.* 1895, 28, 3062); Laubenheimer (*Ber.* 1878, 11, 1157); Ritzenstein (*J. pr. Chem.* 1903, 68, 251); Kehrman and Kragler (*Ber.* 1901, 34, 1102).

Di-*p*-tolylamine; by heating *p*-cresol with ammonium-zinc chloride and ammonium chloride at 330°-340° (Merz and Müller, *Ber.* 1887, 20, 546); by heating a mixture of *p*-bromotoluene, *p*-toluidine, and soda lime at 390° (Merz and Paschkowesky, *J. pr. Chem.* 1893, (2) 48, 463). It melts at 79°, and boils at 328.5°/727.5 mm. or 330.5°/760 mm. (Graebe, *Ann.* 1887, 238, 363).

Nitrosoamine; m.p. 100°-101° (Lehne, *Ber.* 1880, 13, 1544), or 103° (Cosack, *ibid.* 1092). For its nitro-derivatives, see Lellmann (*Ber.* 1882, 15, 831); Jaubert (*ibid.* 1895, 28, 1649); and Lehne (*l.c.*).

Anhydro-formaldehyde-*p*-toluidine; from formaldehyde and *p*-toluidine (Wellington and Tollens, *Ber.* 1885, 18, 3302). It exists in two forms: (a) readily soluble form which crystallises in long needles from ether, m.p. 127°-128° (Eibner, *Ann.* 1898, 302, 352) or 123° (Eberhardt and Welter, *Ber.* 1894, 27, 1804); (b) sparingly soluble form, m.p. 225°-227° (E.), 207°-209° (E. and W.). The lower melting substance is converted on sublimation into the higher melting modification. Both forms have the same molecular weight (Bischoff, *Ber.* 1898, 31, 3253).

For condensation with benzaldehyde and potassium cyanide, see von Müller, Flöchl and Sieber (*Ber.* 1898, 31, 2711).

Methylene-di-*p*-tolylid-imide; by heating a mixture of *p*-toluidine, alcoholic potassium hydroxide, and formaldehyde (Eberhardt and

Welter, Ber. 1894, 27, 1808); by the action of formaldehyde on an alcoholic solution of *p*-toluidine (Eibner, Ann. 1898, 302, 350).

Rhombic tables, m.p. 86° (E. and W.) or 89° (E.). On heating with *p*-toluidine or on long boiling with alcohol it yields anhydroformaldehyde-*p*-toluidine, whilst on heating with *p*-toluidine hydrochloride it yields diaminoditolymethane, silky needles, m.p. 92°. It is also stated that two compounds possessing the constitution $(CH_2 \cdot C_6H_4 \cdot NH)_2CH_3$, are formed by heating 1 mol. of methylene chloride with 4 mols. of *p*-toluidine for 34 hours at 100°. One is a syrup, b.p. above 350° with decomposition and forms the salts, $BHCl$, $B_2H_2PtCl_4$, and $BHAuCl_4$, all of which are amorphous. The other is an amorphous solid, m.p. about 156°, b.p. above 350°, with decomposition. All the salts of the latter with the exception of the acid oxalate are amorphous and unstable (Grünhagen, Ann. 1890, 256, 286). The same author states that di-methylene-di-*p*-toluidine is sometimes formed during the above reaction.

Tolyl-p-hydroxylamine; by reducing *p*-nitrotoluene with zinc dust in the presence of aqueous alcohol and calcium chloride (Lumière and Seyewitz, Bull. Soc. chim. 1894, (3) 11, 1040; Bamberger, Ber. 1895, 28, 245, 1221); by oxidising *p*-toluidine with a persulphate in presence of ether and in contact with ice (Bamberger and Tschirner, Ber. 1899, 32, 1677; see also Wöhl, Eng. Pat. 11216 of 1894; Fr. Pat. 239173; D. R. P. 84138 of 1893; Kalle & Co., D. R. P. 89978 of 1895). Leaflets, m.p. 92°–93° (L. and S.), 93°5'–94° (B.). At 115° it decomposes into *p*-azoxytoluene, and when warmed with dilute sulphuric acid it yields *p*-azoxytoluene, *p*-cresol, amino-cresol, *p*-hydrotoluquinone, and a little *p*-toluidine. Oxidation with chromic acid yields *p*-nitrosotoluene. On treatment with thionyl-aniline in benzene solution it yields *p*-toluidine phenylsulphonamide, white plates, m.p. 236°, and (probably) *o*-toluene-azo-*p*-toluene, m.p. 68°–72° (Michaelis and Petou, Ber. 1898, 31, 988).

Nitroso-p-tolylhydroxylamine; from *p*-nitrotoluene and hydroxylamine in presence of sodium ethylate (Angeli and Angelico, Atti R. Accad. Lincei, 1899, (v.) 8, ii, 28); from *p*-nitrosotoluene and the sodium salt of nitrohydroxylaminic acid (Angeli and Angelico, *ibid.* 1901, (v.) 10, i, 167). Leaflets, m.p. 59°–59°5'.

2-Nitrotolyl-p-hydroxylamine; by electrolytic reduction of 2:4-dinitrotoluene in nearly neutral solution (Brand and Zöller, Ber. 1907, 40, 3324). Compact yellow crystals, m.p. 99° (B. and Z.) or 106° (Burton and Kenner, Chem. Soc. Trans. 1921, 119, 1052).

2:6-Dinitrotolyl-*p*-hydroxylamine; together with 4:6-dinitro-*o*-toluidine by reduction of 2:4:6-trinitrotoluene in cold alcoholic ammoniacal solution with hydrogen sulphide (Anschütz and Zimmermann, Ber. 1915, 48, 152; cf. Cohen and Dakin, Chem. Soc. Trans. 1902, 81, 27; Cohen and McCandlish, *ibid.* 1905, 87, 1205); together with 4:6-dinitrotolyl-*o*-hydroxylamine by reducing 2:4:6-trinitrotoluene in almost neutral solution at a silver cathode (Brand and Eisenmenger, J. pr. Chem. 1913, (2) 87, 487; Ber. 1916, 49, 673). It melts at 135°–136°, and is converted by boiling concentrated

hydrochloric acid into 2:6-dinitro-*p*-toluidine and 2:6-dinitro-4-azoxytoluene.

o-Toluidine 3-sulphonic acid; by reduction of 2-nitrotoluene 3-sulphonic acid (von Pechmann, Ann. 1874, 173, 215); from tolyl-*o*-hydroxylamine and sulphurous anhydride (Brottschneider, J. pr. Chem. 1897, (2) 55, 291). Microscopic needles. The aqueous solution forms an intensive reddish-yellow colour when warmed with ferric chloride.

o-Toluidine 4-sulphonic acid; by reducing the corresponding nitro-acid (Bek, Zeit. f. Chem. 1869, (2) 5, 211; Beilstein and Kuhlberg, Ann. 1870, 155, 21) or *o*-nitrotoluene *p*-sulphonyl chloride with tin and hydrochloric acid (Reverdin and Crépieux, Ber. 1901, 34, 2993); sulphonation of *o*-toluidine sulphate with 30 p.c. or 50 p.c. fuming sulphuric acid (Claus and Immel, Ann. 1891, 265, 71; cf. Weckwarth, *ibid.* 1874, 172, 193; Hayduck, *ibid.* 1874, 172, 204; 1874, 174, 343; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 745). Long needles or four-sided prisms. The aqueous solution forms a dark violet coloration with ferric chloride (Herzfeld, Ber. 1884, 17, 904). With bromine it yields a dibromo-derivative. $NaA' + H_2O$, small lustrous scales (W. and B.), $+ 3H_2O$ (C. and I.), $+ 4H_2O$ (B.); $KA' + H_2O$ (W. and B.); $CaA'_2 + 6H_2O$, small prisms (W. and B.); $BaA'_2 + 2H_2O$, tables (W. and B.); PbA'_2 , anhydrous (H.).

Amide; by reduction of 2-nitrotoluene 4-sulphonamide with ammonium sulphide (Paysan, Ann. 1883, 221, 210; cf. Reverdin and Crépieux, *l.c.*). Large four-sided columns, m.p. 175°. $BHCl$, long silky needles, m.p. 240°.

o-Toluidine 5-sulphonic acid; by heating *o*-toluidine with fuming sulphuric acid at 160°–180° (Gerver, Ann. 1873, 169, 374), or *o*-toluidine ethylsulphate at 200° (Pagel, Ann. 1875, 176, 292); by reducing 2-nitrotoluene 5-sulphonic acid with ammonium sulphide (Foth, Ann. 1864, 230, 306); by heating *o*-toluidine hydrogen sulphate at 220°–230° (Neville and Winther, Chem. Soc. Trans. 1880, 37, 626; Wynne, *ibid.* 1892, 61, 1037; cf. Claus and Immel, Ann. 1891, 265, 67); by heating di-*o*-tolylurea at 150° with concentrated sulphuric acid (Cazeneuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 23). Large monoclinic prismatic crystals $+ H_2O$ (Zepharovich, Ber. 1888, 21, 1803; cf. Hassé, Ann. 1885, 230, 287) or needles $+ H_2O$ (Wynne). $NaA' + 4H_2O$, tables (N. and W.; Wynne); $KA' + H_2O$, tables and prisms (N. and W.); $BaA'_2 + 7H_2O$ (N. and W.; Foth); PbA'_2 , long flat prisms; AgA' , anhydrous prisms.

The aqueous solution when treated with a little lead peroxide is coloured rose-red, then green and finally, on adding more lead peroxide, blackish-violet. On bromination it yields monobromo-*o*-toluidine 5-sulphonic acid and 3:5-dibromo-*o*-toluidine. On nitration the chief product is 3:5-dinitro-2-nitroaminotoluene, yellow explosive crystals, m.p. 92° (Zincke and Malkomesius, Ann. 1905, 339, 202).

Acetyl-derivative, needles (Junghahn, Ber. 1900, 33, 1366).

o-Toluidine 3:5-disulphonic acid; by sulphonating 2-toluidine 5-sulphonic acid at 160°–170° for $\frac{1}{2}$ hour (Neville and Winther, Chem. Soc. Trans. 1882, 41, 421; Ber. 1882, 15, 2983;

Hasse, Ann. 1885, 230, 238; cf. Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 731). Slender needles + $1\frac{1}{2}$ H₂O. Decomposed at 240°, forming 2-toluidine 5-sulphonic acid.

Salts (see Hasse). Na₂A'' + 6H₂O, tables; K₂A'' (anhydrous) (W. and B.); K₂A'' + 2H₂O, monoclinic plates (H.); CaA'' + 5H₂O, tables; Ba₂A'' + $3\frac{1}{2}$ H₂O, microscopic needles or prisms; BaA'' + 3H₂O, triclinic crystals; PbA'', + $6\frac{1}{2}$ H₂O, quadratic prisms; PbA'' + 2H₂O, columns.

Chloride, pale yellow prismatic crystals, m.p. 95° (W. and B.), 132° (H.).

o-Toluidine 4:5-disulphonic acid; by sulphonating *o*-toluidine 4-sulphonic acid, finally at 160° (Wynne and Bruce, l.c.). Needles, K₂A'' + 2H₂O, thin scales; K₂A'', short slender anhydrous needles; BaA'' + $1\frac{1}{2}$ H₂O, small thin scales (W. and B.).

3-Bromo-o-toluidine 5-sulphonic acid; by brominating *o*-toluidine 5-sulphonic acid (Neville and Winther, Ber. 1880, 13, 1942; Chem. Soc. Trans. 1880, 37, 429, 625; Claus and Immel, Ann. 1891, 265, 68; Wynne, Chem. Soc. Trans. 1892, 6, 1037). Lustrous needles or prisms + H₂O. On heating with water or hydrochloric acid at 160° a mixture of bromo-*o*-toluidine, m.p. 56°, dibromo-*o*-toluidine, m.p. 46°, and a liquid bromotoluidine is obtained.

KA', anhydrous thin scales (W.); NaA' + 18H₂O, small rectangular prisms, which rapidly lose $17\frac{1}{2}$ H₂O on exposure to air; BaA' + 3H₂O, long lustrous needles (C. and I.; W.).

Pagel (Ann. 1875, 176, 200) by heating *o*-toluidine with sulphuric acid obtained *o*-toluidine sulphonic acid, the amino-group of which was replaced by bromine, and the bromosulphonic acid nitrated and reduced. The product formed microscopic prisms; BaA' + H₂O, thick needles; whilst Gerver (Ann. 1873, 169, 380) by treating an aqueous solution of *o*-toluidine 5-sulphonic acid with bromine obtained a dibromo-*o*-toluidine 5-sulphonic acid together with a tribromo-*o*-toluidine, m.p. 112°. The former compound yielded BaA' + 4H₂O, long needles; PbA' + 3H₂O, needles or prisms. The validity of the latter author's work is questioned by Neville and Winther.

3:5-Dibromo-o-toluidine 4-sulphonic acid; by brominating *o*-toluidine 4-sulphonic acid (Hayduck, Ann. 1874, 172, 211). Long slender needles + H₂O (see also Kornatzki, Ann. 1883, 221, 191); BaA' + 9H₂O, aggregates of small needles (H.).

4-Iodo-o-toluidine 5-sulphonic acid; by heating diazotised 2-nitro-*p*-toluidine 5-sulphonic acid with concentrated hydriodic acid (Foth, Ann. 1885, 230, 308). Slender silky needles + H₂O; BaA', rhombic plates.

3-Nitro-o-toluidine 5-sulphonic acid; by nitrating acetyl-*o*-toluidine 5-sulphonic acid (Nistaki and Pollini, Ber. 1890, 23, 138); by heating aceto-*o*-toluidine with 3 parts of 20 p.c. fuming sulphuric acid at 100° and nitrating the cold product with mixed acids (Gnehm and Blumer, Ann. 1899, 304, 105). Small yellow crystals. On heating with dilute sulphuric acid it yields 3-nitro-*o*-toluidine.

6-Nitro-o-toluidine 4-sulphonic acid; by passing hydrogen sulphide into an ammoniacal solution of 3:6-dinitrotoluene 4-sulphonic acid (Marckwald, Ann. 1893, 274, 353). Slender

needles. KA', leaflets; CaA', needles; BaA' + $2\frac{1}{2}$ H₂O, needles; AgA' + $\frac{1}{2}$ H₂O, needles.

Methyl-o-toluidine 4-sulphonic acid; by treating methyl-*o*-toluidine with 30 p.c. fuming sulphuric acid with cooling and then heating to 50° (Gnehm and Blumer, Ann. 1899, 304, 109). Leaflets or tables. NaA', leaflets; BaA' + 2H₂O, small irregular crystals.

Acetyl-derivative; by acetylation of the amino-acid or sulphonation of methylaceto-*o*-toluidine. BaA', flat prisms (G. and B.).

Methyl-o-toluidine (?)sulphonic acid; by sulphonation of methyl-*o*-toluidine with monohydrate at 180°-210° (G. and B.). Needles. BaA', readily soluble in water.

Dimethyl-o-toluidine (?)sulphonic acid; by heating dimethyl-*o*-toluidine with 4 parts of sulphuric acid at 180°-210° (Michler and Sampaio, Ber. 1881, 14, 2168). Large glistening prisms which become opaque on exposure to air. CaA', nodules; BaA', leaflets; ZnA', needles.

m-Toluidine 2-sulphonic acid; together with *m*-toluidine 2:4-disulphonic acid by heating *m*-toluidine with fuming sulphuric acid at 160°-175° (Lorenz, Ann. 1874, 172, 185). The products are separated by crystallisation from water in which the disulphonic acid is more soluble.

Rhombic tables or leaflets, charring above 275° without melting. BaA' + 9H₂O, thin tables or long prisms; PbA' + $3\frac{1}{2}$ H₂O, nodules.

m-Toluidine 4-sulphonic acid; 2-bromotoluene 4-sulphonic acid is nitrated, reduced and then treated with sodium amalgam to remove the bromine (Hayduck, Ann. 1874, 174, 350). Microscopic needles. BaA', amorphous; PbA', voluminous flocks.

6-Chloro-m-toluidine 4-sulphonic acid; by reducing sodium 2-chloro-5-nitrotoluene *p*-sulphonate with iron filings and dilute acetic acid. Thin small colourless anhydrous plates which turn red on exposure to air and light (Davies, Chem. Soc. Trans. 1921, 119, 865).

m-Toluidine 2:4-disulphonic acid; by heating *m*-toluidine with fuming sulphuric acid (Lorenz, Ann. 1874, 172, 185). One sulphonic group is removed readily with formation of *m*-toluidine sulphonic acid. BaA'' + $12\frac{1}{2}$ (?)H₂O, needles; PbA'' + 2H₂O, crusts.

Aceto-p-toluidide 2-sulphonic acid, small colourless needles, m.p. about 160° (decomp.), is obtained by the action of aqueous sodium sulphite on aceto-*p*-toluidide-2-sulphonylchloride (Johnson and Smiles, Chem. Soc. Trans. 1923, 123, 2384).

p-Toluidine 2-sulphonic acid; together with *p*-toluidine 3-sulphonic acid and *p*-toluidine disulphonic acid by heating *p*-toluidine with fuming sulphuric acid (Sell, Ann. 1863, 126, 155; Malyschew, Zeit. f. Chem. 1869, (3) 5, 213); by reducing 4-nitrotoluene 2-sulphonic acid (Ballstein and Kuhlberg, Ann. 1874, 172, 230; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 743; cf. Brackett and Hayes, Amer. Chem. J. 1887, 9, 400); from *p*-nitrotoluene (Jensen, Ann. 1874, 172, 233); by heating di-*p*-toluidene with concentrated sulphuric acid at about 150° (Caseneuve and Moreau, Bull. Soc. chim. 1899 (3) 19, 22). Monoclinic crystals + H₂O (Koprovich, Ber. 1888, 21, 2188) or rhombic (Hinsikka, Ann. Acad. Sci. Fennica, 1911

[A] 10, 1). The cold aqueous solution is coloured yellowish-red on treatment with lead peroxide, and with ferric chloride a bordeaux-red colour is produced on warming (Janowsky and Reimann, Ber. 1888, 21, 1217). It reduces ammoniacal silver solution forming a mirror. On diazotisation and boiling with absolute alcohol toluene *o*-sulphonic acid is formed (Ascher, Ann. 1872, 161, 8; Jønsen and Palmer, Amer. Chem. J. 1886, 8, 245). KA' , leaflets or prisms; BaA' , $+H_2O$, leaflets; PbA' , crystalline powder.

Acetyl-derivative; by sulphonating aceto-*p*-toluidide; *acetylsulphonylchloride*, m.p. 124°; *acetylsulphonanilide*, m.p. 220°–221° (Zincke and Rollhauser), or 230° (Johnson and Smiles, Chem. Soc. Trans. 1923, 123, 2384). The acetyl-sulphonyl chloride when reduced with zinc dust yields 4-acetyl-amino-*o*-tolylmercaptan, m.p. 95°, which, on hydrolysis, yields 4-amino-*o*-tolylmercaptan, m.p. 47° (Hess, Ber. 1881, 14, 488, gives 42°) (Zincke and Rollhauser, Ber. 1912, 45, 1495; see also Johnson and Smiles, l.c.).

Amide; by reducing 4-nitrotoluene 2-sulphonamide with hydrogen sulphide in warm ammoniacal solution (Heffter, Ann. 1883, 221, 208). Silky needles or pearly plates, m.p. 164°. By the action of nitrous acid on a mixture of the amide and concentrated hydrochloric acid, *p*-chlorotoluene *o*-sulphonamide is formed, and with nitrous acid and alcohol toluene *o*-sulphonamide is obtained.

p-Toluidine 3-sulphonic acid; by baking *p*-toluidine sulphate or hydrogen sulphate (Neville and Winther, Ber. 1880, 13, 1947; Chem. Soc. Trans. 1880, 37, 631; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 739); together with *p*-toluidine 2-sulphonic acid and a disulphonic acid by heating *p*-toluidine with twice its weight of fuming sulphuric acid at 180°. In the latter case, the chief product is *p*-toluidine 3-sulphonic acid, but on further heating a greater proportion of the other products is obtained (von Pechmann, Ann. 1874, 173, 195); by treating tolyl-*p*-hydroxylamine in cold 60 p.c. alcoholic solution with sulphur dioxide (Bretschneider, J. pr. Chem. 1897, (2) 55, 292); by heating di-*p*-tolylurea with concentrated sulphuric acid at 150° (Cazeneuve and Moreau, Bull. Soc. chim. 1898, (3) 19, 22).

The 2- and 3-acids may be separated by means of alcohol, in which only the latter is soluble (Buff, Ber. 1870, 3, 796; cf. von Pechmann), or by means of the lead salts, that of the 3-acid being the less soluble; or by means of aqueous potassium hydroxide (Schneider, Amer. Chem. J. 1886, 8, 274). Yellow needles $+ \frac{1}{2}H_2O$ or H_2O (P.). Its aqueous solution gives a wine-red colour with a little lead peroxide (Janowsky, Ber. 1888, 21, 1804). On bromination it yields 5-bromo-*p*-toluidine 3-sulphonic acid and 2:5-dibromo-*p*-toluidine (N. and W.). The sulphonic group is hydrolysed by water at 180°. $KA' + \frac{1}{2}H_2O$ (Malyschew, Zeit. f. chem. 1869, 212; Schneider); $BaA' + 3H_2O$, six-sided plates (P.); $PbA' + 2H_2O$, long needles (P.); AgA' , shining crystals.

Acetyl-derivative; by sulphonating aceto-*p*-toluidide (Jungmann, Ber. 1900, 33, 1366). Leaflets.

p-Toluidine 2:5-disulphonic acid; by heat-

ing *p*-toluidine 2-sulphonyl chloride with chloro-sulphonic acid at 160° or with fuming sulphonic acid at 180° (Richter, Ann. 1885, 230, 331; Wynne and Bruce, Chem. Soc. Trans. 1898, 73, 743). Long silky needles $+ 2\frac{1}{2}H_2O$, hydrolysed at 200° with formation of *p*-toluidine 2-sulphonic acid.

$KA' + 2H_2O$, long needles; $BaH_2A' + \frac{1}{2}H_2O$, nodules; $+ \frac{1}{2}H_2O$, silky needles; $BaA' + H_2O$, tables; $PbA' + \frac{1}{2}H_2O$.

p-Toluidine 3:5-disulphonic acid; by heating *p*-toluidine with fuming sulphuric acid at 200° (von Pechmann, Ann. 1874, 173, 217); by heating *p*-toluidine 3-sulphonic acid with chloro-sulphonic acid for 2 hours at 120° and then for 2 hours at 140°–160°, or by heating with fuming sulphuric acid for $\frac{1}{2}$ hours at 160° (Richter, Ann. 1885, 230, 315). The product obtained by the latter author was originally regarded as *p*-toluidine 2:3-disulphonic acid, but was shown by Wynne and Bruce (Chem. Soc. Trans. 1898, 73, 739) to be the 3:5-disulphonic acid. Microscopic needles $+ 2H_2O$, converted by heating at 200°, or with water at 140°, into *p*-toluidine 3-sulphonic acid. Salts (Richter). $KA' + 2H_2O$, long acicular prisms; $BaH_2A' + 3H_2O$, nodules; $BaA' + 3H_2O$, leaflets or tables; $PbA' + 2H_2O$, slender needles; PbA' , silky needles.

Bromo-p-toluidine 2-sulphonic acid; by adding bromine to a boiling solution of *p*-toluidine 2-sulphonic acid (Jønsen, Ann. 1874, 172, 234). Slender needles. $KA' + H_2O$, prisms; $BaA' + 7H_2O$, prisms or needles.

5(?) *Bromo-p*-toluidine 3-sulphonic acid; together with 3:5-dibromo-*p*-toluidine by treating *p*-toluidine 3-sulphonic acid with bromine (von Pechmann, Ann. 1874, 173, 210; Neville and Winther, Chem. Soc. Trans. 1880, 37, 631). Yellowish nodules consisting of grouped needles $+ \frac{1}{2}H_2O$, or fine sulphur-yellow needles $+ \frac{1}{2}H_2O$. KA' , thick prisms; $BaA' + 2H_2O$, small rhombic tables; PbA' , glistening needles; AgA' , long colourless needles (P.).

2-Nitro-*p*-toluidine 5-sulphonic acid; from 2-nitro-*p*-toluidine and fuming sulphuric acid at 135°–150° or chlorosulphonic acid at 160° (Foth, Ann. 1885, 230, 300). Yellow needles, which carbonise without melting. $KA' + H_2O$, small orange-red prisms; $BaA' + 4H_2O$, small yellowish-red prisms $+ H_2O$, red nodules; $PbA' + 3\frac{1}{2}(?)H_2O$, small red needles; ammonium salt, golden-yellow needles; silver salt, white prisms, blackened by light.

Ethyl-p-toluidine 2-sulphonic acid; by sulphonating ethyl-*p*-toluidine (Schmidt, J. pr. Chem. 1893, (2) 48, 62). Yellow prisms $+ H_2O$. $KA' + H_2O$, yellow tables.

Diethyl-p-toluidine 2-sulphonic acid; by sulphonation of diethyl-*p*-toluidine at 180°–200° (Schmidt); by ethylation of potassium-*p*-toluidine 2-sulphonate with ethyl bromide and absolute alcohol at 150° (Schmidt). Prisms $+ H_2O$. $KA' + 2H_2O$, triclinic tables; $CaA' + 3H_2O$; $BaA' + 4H_2O$, triclinic tables.

Diethyl-p-toluidine 3-sulphonic acid; by ethylating potassium *p*-toluidine 3-sulphonate in a similar manner (Schmidt). Monoclinic prisms $+ H_2O$, m.p. 243°. $KA' + \frac{1}{2}H_2O$, tables, m.p. 297°.

Some toluidine sulphonic acids of unknown orientation are described by Pagel (Ann. 1875,

176, 305); Hayduck (*ibid.* 1876, 177, 57); Schäfer (*ibid.* 1874, 174, 360).

2:3-Toluylenediamine; by reducing 3-nitro-*o*-toluidine with tin and hydrochloric acid (Leilmann, Ann. 1885, 228, 243) or with hydriodic acid (Gabriel and Thieme, Ber. 1910, 52, 1079). Crystals, m.p. 61°-62°, b.p. 255° (L.), or m.p. 63°-64° (G. and T.).

6-Chloro-2:3-toluylenediamine; by reducing 6-chloro-2:3-dinitrotoluene with stannous chloride and hydrochloric acid (Cohn, Monatah. 1901, 22, 477); by reducing 6-chloro-3-nitro-*o*-toluidine with zinc dust and ammonium chloride in dilute alcohol (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 788). Colourless needles, m.p. 46°-47°.

Hydrochloride, nacreous leaflets, decomposing at 263° (M. and D.).

Acetyl-derivative; m.p. 201°-203° (M. and D.).

4:6-Dichloro-2:3-toluylenediamine; by reducing 2:4-dichloro-5:6-dinitrotoluene (Seelig, Ann. 1887, 237, 164). Leaflets, m.p. 110°. On boiling with acetic anhydride for 25 hours it yields an *anhydro-base*, m.p. 170°.

4:5:6-Trichloro-2:3-toluylenediamine; by reducing the corresponding dinitro-compound with stannous chloride in hot 50 p.c. alcoholic solution (Seelig, Ber. 1885, 18, 82; Prenntzell, Ann. 1897, 298, 182). M.p. 195°-207°.

Anhydro-base; by boiling with acetic anhydride for 40-50 hours. Glistening brown needles, m.p. about 300° (S.).

5-Bromo-2:3-toluylenediamine; by successive bromination, nitration, hydrolysis, and reduction of aceto-*o*-toluidide (Hübner and Schupphaus, Ber. 1884, 17, 776). Small needles, m.p. 59°. B'HCl, needles; B'H₂SO₄, plates.

5-Nitro-2:3-toluylenediamine; by reducing 3:5-dinitro-*o*-toluidine with sodium sulphide. Orange-red felted needles.

Diacetyl-derivative; obtained by warming the base with acetic anhydride. Pale yellow needles, m.p. 234°. When the free base is boiled with glacial acetic acid and formic acid it is converted into 5-nitro-2:7-dimethylbenzimidazole, glistening needles, m.p. 186°, and 5-nitro-7-methylbenzimidazole, white needles, m.p. 199°-200°.

6-Chloro-2-methyl-2:3-toluylenediamine; by reducing 6-chloro-3-nitromethyl-*o*-toluidine with zinc dust and ammonium chloride in aqueous alcoholic solution. Oil. B'HCl, colourless needles. **Diazotimine**, flesh-coloured prismatic needles, m.p. 238°-239° (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 191).

2:3-Toluylenediamine 5-sulphonic acid; by reducing 3-nitro-*o*-toluidine 5 sulphonic acid with stannous chloride and hydrochloric acid (Nietzki and Pollini, Ber. 1890, 23, 139). Needles.

2:4-Toluylenediamine, *m-toluylenediamine*; by reducing 2:4-dinitrotoluene (Hofmann, Jahresbericht, 1861, 513) or 4-nitro-*o*-toluidine with tin and hydrochloric acid (Nölting and Collin, Ber. 1884, 17, 288); by treating 2:4-dinitrobenzyl chloride with tin and hydrochloric acid (Krasusky, J. Russ. Phys. Chem. Soc. 1905, 37, 837). Long needles, or rhombic prisms, m.p. 99°, b.p. 280°. Its aqueous solution darkens in the air. When treated with sodium peroxide solution at a moderate temperature 4-nitro-*o*-toluidine is obtained, whilst when the mixture is boiled 2:4-dinitrotoluene is

formed (O. Fischer and Trost, Ber. 1893, 26, 3084).

Salts, see Hofmann; Hell and Schoop, Ber. 1870, 12, 723. B'HCl (Bernthsen and Trompeter, Ber. 1878, 11, 1759); B'2HCl, B'H, PtCl₄; B'2HBr; B'H₂SO₄+2H₂O, long monoclinic prisms (Strauss, Ann. 1868, 148, 187; cf. Beilstein and Kuhlberg, Ann. 1871, 158, 251). Reactions with sulphur, see Kalle and Co., D. R. P. 86096 of 1894; Clayton Aniline Co., Eng. Pat. 4792 of 1900; D. R. P. 120504 of 1900; Cassella & Co., Eng. Pat. 11771 of 1902; U.S. Pat. 714542; Fr. Pat. 321122; D. R. P. 139430 of 1902.

With formaldehyde in neutral aqueous or alcoholic solution it yields *anhydroformaldehyde-m-toluylenediamine*, powder, m.p. 150°-180°, whilst in acid solution 3:3'-dimethyl-4:6:4':6'-tetraaminodiphenylmethane, m.p. 203°-204°, is formed (Ullmann and Naef, Ber. 1900, 33, 913; D. R. P. 130943 of 1898).

2-Acetyl-derivative; by reducing 4-nitro-aceto-*o*-toluidide, needles, m.p. 140° (Wallach, Ann. 1886, 234, 360).

4-Acetyl-derivative; by prolonged boiling of 2:4-toluylenediamine with acetic acid (Tiemann, Ber. 1870, 3, 221; Schiff and Ostrogovich, Ann. 1896, 293, 371), or by heating 1 part of the diamine with $\frac{1}{2}$ part of acetamide initially at 110° and finally at 160°-170° (S. and O.). Long yellow prisms or needles, m.p. 161.5° (S. and O.) or 159°-160° (T.).

Diacetyl-derivative (Koch, Ann. 1870, 153, 132; Tiemann, Ber. 1870, 3, 8; Ladenburg, *ibid.* 1875, 8, 1211). Long needles, m.p. 221° (T.) or 224° (L.). By boiling with 1 mol. of potassium hydroxide 4-acetamino-2-aminotoluene is obtained (K.).

Formyl-derivative; transparent pyramids, m.p. 113°-114°; **disformyl-derivative**; bunches of white needles, m.p. 176°-177° (Geigy & Co., U.S. Pat. 722630; Fr. Pat. 306655; D. R. P. 138839 of 1902).

4-Benzoyl-derivative; by reducing *o*-nitro-4-benzoylamino-toluene with tin and hydrochloric acid (Bell, Ber. 1874, 7, 1506). Prisms, m.p. 142°.

Dibenzoyl-derivative; tables, m.p. 224° (Ruhemann, Ber. 1881, 14, 2656).

Benzylidene-derivative; yellow tables, m.p. 90°-91° (Meyer and Gross, Ber. 1898, 31, 2358); **dibenzylidene-derivative**; yellowish crystalline mass, m.p. 122°-123° (Schiff, Ann. 1866, 146, 98).

5-Chloro-2:4-toluylenediamine; by reducing 5-chloro-2:4-dinitrotoluene with tin and hydrochloric acid (Reverdin and Crépieux, Ber. 1900, 33, 2507); by successive chlorination and hydrolysis of diacetyl-2:4-toluylenediamine (Morgan, Chem. Soc. Trans. 1900, 77, 1869). Leaflets or rectangular plates, m.p. 120°-121° (M.) or 123° (R. and G.).

Acetyl-derivative; m.p. 170° (R. and G.); **diacetyl-derivative**, small acicular prisms, m.p. above 290° (R. and G.; Morgan, Chem. Soc. Trans. 1902, 81, 95).

Disformyl-derivative; colourless silky needles, m.p. 166° (Morgan).

Dibenzoyl-derivative; colourless acicular lamellae, m.p. 205° (M.).

6-Chloro-2:4-toluylenediamine; by reducing 2-chloro-4:6-dinitrotoluene with stannous

chloride and hydrochloric acid in presence of alcohol, or with zinc dust, ammonium chloride and alcohol (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 788).

5:6-Dichloro-2:4-toluylenediamine; by reduction of 2:3-dichloro-4:6-dinitrotoluene (Seelig, Ann. 1887, 237, 164). Slender needles, m.p. 137°.

5-Bromo-2:4-toluylenediamine; by reducing either 5-bromo-2:4-dinitrotoluene (Grete, Ann. 1875, 177, 231) or 5-bromo-4-nitro-*o*-toluidine (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 950); by brominating dibenzoyl-2:4-toluylenediamine (Ruhemann, Ber. 1881, 14, 2659; Morgan and Clayton) or diacetyl-2:4-toluylenediamine (Tiemann, Ber. 1870, 3, 220) and hydrolysing the product. Lustrous needles, m.p. 104°-107° (decomp.) (M. and C.), rhombic tables 107° (G.), leaflets 104° (R).

Monoacetyl-derivative, leaflets, m.p. below 100° (Koch, Ann. 1870, 153, 134).

Acetyl-derivative, m.p. 254° (M. and C.). Dibenzoyl-derivative, m.p. 214° (R).

Dibromo-4-acetyl-2:4-toluylenediamine; by brominating 4-acetyl-2:4-toluylene-diamine (Tiemann, l.c.). Long needles, m.p. 208° with blackening.

3:5:6-Tribromo-2:4-toluylenediamine; by reducing the corresponding dinitro-compound or 3:5:6-tribromo-4-nitro-*o*-toluidine with iron and acetic acid (Blanksma, Chem. Weekblad, 1914, 11, 185). Colourless crystals, m.p. 180°.

Nitroso-2:4-toluylenediamine; m.p. 195° (Täuber and Walder, D. R. P. 123375 of 1900).

6(?) Nitro-2:4-toluylenediamine; by successive nitration and hydrolysis of diacetyl or dibenzoyl-2:4-toluylenediamine (Tiemann, Ber. 1870, 3, 219; Ladenburg, *ibid.* 1875, 8, 1211; Ruhemann, *ibid.* 1881, 14, 2656). Reddish-yellow needles, with a violet sheen, m.p. 154°. Weak base, whose salts are decomposed by water.

Diacetyl-derivative; needles, m.p. 253° (decomp.) (L.). Dibenzoyl-derivative; citron-yellow needles, m.p. 245° (R.).

6-Nitro-2:4-toluylenediamine(?); by reducing 2:4:6-trinitrotoluene with alcoholic ammonium sulphide (Tiemann, l.c.). Small red prisms, m.p. 132°; hydrochloride, yellow needles.

3:5-Dinitro-2:4-toluylenediamine; together with a mononitro-derivative by nitration of diacetyl-2:4-toluylenediamine in presence of urea nitrate, followed by hydrolysis with dilute sulphuric acid (Nietzki and Rösel, Ber. 1890, 23, 3218); from 2:4-dibromo-3:5-dinitrotoluene and alcoholic ammonia at 150° (Blanksma, Chem. Weekblad, 1912, 9, 968); by heating 3:4:5-trinitro-2-methoxytoluene with ammonia in a sealed tube (Blanksma, Rec. trav. chim. 1910, 29, 410). Dark brown crystals, m.p. 254°.

Acetyl-derivative; does not melt below 300° (B.).

2-Methylamino-4-aminotoluene; by reducing 4-nitro-methyl-*o*-toluidine with tin or zinc dust (Gnehm and Blumer, Ann. 1899, 304, 106). Colourless oil, b.p. 273°.

2-Amino-4-methylaminotoluene; colourless viscid oil, b.p. 276°-276.5° (corr.), coloured brown by exposure to air; sulphate, white needles. For its use in the preparation of azines and indulines, see Bayer & Co., Eng. Pat. 16915 of

1892; Fr. Pat. 225086; D. R. P. 92014 of 1892; B. A. S. F., D. R. P. 77228 of 1892.

Nitrosoamine; yellow needles, m.p. 83°; picrate, needles, m.p. 103°-105° (Pinnow and Oesterreich, Ber. 1898, 31, 2928).

Nitroamine; by heating 2-nitromethyl-*p*-toluyl-nitroamine with alcoholic ammonium sulphide at 100°. Dull red prisms, m.p. 83.5° (P. and O.).

5-Nitro-2-amino-4-methylaminotoluene; from 2:5-dinitromethyl-*p*-toluidine and alcoholic ammonium sulphide (Pinnow, J. pr. Chem. 1900, (2) 62, 508). Brown leaflets with a bronze lustre, m.p. 168°.

Acetyl-derivative; yellowish-brown needles, m.p. 205.5°-207° (P.).

3:5-Dinitro-2-amino-4-methylaminotoluene; by heating 2:3:5-trinitromethyl-*p*-toluidine with alcoholic ammonia at 130° (Sommer, J. pr. Chem. 1903, (2) 67, 535); from 3:5-dinitro-2-amino-*p*-toluyl-nitroamine by heating with twice its weight of phenol for 2 hours at 140°-160° (S.); from the ethyl-ether of 3:5-dinitro-4-methylamino-*o*-cresol by heating with concentrated absolute alcoholic ammonia at 100° (Sommer, l.c. 559). Orange needles with a yellow reflex, m.p. 206°-208°.

Nitrosoamine; by the action of ammonia on the nitrosoamine of 2:3:5-trinitromethyl-*p*-toluidine. Brownish-yellow prisms, m.p. 164° (Sommer, l.c. 562).

2-Dimethylamino-4-aminotoluene; by reducing 4-nitrodimehyl-*o*-toluidine with stannous chloride and hydrochloric acid (Ullmann and Mühlhauser, Ber. 1902, 35, 332; Möhlau, Klimmer and Kahl, Zeit. f. Farb. u. Textilchem, 1902, 1, 313). Yellowish oil, coloured red by air, b.p. 248° (M., K. and K.) or 257°-259°/730 mm. with slight decomposition (U. and M.).

Dihydrochloride; columns, m.p. 208°; sulphate; m.p. 209° (M., K. and K.).

Acetyl-derivative; needles, m.p. 103° (M., K. and K.).

2-Amino-4-dimethylaminotoluene; by reducing 2-nitrodimehyl-*p*-toluidine (M. L. B., D. R. P. 69188 of 1891) with tin and hydrochloric acid (Morgan and Clayton, Chem. Soc. Trans. 1905, 87, 948).

Acetyl-derivative; white needles, m.p. 135° (M. and C.).

For the use of this base in the preparation of azines, see M. L. B., D. R. PP. 69188 of 1891; 85231, 85232 of 1892; 87500 of 1895; of safranines, Leonhardt & Co., D. R. P. 86806 of 1892; and of other dyes, Act. Ges. f. Anilfabr., Eng. Pat. 12899 of 1900; Fr. Pat. 301793; D. R. P. 118392 of 1900.

5-Bromo-2-amino-4-monoethylaminotoluene; by brominating 2-acetyl-amino-4-dimethylaminotoluene in glacial acetic acid, followed by hydrolysis (Morgan and Clayton, l.c.); by reducing 3-bromo-6-nitrodimehyl-*p*-toluidine with tin and hydrochloric acid (M. and C.). Pearly leaflets, m.p. 40°.

Acetyl-derivative; crystals, m.p. 163°; benzoyl-derivative; m.p. 177°-178°; 2-benzene-sulphonyl-derivative; m.p. 178°-179° (M. and C.).

3:5-Dinitro-2:4-monomethylaminotoluene; by the action of methylamine on a concentrated boiling alcoholic solution of 2:3:5-trinitro-methyl-*p*-toluidine (Sommer, J. pr. Chem. 1903, (2) 67, 547). It exists in two modifications:

(a) red plates, m.p. 168° – 170° ; (b) yellow needles, m.p. 110° , converted into the red modification at 140° . Both modifications yield with aqueous potassium hydroxide according to the concentration 3:5-dinitro-2:4-dihydroxytoluene and 3:5-dinitro-2-methylamino-*p*-cresol (S.).

4-Nitrosoamine; from the nitrosoamine of 2:3:5-trinitromethyl-*p*-toluidine and methylamine. Small yellow needles, m.p. 186° – 187° .

2:4-Dinitrosoamine; from either of the above compounds in acetic acid solution with sodium nitrite. Very stable white leaflets, or glistening cubes, m.p. 132° (S.).

3:5-Dinitro-2-dimethylamino-4-methylaminotoluene; from 2:3:5-trinitromethyl-*p*-toluidine and dimethylamine in alcoholic solution (Sommer, l.c. 565). Yellow needles, m.p. 115° .

3:5-Dinitro-2:4-di(methylnitrosoamino)-toluene; colourless crystals, m.p. 169° (Blanksma, Rec. trav. chim. 1910, 29, 410).

Tetramethyl-2:4-toluylenediamine; together with the methylammonium bromide; by heating 2:4-toluylenediamine hydrobromide with methyl alcohol in a sealed tube at 180° (Morgan, Chem. Soc. Trans. 1902, 81, 653). Yellowish-brown oil, b.p. 148° – 150° /24–26 mm., 255° – 256° /757 mm.; D_{20}^{25} 0.9661. BH_2PtCl_6 , yellow prisms; picrate, yellow prisms, m.p. 162° – 163° .

2-Ethylamino-4-aminotoluene; by reducing 4-nitroethyl-*o*-toluidine with zinc dust and hydrochloric acid (MacCallum, Chem. Soc. Trans. 1895, 67, 247). Liquid, b.p. 274° – 275° .

2-Amino-4-ethylaminotoluene; by reducing the corresponding nitro-compound (Nölting and Stricker, Ber. 1886, 19, 549). Liquid, b.p. 280° – 283° (N. and S.) or 289° – 291° (Jaubert, Bull. Soc. chim. 1899, (3) 21, 20).

2-Diethylamino-4-aminotoluene; by reducing 4-nitrodiethyl-*o*-toluidine with stannous chloride and hydrochloric acid (Ullmann and Mühlhauser, Ber. 1902, 35, 335; Möhlau, Kluhmer and Kahl, l.c.). Yellowish oil, b.p. 259° (M., K. and K.), 265° – 266° /730 mm. (U. and M.). Volatile with steam. $B_2HCl + H_2O$, m.p. 213° – 215° (decomp.) (M., K. and K.).

2-Amino-4-phenylaminotoluene; by heating 1 part of 2:4-toluylenediamine with $1\frac{1}{2}$ parts of aniline hydrochloride and 3 parts of aniline at 240° – 250° for 10 hours (Bayer & Co., Eng. Pat. 3610 of 1894; Fr. Pat. 240571; D. R. P. 80977 of 1894). Prisms, m.p. 76° – 77° . Used for the preparation of azines (Bayer & Co., Eng. Pat. 3610 of 1894; Fr. Pat. 240621; D. R. PP. 81963 and 84504 of 1894).

3:5-Dinitro-2-phenylamino-4-methylaminotoluene; from 2:3:5-trinitromethyl-*p*-toluidine and aniline (Sommer, J. pr. Chem. 1903, (2) 67, 137). Thick prisms, m.p. 197° .

4-Nitrosoamine; orange needles, m.p. 122° .

3:5-Dinitrosoamine; sulphur-yellow needles, decomposing at 100° (S.).

2:4-Dinitrophenyl-2:4-toluylenediamine; by boiling a mixture of 2:4-toluylenediamine, chloro-2:4-dinitrobenzene and alcohol (Leymann, Ber. 1883, 16, 1237). Red tables, m.p. 184° .

Acetyl-derivative; m.p. 163° – 164° (L.).

2-Ethylamino-4-phenylaminotoluene; by heating 3-amino-4-phenylaminotoluene with ethyl bromide at 150° – 175° for 10 hours (Bayer & Co., Eng. Pat. 4176 of 1893; Fr. Pat. 240571;

D. R. P. 87467 of 1895). Crystals, m.p. 59° – 60° . Used for the preparation of azines (Bayer & Co., Eng. Pat. 9794 of 1895; Fr. Pat. 240621; D. R. P. 87975 of 1895).

2:4-Toluylenediamine 5-sulphonic acid; by warming 2-nitro-*p*-toluidine 5-sulphonic acid with stannous chloride and hydrochloric acid (Foth, Ann. 1885, 230, 309). Small glistening pyramids or rhombohedra. $KA' + H_2O$, glistening prisms; $BaA' + 5\frac{1}{2}H_2O$, glistening leaflets or tables; $B'HCl + H_2O$, large rhombic prisms, decomposed by boiling water; $B'HBr + H_2O$.

This sulphonic acid is possibly identical with that prepared by Wiesinger (Ber. 1874, 7, 464) by sulphonating 2:4-toluylenediamine, although the water content of some of its salts differs from those enumerated above.

2:4-Toluylenediamine 6-sulphonic acid; by reducing 2:4-dinitrotoluene 6-sulphonic acid. Prisms (Oehler, Fr. Pat. 199568; D. R. P. 51662 of 1889).

Anhydroformaldehyde-2:4-toluylenediamine; from 2:4-toluylenediamine and formaldehyde in neutral aqueous or alcoholic solution (Ullmann and Naef, Ber. 1900, 33, 913; D. R. P. 130943 of 1898). Slightly coloured powder, m.p. 150° – 180° . On heating in dilute acid solution it yields acridines (Ges. f. Chem. Ind. Basel, D. R. P. 136617 of 1902).

2:5-Toluylenediamine, *p*-toluylenediamine; by reducing 5-nitro-*o*-toluidine (Beilstein and Kuhlberg, Ann. 1871, 158, 352), *o*-aminoazotoluene (Nietzki, Ber. 1877, 10, 832) or *m*-aminoazotoluene (Nietzki, l.c. 1158) with tin and hydrochloric acid; by reducing 6-nitro-*m*-toluidine (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 306). Colourless prisms, m.p. 64° , b.p. 273° – 274° . By treating a solution of the base containing a little *o*-toluidine with oxidising agents such as potassium dichromate, manganese dioxide, and ferric chloride an intense green coloration is formed (N.).

Dihydrochloride; leaflets; sulphate, powder.

Diacetyl-derivative; large prisms, m.p. 220° (Nietzki, Ber. 1877, 10, 1157; *ibid.* 1879, 12, 2237).

4-Chloro-2:5-toluylenediamine; by reducing 4-chloro-2:5-toluylenediamine dioxime with stannous chloride and hydrochloric acid in presence of alcohol.

Diacetyl-derivative; silky snow-white needles (Kehrmann, Silva and Keleti, Ber. 1916, 48, 2028).

Chloro-2:5-toluylenediamine; by saturating an alcoholic, ethereal or glacial acetic acid solution of *N*-nitroso-*o*-tolylglycine with cold dry hydrogen chloride (Vörländer and Schröder, Ber. 1901, 34, 1651). White scales rendered violet by air, m.p. 146° . It reduces cold ammoniacal silver nitrate. Ferric chloride, chlorine water, &c., give a green coloration.

Dihydrochloride and sulphate are crystalline.

Diacetyl-derivative; fine white needles, m.p. above 300° (V. and S.).

3:4:6-Trichloro-2:5-toluylenediamine; by reducing a glacial acetic acid solution of 2:4:6-trichlorodinitrotoluene with stannous chloride and aqueous hydrochloric acid (Seelig, Ann. 1887, 237, 143; Ber. 1885, 18, 430). Shaded needles, m.p. 196° .

Tetra-acetyl-derivative; needles, m.p. 238° (S.).

3-Amino-4-dimethylaminotoluene; by

ducing nitroso-dimethyl-*m*-toluidine with tin and hydrochloric acid (Wurster and Riedel, Ber. 1879, 12, 1801). Long needles, m.p. 28°.

Acetyl-derivative; m.p. 158° (W. and R.).

5-Amino-2-dimethylaminotoluene; by reducing 5-nitrodimehyl-*o*-toluidine with zinc dust and hydrochloric acid at 0° (Bernthsen, Ber. 1892, 25, 3134). Oil, which solidifies in a freezing mixture and melts at 47°, b.p. 253°-254°. $B'H_2SO_4$, small needles. Ferric chloride yields a bluish-red colour and potassium dichromate a purple-red colour.

Tetramethyl-2:5-toluylenediamine; by heating 5-dimethylamino-*o*-toluidine with methyl alcohol and hydrochloric acid at 180° (Wurster and Riedel, l.c. 1802). Oil, b.p. 260°. Ferric chloride yields an intensive blue colour which disappears on adding hydrochloric acid.

5-Amino-2-ethylaminotoluene; by reducing 5-nitroso-ethyl-*o*-toluidine (Kock, Ann. 1888, 243, 307) with stannous chloride and hydrochloric acid (Weinberg, Ber. 1892, 25, 1611). Viscid liquid, b.p. (in atmosphere of hydrogen) 264° (K.), 272° (W.).

Dihydrochloride, m.p. 124° (decomp.); *sulphate*, large crystals.

5-Amino-2-diethylaminotoluene; by reducing 5-nitrodiethyl-*o*-toluidine (Bernthsen, Ber. 1892, 25, 3138, 3367); by hydrolysis of its acetyl-derivative (Weinberg). M.p. 24° (Weinberg, Ber. 1893, 26, 308), b.p. 266°-267°.

Hydrochloride; glistening leaflets; *sulphate*, $+2H_2O$, prisms.

2-Ethylamino-5-benzoylamintoluene; small needles, m.p. 174° (O. Fischer, Ann. 1895, 286, 166).

4-Nitro-2:5-toluylenediamine; by nitration of *diacetyl-2:5-toluylenediamine* in glacial acetic acid with a mixture of nitric acid (D 1.47) and glacial acetic acid, followed by hydrolysis (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1398). Needles, varying in different crystallisations from bright red to dark green with a bronze reflex, m.p. 173°.

Diacetyl-derivative; short pale yellow prisms, m.p. 158° (M. and M.).

2:6-Toluylenediamine; by reducing 6-nitro-*o*-toluidine with tin and hydrochloric acid (Cunrath, Ann. 1874, 172, 227; Ullmann, Ber. 1884, 17, 1959). Prisms, m.p. 103.5°-105°. With ferric chloride it yields a deep blue colour, and with *p*-nitrosodimethylaniline first a green and then a dark blue solution.

Hydrochloride, crystals; *sulphate*, $+1\frac{1}{2}H_2O$, small slender needles.

Diacetyl-derivative; sublimes in white woolly flocks, m.p. 202°-203 (Green and Lawson, Chem. Soc. Trans. 1891, 59, 1017).

3:5-Dinitro-2:6-toluylenediamine; by the action of alcoholic ammonia on 2:6-dibromo-3:5-dinitrotoluene at 150° (Blanksma, Chem. Weekblad, 1912, 9, 968).

Acetyl-derivative; colourless crystals, decomposing above 300° (B.).

3:5-Dinitro-2:6-dimethyltoluylenediamine; by the action of methylamine on 2:6-dibromo-3:5-dinitrotoluene (Blanksma). Orange-red crystals, m.p. 216°.

2:6-Toluylenediamine sulphonic acid; by boiling the corresponding thiosulphonic acid with concentrated hydrochloric acid (Perl, Ber. 1885, 18, 69). Silky needles. $B'A' + 2H_2O$, microscopic needles.

2:6-Toluylenediamine-4-sulphonic acid; by reducing 2:6-dinitrotoluene 4-sulphonic acid or 6-nitro-2-aminotoluene 4-sulphonic acid with tin and hydrochloric acid (Schwanert, Ann. 1877, 186, 380; Marckwald, Ann. 1893, 274, 351). Rhombic pillars, not melting at 280° (S.). $B'A' + 4H_2O$, amorphous; $B'HCl + 2H_2O$, small rhombic pillars; $B'HBr + 2H_2O$; $B'HNO_3 + H_2O$, rhombic needles; $B'H_2SO_4 + H_2O$, rhombic plates (S.).

3:4-Toluylenediamine; reduction of 3-nitro-*p*-toluidine or 3-nitro-*p*-aminobenzyl alcohol with tin and hydrochloric acid (Beilstein and Kuhlberg, Ann. 1871, 158, 351; Meyer and Rohmer, Ber. 1900, 33, 254). Scales, m.p. 88.5°, b.p. 265° (B. and K.). Its aqueous solution darkens in the air. $B'2HCl$, needles (Hübner, Ann. 1881, 209, 364); *sulphate*, $+1\frac{1}{2}H_2O$, scales.

3-Acetyl-derivative; by reducing 4-nitro-aceto-*m*-toluidide with iron and acetic acid. Nodular aggregates, melting indefinitely at 95°. The corresponding *anhydro-base* melts at 145°-150° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1400); **4-acetyl-derivative**; by reduction of 3-nitroaceto-*p*-toluidide, leaflets, m.p. 130°-131° (Bössneck, Ber. 1886, 19, 1757); *picrate*, leaflets (Bankiewicz, Ber. 1889, 22, 1399); *diacetyl-derivative*; long slender needles, m.p. 210° (Bistrzycki and Ulfers, Ber. 1890, 23, 1878). The *diacetyl-derivative* yields a *nitro-compound*, long needles, m.p. 230°, and a *dinitro-compound*, fine silky needles, m.p. 251°-252° (Bistrzycki and Ulfers, l.c. 1891).

3-Benzoyl-derivative; by reducing 4-nitro-benzoyl-*m*-toluidine with iron and acetic acid. Colourless felted needles or prismatic crystals, m.p. 158° (Morgan and Micklethwait, Chem. Soc. Trans. 1913, 103, 1403); **4-benzoyl-derivative**; crystals, m.p. 193°-194°, together with phenyl-tolimidazole by reducing 3-nitrobenzyl-*p*-toluidine with tin and hydrochloric acid (Hübner, Ann. 1881, 208, 314) or together with the dibenzoyl-derivative by direct benzoylation (Bistrzycki and Cybulski, Ber. 1891, 24, 633); **dibenzoyl-derivative**; by the further treatment of the 4-benzoyl-derivative with benzoyl chloride (Hübner, Bistrzycki and Cybulski) or from *m*-methylbenzimidazole with benzoyl chloride and sodium hydroxide (Bamberger and Berlé, Ann. 1893, 273, 349). It forms glistening needles, m.p. 263°-264° (Hinsberg and Udransky, Ann. 1889, 254, 255), and yields a *nitro-derivative*, prisms or needles, m.p. 246° (Bistrzycki and Ulfers, Ber. 1892, 25, 1994).

2-Chloro-3:4-toluylenediamine; by reducing 2-chloro-4-nitro-*m*-toluidine with zinc dust, dilute alcohol and ammonium chloride (Morgan and Glover, Chem. Soc. Trans. 1921, 119, 1706). Pale brown needles, m.p. 55°-56°.

6-Chloro-3:4-toluylenediamine; obtained quantitatively as the hydrochloride by reducing 6-chloro-4-nitro-*m*-toluidine with zinc dust, ammonium chloride and dilute alcohol, or with alcoholic stannous chloride (Morgan and Drew, Chem. Soc. Trans. 1920, 117, 790; Morgan and Challenor, *ibid.* 1921, 119, 1539). Pale brownish-yellow leaflets, m.p. 143°.

5-Bromo-3:4-toluylenediamine; by reducing 5-bromo-3-nitro-*p*-toluidine with stannous chloride and hydrochloric acid (Bistrzycki, Ber. 1890, 23, 1045). Long flat needles, m.p. 81°-82°.

4-Acetyl-derivative; by reducing 5-bromo-3-nitroaceto-*p*-toluidide at a low temperature with stannous chloride and hydrochloric acid. It forms crystals, m.p. 167°-168° (Hartmann, Ber. 1890, 23, 1049); diacetyl-derivative; by direct acetylation, glistening needles, m.p. 222°-223°; dibenzoyl-derivative, needles, m.p. 244°.

4-Methylamino-3-aminotoluene; by reducing 3-nitro-4-methylaminotoluene or its nitroso-amine with tin and hydrochloric acid (Gattermann, Ber. 1885, 18, 1487; O. Fischer, Ber. 1893, 26, 194); by reducing methyl-*p*-toluidine-azobenzene 4-sulphonic acid with stannous chloride and hydrochloric acid (Bamberger and Wulz, Ber. 1891, 24, 2082). Quadratic tables, m.p. 46°-44°, b.p. 260°/752 mm. (Pinnow, Ber. 1887, 20, 3121). B²HCl, small glistening prisms, decomposing at 180°-185° (B. and W.) or 175°-180° (F.); B²H₂SO₄, deliquescent needles (F.); B²C₂H₃O₄, glistening needles, m.p. 124° (F.); picrate, small yellow crystals, m.p. 164° (F.). Symm-diacetyl-derivative; hexagonal plates, m.p. 183°-184° (Pinnow, J. pr. Chem. 1900, (2) 62, 514).

6-Chloro-4-amino-3-methylaminotoluene; by reducing 6-chloro-4-nitromethyl-*m*-toluidine with zinc dust, alcohol and ammonium chloride (Morgan and Challenor, Chem. Soc. Trans. 1921, 119, 1542). Sublimes in arborescent needles, m.p. 60°.

5-Nitro-4-methylamino-3-aminotoluene; by reducing 3:5-dinitromethyl-*p*-toluidine with hydrogen sulphide in presence of alcohol and ammonia (Pinnow, J. pr. Chem. 1901, (2) 63, 360). Bluish-red plates or short prisms with a green sheen, m.p. 131.5°-132.5°.

3-Amino-4-dimethylaminotoluene; together with a compound whose picrate melts at 254.5° by the gradual addition of tin to a solution of 3-nitro-4-dimethylaminotoluene in hydrochloric acid (Pinnow, Ber. 1895, 28, 3042; J. pr. Chem. 1901, (2) 63, 354). Oil, b.p. 234°. Coloured red by ferric chloride. B²HCl, crystals, m.p. 192°-193°; B²H₂HgCl₂, crystals, m.p. 205°-206°; picrate, yellow-brown prisms, m.p. 150.5°. Acetyl-derivative; plates, m.p. 111.5°-112.5° (F.).

5-Nitro-3-acetylamino-4-dimethylaminotoluene; by reducing 3:5-dinitrodimethyl-*p*-toluidine with ammonium sulphide, followed by treatment with acetic anhydride (Pinnow and Matovich, Ber. 1898, 31, 2514). Yellow needles or prisms, m.p. 97°.

6-Nitro-3-acetylamino-4-dimethylaminotoluene; by nitrating 3-acetylamino-4-dimethylaminotoluene with mixed acids below 0° (Pinnow, Ber. 1901, 34, 1131). Bright yellow rhombic tables, m.p. 142.5°-143°.

Tetramethyl-3:4-toluylenediamine; from 3:4-toluylenediamine and methyl iodide (Niemenowski, Ber. 1887, 20, 1888; cf. O. Fischer and Rignard, *ibid.* 1902, 35, 1283). Liquid, b.p. 24.5°-22.5°/717 mm. (N.), 259°-260°/740 mm. (F. and R.). Ferric chloride gives a red coloration and red crystalline plates. B²HCl, needles, m.p. 125° (F. and R.).

4-Ethylamino-3-aminotoluene; by reducing nitroethyl-*p*-toluidine with tin and hydrochloric acid (Gattermann, Ber. 1885, 18, 1484; O. Fischer, *ibid.* 1893, 26, 199). Large tables, m.p. 54°-55°. Unstable. B²HCl, m.p. 176° (F.); B²C₂H₃O₄, needles, m.p. 181° (F.).

Symm. diacetyl-derivative; obtained together with 2:5-dimethyl-1-ethylbenzimidazole by the action of acetic anhydride on the base (O. Fischer and Rignard, Ber. 1901, 34, 4206). Crystals, m.p. 177°.

3-Ethylamino-4-aminotoluene; by reducing 4-nitro-ethyl-*m*-toluidine with tin and hydrochloric acid (O. Fischer and Rignard). Needles, m.p. 59°, coloured violet in presence of air and moisture. With ferric chloride it yields a deep red oxidation product.

Symm. diethyl-3:4-toluylenediamine; from the diethyl-derivative of dibenzene-sulphone-3:4-toluylenediamine and concentrated hydrochloric acid at 180° (Hinsberg, Ann. 1891, 265, 191; cf. O. Fischer and Rignard, Ber. 1902, 35, 1265). Liquid, b.p. 265° (H.). B²HCl, needles. With ferric chloride in presence of hydrochloric acid it forms a reddish-brown colour; a colourless precipitate is formed on the addition of potassium ferrocyanide to the aqueous solution (H.).

6-Chloro-3-phenylamino-4-aminotoluene; by reducing 6-chloro-4-nitrophenyl-*m*-toluidine with zinc dust and ammonium chloride (Morgan and Jones, Chem. Soc. Trans. 1921, 119, 191). Pink needles, m.p. 109.5°.

Diazoimine; silky pink needles, m.p. 119°-120° (M. and J.).

3 (or 2)-Nitro-2 (or 3)-amino-4-methylaminotoluene; in small yield by reducing 2:3(γ)-dinitromethyl-*p*-toluidine with ammonium sulphide (Pinnow, J. pr. Chem. 1900, (2) 62, 516). Nearly black prisms, m.p. 127°-128°.

3:5-Toluylenediamine; by reducing 3:5-dinitrotoluene (Städell, Ann. 1883, 217, 200) or 2:4-dibromo-3:5-dinitrotoluene (Davis, Chem. Soc. Trans. 1902, 81, 873). Liquid, b.p. 283°-285° (S.); syrupy liquid (D.). B²HCl, white needles, m.p. 255°-260° (decomp.).

Diacetyl-derivative; pike-shaped hemimorphic prisms, m.p. 235°-236°, which become strongly electrical when dry (D.).

2-Chloro-3:5-toluylenediamine; by reducing 2-chloro-3:5-dinitrotoluene with stannous chloride and hydrochloric acid (Nietzki and Rehe, Ber. 1892, 25, 3006). Long needles, m.p. 73° (N. and R.) or 74° (Morgan, Chem. Soc. Trans. 1902, 81, 97).

2:4-Dinitro-3:5-toluylenediamine; by heating an alcoholic solution of 2:4-dinitro-3:5-dibromotoluene with ammonia in a sealed tube at 150° (Blankama, Rec. trav. chim. 1904, 23, 125). Yellow crystals, m.p. 199°.

Trinitro-3:5-toluylenediamine; by the action of alcoholic ammonia on 3:5-dibromo-trinitrotoluene at 100° (Palmer, Ber. 1898, 31, 3501). Small yellow prisms, m.p. 232°.

2:4-Dinitro-3:5-dimethylaminotoluene; from 2:4-dinitro-3:5-dibromotoluene and dimethylamine (Blankama). Bright red crystals, m.p. 140°. On nitration it yields 2:4:6-trinitrodimethylaminotoluene; colourless crystals, m.p. 199°-200° (decomp.) (B.).

2:4-Dinitro-3:5-diphenylaminotoluene; similarly to the preceding dimethyl-compound using aniline (B.). Red crystals, m.p. 165°.

2:4:6-Trinitro-3:5-dimethylaminotoluene; red crystals, m.p. 156°. On treatment with nitric acid (1:52) it yields 2:4:4-trinitrodimethylaminotoluene (B.).

2:4:6-Trinitro-3:5-diphenylaminotoluene; red crystals, m.p. 206° (B.).

4-Chloro-3:5-toluylenediamine 1-sulphonic acid; by reducing 3:5-dinitro-4-chlorobenzyl-sulphonic acid with iron and acetic acid (B. A. S. F., D. R. P. 134988 of 1901). White needles. An aqueous solution on treatment with ferric chloride gives a red colour which gradually changes through violet to blue.

6-Aminodiacyl-3:4-toluylenediamine; by nitration and reduction of diacyl-3:4-toluylenediamine (Maron and Salzberg, Ber. 1911, 44, 2999). M.p. 238°.

Triacyl-derivative; m.p. 273°-274° (M. and S.).

5-Aminodiacyl-2:4-toluylenediamine; by nitration and reduction of diacyl-2:4-toluylenediamine (Maron and Salzberg, *l.c.*; Kym and Ringer, *ibid.* 1915, 48, 1671). M.p. 252°-253°.

Triacyl-derivative (M. and S.; K. and R.).

2-Acetyl-amino-3:5-toluylenediamine; from 3:5-dinitroaceto-o-toluidide and reducing agents, such as iron and acetic acid or mineral acids (Bayer & Co., U.S. Pat. 742845 of 1903; D. R. P. 183843 of 1902). Yellow needles, m.p. 210°-211°.

Triaminotoluene; by reducing trinitrotoluene with iron and dilute hydrochloric acid at 60°-80°. It serves as an intermediate product, as a dye for cotton, silk and wool, and as a photographic developer (Bielous, Eng. Pats. 137529, 166934 of 1920).

ALDEHYDE DERIVATIVES.

Tolualdehydes are obtained from *o*-, *m*-, and *p*-xylene by passing the vapour mixed with air over a metallic oxide, other than vanadium oxide, of the fifth or sixth periodic group at 300° to a dull red heat, the period of contact being about 0.3 second (The Barrett Co., Eng. Pat. 189107).

o-Tolualdehyde, *o*-toluic aldehyde; by boiling *o*-chloro-*o*-xylene with lead nitrate solution (Lauth and Grimaux, Bull. Soc. chim. 1867, (2) 7, 233; Rayman, *ibid.* 1877, (2) 27, 498); by oxidation of *o*-xylene with chromyl chloride (Bornemann, Ber. 1884, 17, 1467), or with manganese dioxide and sulphuric acid (Fournier, Compt. rend. 1901, 133, 635), or of *o*-tolylcarbinol with potassium dichromate and sulphuric acid (Fournier, *ibid.* 1903, 137, 718). Liquid, b.p. 90°/20 mm., or 197°/atm. (F.). *Anti*-oxime, m.p. 48°-49°, obtained in the usual manner (Dollfus, Ber. 1892, 25, 1922) or together with *p*-tolualdoxime and the nitrile by treating toluene with mercury fulminate and aluminium chloride containing small quantities of the hydrated chloride and aluminium hydroxide. The oximes are primarily obtained in the syn-form, but on separating from the nitrile, alkalis are used and the anti-forms are produced (Scholl and Kaber, Ber. 1903, 36, 322); *semicarbazone*, small white needles, m.p. 196° (Law and Perkin, Trans. Faraday Soc. 1904, 1) or 209° (Fournier); *phenylbenzylhydrazone*, m.p. 87° (Fournier); *diphenylhydrazone*, white needles, m.p. 103°-104° (Maurenbrecher, Ber. 1906, 39, 3583; Rorive and Tollens, *ibid.* 1907, 40, 3107); *5-dimethylamino-derivative*, from dimethyl-*m*-toluidine and formaldehyde, leaflets, m.p. 67° (Geigy & Co., D. R. P. 105103 of 1898).

p-Chloro-*o*-tolualdehyde; by chlorinating 4-keto-1-methyl-1-dichloromethylidihydrobenzene

with phosphorus pentachloride and heating the crude product with water at 160°-180° (Auwers and Keil, Ber. 1905, 38, 1693). Oil, b.p. 228°, solidifying to colourless crystals; D_{17}^{20} 1.277.

Semicarbazone; colourless needles, m.p. 224° (A. and K.).

m-Tolualdehyde; by boiling *o*-chloro-*m*-xylene with lead nitrate solution (Gundelach, Bull. Soc. chim. 1876, (2) 26, 44; Müller, Ber. 1887, 20, 1213; cf. Lauth and Grimaux, *l.c.*); by treating *m*-xylene with chromyl chloride (Étard, Ber. 1881, 14, 848; Ann. Chim. 1881, (5) 22, 218; Bornemann, Ber. 1884, 17, 1464); together with 3:3'-dimethyldibenzyl by oxidising *m*-xylene with potassium persulphate (Moritz and Wolfenstein, Ber. 1899, 32, 2533); by oxidising *m*-xylyl alcohol with potassium dichromate and dilute sulphuric acid (Sommer, Ber. 1900, 33, 1078). Liquid, with an almond odour, b.p. 199°; D_0^{20} 1.037; D_{20}^{20} 1.024. It forms an *anilide*, b.p. 313°-314°; *semicarbazone*, needles, m.p. 216° (Sommer); *phenylhydrazone*, prisms, m.p. 91° (B.) or 88° (Rudolph, Ann. 1888, 248, 100); *diphenylhydrazone*, light yellow plates, m.p. 74°-75° (Maurenbrecher; Rorive and Tollens). For condensation products with ammonia and ethyl cyanoacetate, see Guarschi (Atti R. Accad. Sci. Torino, 1901-02, 37, 593).

2-Nitro-*m*-tolualdehyde; together with the 4-nitro-isomeride by nitrating *m*-tolualdehyde (Mayer, Ber. 1914, 47, 406; cf. Gilliard, Monnet and Cartier, Eng. Pat. 25634 of 1898; U.S. Pats. 662074, 662075; D. R. P. 113604 of 1898). The isomerides are separated by fractionation *in vacuo*. The product obtained by Bornemann (Ber. 1884, 17, 1473) and M. L. B. (Eng. Pat. 3216 of 1882; U.S. Pats. 276889, 276890; Fr. Pat. 149935; D. R. P. 21683 of 1882) is a mixture of the isomerides. Crystals, m.p. 64° (G., M. and C.; M.) or 61° (Reissert and Scherk, Ber. 1898, 31, 392); b.p. 135°-145°/2 mm. With acetone it yields the greenish-blue dimethylindigotin. *Ammonia-derivative*, m.p. 93°; *anilide*, m.p. 79°; *oxime*, m.p. 134°-135°; *phenylhydrazone*, m.p. 131°-132°; *hydrobenzamide*, m.p. 93°.

4-Nitro-*m*-tolualdehyde (see above). Yellow needles, m.p. 44°. With acetone it yields the reddish-blue dimethyl-indigotin. *Ammonia-derivative*; m.p. 140°; *anilide*, m.p. 51°-5°; *oxime*, m.p. 104°-105°; *phenylhydrazone*, m.p. 141°-142°; *hydrobenzamide*, m.p. 140° (G., M. and C.).

Dinitro-*m*-tolualdehyde; long silky needles, m.p. 110°-112° (Bornemann).

2-Iodo-*m*-tolualdehyde; m.p. 55°-56° (Mayer, Ber. 1914, 47, 406).

4-Iodo-*m*-tolualdehyde; m.p. 83°-84° (M.).

6-Amino-*m*-tolualdehyde; by heating 4-nitro-*m*-xylene with a solution of sulphur in sodium hydroxide (Geigy & Co., D. R. P. 87255 of 1895; see also Böhringer, D. R. P. 108026 of 1898). Sinters above 90° and melts at 99°-101° (B.) or 92° (G.).

4-Chloro-*derivative*; yellow crystals, m.p. 153° (Geigy & Co., D. R. P. 105103 of 1898).

6-Methylamino-*m*-tolualdehyde; colourless leaflets or needles, m.p. 114° (Geigy & Co., Fr. Pat. 280514; D. R. P. 103578 of 1898); 4-chloro-*derivative*, yellowish needles, m.p. 157° (Geigy & Co., D. R. P. 105103 of 1898); the

p-dimethylaminoanilide, yellowish-green prisms, melts at 162° and the phenylhydrazone at 124° (Ullmann and Frey, Ber. 1904, 37, 863).

6-Ethylamino-*m*-tolualdehyde, needles or pale yellow prisms, m.p. 70°; 4-chloro-derivative, yellowish needles, m.p. 78°–79° (Geigy & Co.); oxime, m.p. 82°; phenylhydrazone, m.p. 95° (U. and F.; G.).

m-Tolualdehyde *o*-sulphonic acid; by sulphonation of *m*-tolualdehyde at low temperatures. With aromatic amines it yields dyes fast to alkalis (Fr. Pat. 311739 of 1901).

p-Tolualdehyde; by heating a mixture of calcium *p*-toluate and calcium formate (Cannizzaro, Ann. 1882, 124, 254); by oxidising *p*-xylene with chromyl chloride (Bornemann, Ber. 1884, 17, 1467); by the action of hydrocyanic acid and hydrochloric acid on toluene in presence of aluminium chloride (Bayer & Co., Eng. Pat. 19204 of 1897; Fr. Pat. 270334; D. R. P. 99568 of 1897); by passing a mixture of carbon monoxide and hydrogen chloride through toluene in presence of aluminium chloride and cuprous chloride (Gattermann and Kock, Ber. 1897, 30, 1623; Bayer & Co., Eng. Pat. 13709 of 1897; Fr. Pat. 268168; D. R. P. 98706 of 1897; cf. Reformatzki, J. Russ. Phys. Chem. Soc. 1901, 33, 157); by the action of boiling dilute sulphuric acid on *p*-methylbenzylazoisimide (Curtius and Darapsky, Ber. 1902, 35, 3229); together with a little *p*-toluic acid by electrolytic oxidation of a warm solution of *p*-xylene with an excess of current at a lead peroxide anode (Fichter and Grisard, Helv. Chim. Acta. 1921, 4, 928); by heating *p*-tolylglyoxylic acid with aniline and hydrolysing the product (Bouveault, Bull. Soc. chim. 1897, (3) 17, 367); by the action of nickel carbonyl on toluene in presence of aluminium chloride (Dewar and Jones, Chem. Soc. Trans. 1904, 85, 212) and by other methods (Fournier, Compt. rend. 1903, 136, 557; Bodroux, Compt. rend. 1904, 138, 92; Bull. Soc. chim. 1904, (3) 31, 586). Oil with a peppery odour, b.p. 204° (G.); D_{20}^{15} 1.072; n_D^{14} 1.5484 (Hanzlik and Bianchi, Ber. 1899, 32, 1286).

p-Tolualdehyde ammonia; m.p. 43°–44° (Francis, Ber. 1909, 42, 2216); hydro-*p*-toluamide, white needles, m.p. 92° (Gattermann, Ann. 1906, 347, 347); bisulphite-compound, scales; semicarbazone, m.p. 215° (Fournier); diacetate colourless glistening leaflets, m.p. 69°, forming a leuco-malachite Green with dimethyl-aniline and zinc chloride (Claussner, Ber. 1905, 38, 2860); phenylhydrazone, yellow compound, m.p. 113°, coloured red by exposure to light (Law and Perkin, Trans. Faraday Soc. 1904, 1); phenylbenzylhydrazone, m.p. 140° (Fournier, Compt. rend. 1903, 137, 716); diphenylhydrazone, white needles, m.p. 83°–84° (Maurenbrecher, l.c.; Rorive and Tollens, l.c.); anti-oxime, m.p. 79°–80°; syn-oxime, m.p. 108°–110° (Hantzsch, Zeitsch. physikal. Chem. 1904, 13, 523); diaxime peroxide, white shining plates, decomposing with a slight explosion at 121° (Ponzo, Atti R. Accad. Lincei, 1906, [v.] 15, ii. 42, 118; Tschugaeff and Spiro, Ber. 1908, 41, 2219); nitroso-derivatives, silvery needles, m.p. 128° (Gattermann, l.c.).

p-Tolualdehyde when exposed to light in the presence of iodine for 3 years yields *p*-

toluic acid, a trimeric tolualdehyde, thin colourless prismatic crystals, m.p. 215° and *p*-tolyl *p*-toluate, pale yellow oil, b.p. 213°–217°/15 mm. (Muscarelli and Russi, Atti R. Accad. Lincei, 1910, [v.] 19, ii. 239). With ethyl iodide and magnesium it yields *p*-polyethylethylcarbinol, a dimeride of *p*-tolualdehyde, m.p. 130°, and *p*-xylyl alcohol (Oddo, Gazz. chim. ital. 1911, 41, i. 273).

2-Nitro-*p*-tolualdehyde; by nitration of *p*-tolualdehyde with mixed acids below 0° (Hanzlik and Bianchi, Ber. 1899, 32, 1288). Needles, m.p. 43°–44° (H. and B.) or 48°–49° (Gattermann, Ann. 1906, 347, 347). Diacetate, monoclinic tables, m.p. 98°–98.5° (Hanzlik and Bianchi, l.c., 2286); phenylhydrazone, orange crystals, m.p. 112°; *p*-nitrophenylhydrazone, reddish-brown crystalline powder, m.p. 223°–224° (H. and B.).

3-Nitro-*p*-tolualdoxime; needles, m.p. 128° (M. L. B., Fr. Pat. 290643 of 1899; D. R. P. 107095 of 1898).

CARBOXYLIC ACID DERIVATIVES.

o-Toluic acid; by boiling *o*-xylene with dilute nitric acid (1 vol. D 1.4 to 2 vols. water) (Fittig and Bieber, Ann. 1870, 156, 242); by the action of sodium amalgam on a mixture of ethylchloroformate and *o*-iodotoluene, followed by hydrolysis of the ester formed (Kekulé, Ber. 1874, 7, 1007); in a yield of 97 p.c. by boiling phthalide (phthalic aldehyde) with hydriodic acid (b.p. 127°) and yellow phosphorus in an atmosphere of carbon dioxide (Hessert, Ber. 1878, 11, 238; Racine, Ann. 1887, 239, 72); from toluene *o*-sulphonic acid by heating with potassium cyanide and hydrolysing the product (Fittig and Ramsay, Ann. 1873, 168, 246; Zeit. f. Chem. 1871, (2) 7, 584); by boiling the nitrile (Weith, Ber. 1874, 7, 722); from *o*-toluidine via the nitrile (Cahn, Ann. 1887, 240, 280); by heating naphthalene 1:3-disulphonic acid, 1:3-dihydroxynaphthalene, α -naphthol or α -naphthylamine 3-sulphonic acid, β -naphthol or β -naphthylamine 4-sulphonic acid with sodium hydroxide at 150°–300° (Kalle & Co., Eng. Pat. 16559 of 1894; Fr. Pat. 241109; D. R. P. 79028 of 1893; Friedländer and Rüdert, Ber. 1896, 29, 1611). Crystals, readily volatile with steam, m.p. 103.5°–104° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 221); b.p. 258.5°–259°/751 mm. (Serkow, J. Russ. Phys. Chem. Soc. 1893, 25, 633); D_{20}^{14} 1.0621; molecular refractive power 62 (Eykmann, Rec. trav. chim. 1893, 12, 178). Oxidised to phthalic acid with permanganate or dilute nitric acid, whilst it is charred by chromic acid mixture. Bromine vapour above 100° yields phthalide, whilst in the cold bromine forms bromo-*o*-toluic acid, m.p. 167°. It condenses with tertiary aromatic amines to form dyestuffs of the Malachite Green series (Bayer & Co., D. R. P. 101426 of 1897). $\text{NaA} + 2\text{H}_2\text{O}$, glistening leaflets, m.p. 227°–228° (R.); $\text{CaA}_2 + 2\text{H}_2\text{O}$, small needles (F. and B.); $\text{BaA}_2 + 2\text{H}_2\text{O}$, small needles (F. and B.).

Hydroxylamine salt, m.p. 105° (Oesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 2424).

Methyl-ester b.p. 207°–208° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 245) or 213°; D_{20}^{15}

1-073 (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

Ethyl-ester; b.p. 219.5°/713 mm. (Ador and Rilliet, Ber. 1879, 12, 2301) or 227°; D_4^{25} 1.0479,

D_{15}^{15} 1.039, D_{25}^{25} 1.0321; magnetic rotatory power 15-064 at 15.2° (Perkin, Chem. Soc. Trans. 1896, 69, 1238).

Benzyl-ester; oil, b.p. 315°, D_{17}^{17} 1.12 (Hodgkinson, Chem. Soc. Proc. 1891, 7, 167).

Chloride; b.p. 211°/733 mm. (A. and R.), 110°-111°/29 mm. (Klages and Lickroth, Ber. 1899, 32, 1561), 102°/7 mm. (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1311; cf. Frankland and Aston, *ibid.* 1899, 75, 494).

Anhydride; m.p. 36°-38° (Racine, Ann. 1887, 239, 74) or 39° (K. & L.), b.p. above 325° (R.) or 220°-221°/11 mm. (K. and L.).

Peroxide; irregular prisms, m.p. 60° (Vanino and Thiele, Ber. 1896, 29, 1727).

Amide; needles, m.p. 138° (Weith, Ber. 1873, 6, 420), 142.8° (Remsen and Reid, Amer. Chem. J. 1899, 21, 290). *Sodium-derivative* (Wheeler, *ibid.* 1900, 23, 466).

Methylamide; colourless needles, m.p. 75°; *dimethylamide*, b.p. 147°, D_{25}^{25} 1.033 (van S.).

Nitrile; by heating potassium toluene *o*-sulphonate or tri-*o*-tolyl phosphate with potassium cyanide (Heim, Ber. 1883, 16, 1776); by heating tolyl isothiocyanate with copper powder (Weith, Ber. 1873, 6, 419); by the action of heat on tolyl isocyanide (Weith, Ber. 1874, 7, 722); by heating *o*-iodotoluene with silver cyanide at 350° (Merz and Weith, Ber. 1877, 10, 751); by boiling the formyl-derivative of *o*-toluidine with zinc dust (Gasiotowski and Merz, Ber. 1884, 17, 74; 1885, 18, 1004); from *o*-toluidine by Sandmeyer's reaction (Cahn, Ber. 1886, 19, 756); by the action of mercury fulminate on toluene in presence of aluminium chloride (Scholl, Ber. 1903, 36, 10). Liquid, b.p. 203°-204° (W.), or 205.2°; D_4^{25} 1.0061, D_{15}^{15} 0.9975, D_{25}^{25} 0.9912; magnetic rotatory power 12.98 at 15.7° (Perkin, Chem. Soc. Trans. 1896, 69, 1244). On boiling with alcoholic potassium hydroxide it yields the amine and with concentrated hydrochloric acid at 200° it yields *o*-toluic acid. In a well-cooled solution *o*-toluonitrile is converted at a lead peroxide anode into *o*-cyanobenzoic acid. If the cooling is not efficient the nitrile is hydrolysed to *o*-toluic acid which is oxidised to phthalic acid (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). Fuming sulphuric acid at 60°-70° forms *iminodi-o-toluidine*, prisms, m.p. 103° (Kraft and Karstens, Ber. 1892, 25, 455). Concentrated hydriodic acid yields $C_7H_5(CN)2HI$, lemon-yellow crystals, m.p. 135°-140° (decomp.) (Biltz, Ber. 1892, 25, 2540). $(CH_3C_6H_4CN)(Cu_2Cl_2)_2$, white crystals (Rabaut, Bull. Soc. chim. 1898, (3) 19, 787).

Isocyanide; liquid, b.p. 75°/10 mm., 101°/55 mm., 183°-184°/753 mm. (with slight decomp.); D_{24}^{24} 0.968. At 240° it is converted into the nitrile (Nef, Ann. 1892, 270, 309).

3-Chloro-o-toluic acid; by careful addition of sodium nitrite in excess to a hot solution of the amide (Kenner and Witham, Chem. Soc. Trans. 1921, 149, 1458). Long slender needles, m.p. 102°.

Nitrile; from 2-cyano-*m*-toluidine by the

Sandmeyer reaction. Long slender prisms, m.p. 82°-83°, b.p. 143°/38 mm.

Amide; by heating a solution of the nitrile with diluted sulphuric acid at 100°-110° for 1½ hours. Scales, m.p. 167° (K. and W.).

4-Chloro-o-toluic acid; together with 5-chloro-*o*-toluic acid by boiling the corresponding chloroxylylene with nitric acid (D 1.2) (Krüger, Ber. 1885, 18, 1757); together with the 5-acid by passing chlorine through a solution of *o*-toluic acid in glacial acetic acid (Claus and Bayer, Ann. 1893, 274, 308). M.p. 137° (C. and B.), and not 166° as given by Krüger. Its salts are more sparingly soluble than those of the 5-chloro-isomeride. $CaA_2 + 2H_2O$, prisms.

5-Chloro-o-toluic acid; see 4-chloro-*o*-toluic acid. The nitrile is obtained from 5-chloro-*o*-toluidine by the Sandmeyer reaction (Claus and Stapelberg, Ann. 1893, 274, 287). Small needles, m.p. 170° (C. and B.), not 130° as given by Krüger. $KA + H_2O$, needles; $CaA_2 + 3H_2O$, needles; $BaA_2 + 4H_2O$, needles.

Ethyl-ester; oil, b.p. 258° (C. and S.).

Nitrile; long needles, m.p. 67° (C. and S.).

Amide; m.p. 183° (C. and S.).

6-Chloro-o-toluic acid; by boiling 3-chloro-*o*-xylylene with dilute nitric acid (Krüger, Ber. 1885, 18, 1758). Needles, m.p. 154° (Kr.) or 156° (Claus and Bayer). Oxidation with potassium permanganate yields 3-chlorophthalic acid. $CaA_2 + 2H_2O$, long prisms.

3:5-Dichloro-o-toluic acid; from the nitrile which is prepared from 3:5-dichloro-*o*-toluidine by the Sandmeyer reaction (Claus and Stapelberg, Ann. 1893, 274, 292). Glistening needles, m.p. 181°.

Nitrile; needles, m.p. 92° (C. and S.).

A *dichlorotoluic acid* was obtained by Holleman (Ann. 1867, 144, 269) by oxidising crude dichloroxylylene (m.p. 22°) with chromic acid mixture. $CaA_2 + 9H_2O$.

ω-Dichloro-o-toluic acid; needles, m.p. 155°. Its chloride is obtained by chlorinating *o*-toluoyl chloride. The *amide* melts at 117°.

ω-Trichloro-o-toluic acid; obtained by the action of formic acid at 50° on its chloride, which is formed by chlorinating *o*-toluoyl chloride, crystallises from benzene in needles, m.p. 141°-144° (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2213).

4-Bromo-o-toluic acid; by keeping *o*-toluic acid in contact with excess of bromine for 24 hours (Jacobsen and Wieras, Ber. 1883, 16, 1956; Racine, Ann. 1887, 239, 74); from 2-nitro-*p*-toluidine by replacing the amino-group by bromine and the nitro-group by carboxyl (von Meyer and Geiringer, Ber. 1895, 28, 187). Long needles, volatile with steam, m.p. 167°. $CaA_2 + H_2O$; $BaA_2 + 5H_2O$.

Methyl-ester; leaflets, m.p. 44°-48° (R.).

A *bromo-o-toluic acid*, slender needles, m.p. 118°, whose *nitrile* melts at 42°, has been obtained by oxidising bromo-ethoxylylene with dilute nitric acid at 200° (Claus and Fieser, Ber. 1886, 19, 3083; Claus and Kunath, J. pr. Chem. 1889, (2) 39, 489). This acid is not identical with that of Jacobsen (Ber. 1884, 17, 2375), obtained by oxidising bromo-*o*-xylylene with dilute nitric acid. Jacobsen's product forms stellate groups of silky needles, m.p. 174°-176°, yielding $BaA_2 + 2H_2O$, small hard prisms, and is probably identical with the following acid.

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5-Bromo-o-toluic acid; by saponification of the nitrile (Nourrisson, Ber. 1887, 20, 1016). Sublimes in needles, m.p. 187° (N.) or 175° (Konowaloff, J. Russ. Phys. Chem. Soc. 1904, 36, 537). $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (C. and K.).

Amide; pearly plates subliming in needles, m.p. 181°–182°.

Nitrile; long needles, volatile with steam, n.p. 70° (N.).

3:5-Dibromo-o-toluic acid; by hydrolysis of the amide with concentrated hydrochloric acid at 250° (Claus and Beck, Ann. 1892, 269, 215). Needles, m.p. 157°. $\text{BaA}'_2 + \text{H}_2\text{O}$, crystalline crusts.

Amide; glistening needles or columns, m.p. 198°.

Nitrile; from 3:5-dibromo-o-toluidine by Sandmeyer's reaction. Glistening needles, m.p. 86° (C. and B.).

4:5-Dibromo-o-toluic acid; by heating 5-bromo-o-toluic acid with 1 mol. of bromine in the presence of water at 120° for 3 hours (Claus and Beck, Ann. 1892, 269, 213). Glistening needles, m.p. 210°. $\text{BaA}'_2 + \text{CH}_2\text{O}$, glistening needles.

When nitrated at 0°, o-toluic acid yields a mixture of 4-nitro-o-toluic acid, m.p. 178°–178.5°, and 6-nitro-o-toluic acid, m.p. 184°–184.5°, the latter being probably identical with Jacobsen and Wiers's β -nitro-acid, m.p. 145°. The methyl-ester, amide, methyllamide, and dimethylamide of o-toluic acid yield the corresponding derivatives of the 4- and 6-nitro-acids when nitrated at 0°. When nitrated at ordinary temperatures, o-toluic acid and its 4- and 6-mononitro-derivatives yield 4:6-dinitro-o-toluic acid. The methyl-ester under similar conditions yields methyl-4:6-dinitro-o-toluate, m.p. 73°–73.5°. The amide and methyllamide yield the 4:6-dinitro-acid, but the dimethylamide yields the 4-nitro-acid (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

3-Nitro-o-toluic acid; from 3-nitro-o-toluidine via the nitrile (Mayer, J. pr. Chem. 1915, (2) 92, 137) or the amide (Gabriel and Thieme, Ber. 1919, 52, 1079). The latter authors could not prepare it by hydrolysis of the nitrile. Colourless needles, or short rods, m.p. 151°–152° (G. and T.), or colourless silky needles, m.p. between 200°–210° (M.). It sublimes, and it is stated to undergo certain physical changes when exposed to air for a few days, e.g. it becomes less soluble in water, and melts at about 180°–185° (M.).

$\text{NaA}' + 3\frac{1}{2}\text{H}_2\text{O}$; $\text{BaA}'_2 + 3\text{H}_2\text{O}$ (G. and T.).

Amide; by the action of sulphuric acid on the nitrile. Needles, m.p. 158° (G. and T.).

Nitrile; from the amine by the Sandmeyer reaction and treatment of the crude product with alcohol or nitric acid. Silvery leaflets, m.p. 109°–110° (G. and T.), or yellow silky needles on subliming, m.p. 89°–91° (M.).

Methyl-ester; by the action of methyl sulphate. M.p. 72°–75° (M.), or from the acid chloride (m.p. 41°) by the action of methyl alcohol, when needles and leaflets, m.p. 50° are formed (G. and T.). **Ethyl-ester**, oil (G. and T.).

Anhydride; six-sided plates, m.p. 174° (G. and T.).

(a) **4-Nitro-o-toluic acid**; together with the 6-nitro-acid by warming o-toluic acid with nitric acid (D 1.4) at 100° (Jacobsen and Wiers,

Ber. 1883, 16, 1957); together with the 5-nitro-acid by oxidising 4-nitro-o-xylene with dilute nitric acid (Jacobsen, Ber. 1884, 17, 182). Small needles, slowly volatile with steam, m.p. 179°. $\text{KA}' + \text{H}_2\text{O}$, long needles; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, slender needles.

Nitrile; by nitration of o-toluenitrile, needles, m.p. 105°, subliming at 100° (Landsberger, Ber. 1898, 31, 2880).

Amide; by warming the nitrile for $\frac{1}{2}$ hour with six times its weight of concentrated sulphuric acid, fine needles, m.p. 173° (L.); **methyllamide**, slender needles, m.p. 160°; **dimethylamide**, m.p. 105°–106° (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149).

Methyl-ester; oblong prisms, m.p. 69°.

Chloride; colourless needles, m.p. 59°–60° (van S.).

(γ) **5-Nitro-o-toluic acid**; together with the 4-acid by boiling a mixture of 25 grms. of 4-nitro-o-xylene, 250 c.c. of nitric acid (D 1.4) and 500 c.c. of water for 48 hours. The mixture is converted into the barium salts, which are separated mechanically (Jacobsen, Ber. 1884, 17, 162); from 5-nitro-o-toluidine via the nitrile (Mayer, l.c.; Gabriel and Thieme, l.c.). It melts at 152°–153° (G. and T.). $\text{BaA}'_2 + 5\text{H}_2\text{O}$, long transparent flat prisms (J.).

Nitrile; colourless leaflets, m.p. 100° (G. and T.), or long yellow felted needles, which sublime, m.p. 113°–115° (M.).

(β) **6-Nitro-o-toluic acid**; see the 4-nitro-acid, and van Scherpenzeel, l.c. Long needles, m.p. 145° (J. and W.), or 184°–184.5° (van S.). Slowly volatile with steam. $\text{CaA}'_2 + 2\text{H}_2\text{O}$, crusts; $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (J. and W.).

Methyl-ester; pale yellow needles, m.p. 86° (van S.).

Amide; colourless needles, m.p. 163°; **methyllamide**, m.p. 131°–132°; **dimethylamide**, m.p. 69.5°–70° (van S.).

Chloride; m.p. 68°–68.5° (van S.).

Nitrile, m.p. 69.5° (Nölting, Ber. 1904, 37, 1025).

3:4-Dinitro-o-toluic acid; together with 3:4-dinitrophthalic acid by oxidising 3:4-dinitro-o-xylene with dilute nitric acid in a sealed tube (Warner, Chem. Soc. Proc. 1913, 29, 61). Stout colourless needles, m.p. 182°.

Ethyl-ester; colourless rectangular plates, m.p. 63° (W.).

4:6-Dinitro-o-toluic acid; together with 3:5-dinitrophthalic acid by oxidising 3:5-dinitro-o-xylene in a similar manner (Warner); by keeping 4- or 6-nitro-o-toluic acid with a mixture of equal volumes of sulphuric acid and fuming nitric acid for 24 hours (Jacobsen and Wiers). Very long brittle needles, m.p. 206°. With dilute nitric acid at 170° it yields 3:5-dinitrophthalic acid. $\text{BaA}'_2 + 2\text{H}_2\text{O}$ (Racine, Ann. 1887, 239, 77).

Methyl-ester; needles, m.p. 73°–75° (R.).

3:4:6 (or 3:5:6)-Trinitro-o-toluic acid; by oxidising 3:4:6-trinitro-o-xylene with chromic acid (Gius, Gazz. chim. ital. 1922, 52, i. 183). White needles, m.p. 201°–202°. It gives a reddish-brown coloration with alkalis.

α -**Chloro-5-nitro-o-toluic acid**; amide; by warming the nitrile for 2 hours with concentrated sulphuric acid (Gabriel and Landsberger, Ber. 1898, 31, 2734). White felted needles, melting at 228° when heated rapidly. When heated

for some time at 110° it yields 5-nitro-pseudo-phthalimidine, needles, m.p. 158°.

Nitrile; by nitration of *o*-cyanobenzyl chloride (G. and L.).

Yellow crystals, m.p. 94°. When heated with acetic and hydrochloric acids at 140°–150° it yields 5-nitrophthalide.

*5-Chloro-3-nitro-*o*-toluic acid*; from 5-chloro-3-nitro-*o*-toluidine via the nitrile (Claus and Stapelberg, Ann. 1893, 274, 297). Glistening needles, m.p. 189°.

Nitrile; golden-yellow glistening prisms, m.p. 140° (C. and S.).

*5-Chloro-4-nitro-*o*-toluic acid*; together with 5-chloro-6-nitro-*o*-toluic acid, by treating 5-chloro-*o*-toluic acid with nitric acid (D 1.52) at 110°–120° (C. and S.). On pouring into water, the 6-nitro-acid gradually separates. Large glistening prisms, m.p. 193°. $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, prisms; $\text{MgA}'_2 + 4\text{H}_2\text{O}$, four-sided pillars. The salts are more sparingly soluble in water than those of the 6-nitro-isomeride.

Nitrile; from 5-chloro-4-nitro-*p*-toluidine. Thick glistening pillars, m.p. 86° (C. and S.).

*5-Chloro-6-nitro-*o*-toluic acid*; see above. Glistening pillars, m.p. 186°. $\text{KA}' + \text{H}_2\text{O}$, crusts; $\text{MgA}'_2 + 5\text{H}_2\text{O}$, glistening needles (C. and S.).

*3:5-Dichloro-6-nitro-*o*-toluic acid*; by oxidising 3:5-dichloro-6-nitro-*o*-xylene with nitric acid (D 1.15) for 6 hours at 180°–190° (Crossley, Chem. Soc. Trans. 1904, 85, 281). Feathery needles, m.p. 187°–189°.

*5-Chloro-4:6-dinitro-*o*-toluic acid*; by prolonged boiling of 5-chloro-*o*-toluic acid, 5-chloro-4-nitro-*o*-toluic acid, or 5-chloro-6-nitro-*o*-toluic acid with mixed acids (C. and S.). Needles, m.p. 212°.

*5-Bromo-3-nitro-*o*-toluic acid*; from the amide by heating with concentrated hydrochloric acid at 230°–250° for 8–10 hours (Claus and Beck, Ann. 1892, 269, 212). Fine needles, m.p. 226°.

Amide; by boiling the nitrile with 50 p.c. sulphuric acid. Vitreous needles, m.p. 235°.

Nitrile; from 5-bromo-3-nitro-*o*-toluidine by Sandmeyer's reaction. Glistening yellow needles, m.p. 106°–107°.

*5-Bromo-4-nitro-*o*-toluic acid*; together with 5-bromo-6-nitro-*o*-toluic acid, by nitrating 5-bromo-*o*-toluic acid for 6–8 hours at 50°. The greater part of the 5-bromo-4-nitro-*o*-toluic acid separates on cooling (C. and B.). Needles, m.p. 200°, which sublime. $\text{NaA}' + 4\text{H}_2\text{O}$, large pearly plates; $\text{KA}' + \text{H}_2\text{O}$, silky needles; $\text{MgA}'_2 + 7\text{H}_2\text{O}$, vitreous needles; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, long needles.

*5-Bromo-6-nitro-*o*-toluic acid*; see above. The two acids may be separated by means of their magnesium salts. Small needles, m.p. 220°, which sublime. The magnesium salt is extremely soluble in water. $\text{BaA}'_2 + \text{H}_2\text{O}$, nodules.

*3-Amino-*o*-toluic acid*; obtained as the hydrochloride, together with 3-methyl-benzisoxazole-3-one and *m*-toluidine hydrochloride, by reducing 3-nitro-*o*-toluamide with tin and hydrochloric acid, or as the free acid by reducing 3-nitro-*o*-toluic acid with ferrous sulphate in ammoniacal solution (Gabriel and Thieme, Ber. 1919, 52, 1079). Needles, m.p. 125°–126°. According to Mayer (J. pr. Chem. 1915, (2) 92, 187), reduction of the acid with tin and hydro-

chloric acid yields initially the amino-acid, but this could not be isolated, as it was converted into *m*-toluidine during evaporation.

Nitrile; by reducing 3-nitro-*o*-toluonitrile with hydriodic acid and phosphorus. It melts at 127°–128° (G. and T.).

*4-Amino-*o*-toluic acid*; small prisms, m.p. 196° (Jacobsen and Wiers, Ber. 1883, 16, 1959; Jacobsen, *ibid.* 1884, 17, 164).

Nitrile; by reducing 4-nitrotoluonitrile. It melts at 88°, its *hydrochloride* at about 220°, and its *picrate* at 177°–179° (Landsberger, Ber. 1898, 31, 2881).

*5-Amino-*o*-toluic acid*; by reducing 5-nitro-*o*-toluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1884, 17, 164); by heating *p*-nitrophthalide with hydriodic acid and phosphorus at 205° (Hönig, Ber. 1885, 18, 3449). Needles which sublime, m.p. 153° (H.) or 165° (decomp.) (J.).

Nitrile; by reducing 5-nitro-*o*-toluonitrile with stannous chloride and hydrochloric acid. Rhombic crystals, m.p. 90° (G. and T.).

*6-Amino-*o*-toluic acid*; small vitreous needles, m.p. 191° (Jacobsen; Jacobsen and Wiers).

Nitrile; silky needles, m.p. 95.5° (Nörling, Ber. 1904, 37, 1025).

m-Toluic acid; by reducing bromo-*m*-toluic acid (Ahrens, Zeit. f. Chem. 1869, (2) 5, 106; Richter, Ber. 1872, 5, 424; Böttiger and Ramsay, Ann. 1873, 168, 255); by oxidising *m*-xylene with dilute nitric acid (Tawildarow, Ber. 1873, 4, 410; Brückner, Ber. 1876, 9, 406; Reuter, Ber. 1884, 17, 2028); by hydrolysing the nitrile (Weith and Landolt, Ber. 1875, 8, 720) or the 6-sulphonamide (Jacobsen, Ber. 1881, 14, 2349); by boiling ω -chloroxyline with dilute nitric acid (Senff, Ann. 1883, 220, 247; cf. Ador and Rilliet, Ber. 1879, 12, 2300; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149). Very long needles, volatile with steam, m.p. 110.5° (Jacobsen; Bornemann, Ber. 1887, 20, 1382) or 108°–109° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 221), b.p. 263° (J.); D_{20}^{1116} 1.0543; molecular refractive power 62.01 (Eykmann, Rec. trav. chim. 1893, 12, 178). $\text{CaA}'_2 + 3\text{H}_2\text{O}$, flat needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, small plates; AgA' ; $(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{HK}$, long needles; $(\text{CH}_3\text{C}_6\text{H}_4\text{COO})_2\text{H}\cdot\text{NH}_4$, tabular crystals (Farmer, Chem. Soc. Trans. 1903, 83, 1443).

Hydroxylamine salt; m.p. 83° (Oesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 2424).

Methyl-ester; b.p. 214°–215° (Kellas) or b.p. 220.5°–221°/758 mm., D_{15}^{1066} 1.066 (van S.).

Ethyl-ester; b.p. 224.5°–226.5°/710 mm. (Ador and Rilliet).

Chloride; b.p. 218°/724 mm. (A. and R.), 120°/38 mm. (Klages and Lickroth, Ber. 1899, 32, 1560), 109°/8 mm. (Frankland and Wharton, Chem. Soc. Trans. 1898, 69, 1311), 109°/15 mm. (Frankland and Aston, *ibid.* 1899, 75, 494), 219°–220°/773 mm. (van S.); m.p. –23° (van S.); D_{20}^{1017} 1.173 (K. and L.).

Amide, m.p. 94° (Remsen and Reid, Amer. Chem. J. 1899, 21, 290; van S.); *methylamide*, m.p. 44.5°–45° (van S.); *dimethylamide*, oil, b.p. 148°, D_{15}^{1043} 1.043 (van S.).

Nitrile; from *m*-toluidine by the Sandmeyer

reaction (Buchka and Schachtebeck, Ber. 1899, 22, 841). Liquid, b.p. 208°-210° (B. and S.) or 212°-214° (Biltz, Ber. 1892, 25, 2539). See also Weith and Landolt (l.c.).

Mercaptan; b.p. 195.4°/760 mm., D₄²⁰ 1.06251 (Bourgeois, Rec. trav. chim. 1899, 18, 426).

Anhydride; m.p. 71°, b.p. 230°/17 mm. (Denham, Chem. Soc. Trans. 1909, 95, 1240).

Pseudo-m-toluic acid; m.p. 47° (Perkin and Simonis, *ibid.* 1907, 91, 840).

4-Chloro-m-toluic acid; by oxidising 3-acetyl-*p*-chlorotoluene (Claus, J. pr. Chem. 1892, (2) 46, 27). Needles, m.p. 167°.

5-Chloro-m-toluic acid; together with a chloronitroxyline and other products by boiling dihydro-5-chloroxyline with 30 p.c. nitric acid for 20 hours (Klages and Knoevenagel, Ber. 1895, 28, 2045). Needles, m.p. 178°. With potassium permanganate it yields 5-chloroisophthalic acid and a little 5-hydroxyisophthalic acid.

6-Chloro-m-toluic acid; by replacing the nitro-group by chlorine in 6-nitro-*m*-toluic acid (Beilstein and Kreisler, Ann. 1867, 144, 182; Remsen and Kuhara, Amer. Chem. J. 1881, 3, 431); by oxidising 4-chloro-*m*-xylene with chromic acid mixture (Vollrath, Ann. 1867, 144, 266; Bull. Soc. chim. 1867, (2) 7, 342; Jacobsen, Ber. 1885, 18, 1761). M.p. 203° (V.), 204° (corr.) (R. and K.), 210° (corr.) (J.). CaA' + 3H₂O, fine needles; BaA' + 3H₂O (V.).

Ethyl-ester; b.p. 260°-265° (V.).

ω-Chloro-m-toluic acid; by boiling the nitrile with concentrated hydrochloric acid (Reinglass, Ber. 1881, 24, 2418). Fine needles, m.p. 135°.

Amide; m.p. 124°.

Nitrile; by chlorination of *m*-toluonitrile at 150°. Plates or prisms, m.p. 67°, b.p. 258°-260° (R.).

4:6-Dichloro-m-toluic acid; by heating 1 part of 4:6-dichloro-*m*-xylene with 15 parts of dilute nitric acid (D 1-18) (Claus and Burstert, J. pr. Chem. 1890, (2) 41, 557; cf. Hollemann, Ann. 1867, 144, 269). Vitreous needles, m.p. 170°. BaA' + 2H₂O, needles or pillars. Hollemann's product melted at 161° and yielded CaA' + 9H₂O and AgA'.

ω-Dichloro-m-toluic acid; m.p. 132°, is formed from its chloride, m.p. 49°.

ω-Trichloro-m-toluic acid: obtained from its chloride, which is formed by chlorinating *m*-toluoyl chloride (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2214). Sparkling laminae, m.p. 142°.

4-Bromo-m-toluic acid; together with the 3-bromo-isomeride by keeping a mixture of *m*-toluic acid and an excess of bromine (Jacobsen, Ber. 1884, 14, 2351); by heating 4-bromoisoxymene with dilute nitric acid at 130°-135° (Kelbe and Czarnowski, Ann. 1886, 235, 295); from 4-bromo-2-nitro-toluene by heating with alcohol and potassium cyanide at 220°, and hydrolysing the nitrile with alcoholic potassium hydroxide (Richter, Ber. 1872, 5, 425); by oxidising 3-acetyl-4-bromotoluene with permanganate (Claus, J. pr. Chem. 1892, (2) 46, 21). Slender needles, m.p. 152°-153° (K. and C.). Alkaline fusion yields 4-hydroxy-*m*-toluic acid, and oxidation yields 4-bromoisophthalic acid.

CaA', long needles (J.); BaA' + 4H₂O, needles (C.).

6-Bromo-m-toluic acid; by oxidising bromo-*m*-xylene with chromic acid mixture (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 32; Jacobsen, Ber. 1881, 14, 2352); together with the 4-acid by brominating *m*-toluic acid (Jacobsen); by oxidising 6-bromoisoxymene with dilute nitric acid (Kelbe, Ber. 1882, 15, 41); from 6-nitro-*m*-toluic acid (Remsen and Kuhara, l.c.). Crystalline powder, m.p. 209° (Jacobsen). Sodium amalgam yields *m*-toluic acid, and alkaline fusion yields 6-hydroxy-*m*-toluic acid. CaA' + 3H₂O, needles; BaA' + 4H₂O, long needles; AgA'.

Ethyl-ester; solidifies at -5°, b.p. 270°-275° (F., A. and M.).

Bromo-m(?) -toluic acid; together with 6-bromo-*m*-toluic acid by oxidising crude bromo-*m*-xylene (b.p. 200°-208°) with chromic acid mixture (Ahrens, Zeit. f. Chem. 1869, (2) 5, 106), m.p. 185°-190°. CaA' + 8H₂O, small needles, more soluble in water than the salt of 6-bromo-*m*-toluic acid.

Dibromo(?) -toluic acid; by oxidising crude dibromoxyline with chromic acid mixture (F., A. and M.). Microscopic needles, m.p. 185°-186°. BaA' + 9H₂O, long needles; AgA'.

ω-Bromo-m-toluic acid; by brominating *m*-toluic acid in bromoform (Zalkind and Semenow, J. Russ. Phys. Chem. Soc. 1914, 46, 512). White crystals, m.p. 151°-152°.

Ethyl-ester; b.p. 160°-161°/10 mm.

4:6-Dibromo-m-toluic acid; by oxidising 4:6-dibromo-*m*-xylene with nitric acid (Eckert and Seidel, J. pr. Chem. 1921, (2) 102, 338). White crystals, m.p. 174°.

Methyl-ester; m.p. 43°, b.p. 203°-206°/758 mm.

Amide; white needles, m.p. 188°.

2-Nitroso-m-toluic acid; grey prisms, m.p. 172°-173° (Freundler, Bull. Soc. chim. 1911, [4] 9, 657).

2-Nitro-m-toluic acid; together with 4-nitro-*m*-toluic acid (Jacobsen, Ber. 1881, 14, 2347; Findelee, *ibid.* 1905, 38, 3553; Jürgens, *ibid.* 1907, 40, 4409; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; Wheeler and Hoffman, Amer. Chem. J. 1910, 44, 113, 507) and the 6-nitro-acid (Müller, Ber. 1909, 42, 430) when *m*-toluic acid is nitrated. The 2-nitro-acid is formed also by boiling 2-nitro-*m*-xylene with nitric acid (D 1-4) (Nölting and Gachot, Ber. 1906, 39, 73). Monoclinic prisms, m.p. 219° (Jacobsen; Findelee; Müller; Jürgens), 217.5°-218° (Nölting and Gachot).

The 2- and 4-nitrotoluic acids may be separated by means of their barium salts. BaA' + 2H₂O. This acid is identical with one of the three acids which Ahrens (Zeit. f. Chem. 1867, (2) 3, 525; 1869, (2) 5, 106) obtained by the action of nitric acid on a mixture of toluic acids.

Amide; m.p. 192° (Jürgens).

Nitrile; needles, m.p. 84° (Gabriel and Thieme, Ber. 1919, 52, 1079; Jürgens; cf. Reissert and Scherk, Ber. 1898, 31, 390).

Methyl-ester; m.p. 74° (Jürgens).

4-Nitro-m-toluic acid; see 2-nitro-*m*-toluic acid. It melts at 182° (Jacobsen) or 134° (F.; M.). The barium salt is sparingly soluble (Jacobsen).

Amide; about flat needles, m.p. 176°-177° (F.).

Methyl-ester; stout needles, m.p. 78°-79° (M.).

A number of derivatives of both 2- and 4-nitro-*m*-toluic acids have been prepared by van Scherpenzeel (Rec. trav. chim. 1901, 20, 149), but are of doubtful orientation.

5-Nitro-m-toluic acid; by warming an acetic acid solution of 5-nitro-*m*-xylene with potassium permanganate on the water-bath (Thöl, Ber. 1885, 18, 359) or by heating with nitric acid (D 1:16) in a sealed tube for 50 hours at 100° (Müller, *ibid.* 1909, 42, 430). Long silky needles, m.p. 170° (M.) or 167° (T.). $\text{BaA}_2 + 4\text{H}_2\text{O}$, groups of microscopic needles (T.).

Nitrile; m.p. 104°-105° (G. and T.).

Amide; small needles, m.p. 164°-165° (G. and T.).

Methyl-ester; tables, m.p. 84°-85° (M.).

6-Nitro-m-toluic acid; by oxidising crude nitroxylenes (Beilstein and Kreusler, Ann. 1867, 144, 168; Kreusler, Zeit. f. Chem. 1866, (2) 2, 320) or nitroisocymene (Kelbe, Ann. 1883, 221, 161); together with the 2- and 4-nitro-acids by nitrating *m*-toluic acid (Müller, *l.c.*).

Crystalline powder, m.p. 211° (B. and K.), 214° (K.), or pointed needles, m.p. 215°-216° (M.). $\text{NH}_4\text{A} + 2\text{H}_2\text{O}$; $\text{MgA}_2 + 7\text{H}_2\text{O}$; $\text{CaA}_2 + 2\text{H}_2\text{O}$ yellow prisms; $\text{BaA}_2 + 4\text{H}_2\text{O}$, fine needles.

Nitrile; m.p. 80° (B. and K.; G. and T.).

Amide; leaflets, m.p. 151° (B. and K.), or prisms, m.p. 190° (Wheeler and Hoffman, Amer. Chem. J. 1910, 44, 113, 507).

Methyl-ester; m.p. 81°-82° (M.) or 72° (Herre, Ber. 1895, 28, 597).

2:4-Dinitro-*m*-toluic acid; m.p. 173°.

Methyl-ester, m.p. 104°-105° (van Scherpenzeel).

Bromonitro-m-toluic acid; by warming bromo-*m*-toluic acid with fuming nitric acid (Fittig, Ahrens and Mattheides, Ann. 1868, 147, 347). Crystals, m.p. 175°-176°. $\text{CaA}_2 + 3\text{H}_2\text{O}$, nodules; $\text{BaA}_2 + 3\text{H}_2\text{O}$, long needles.

2-Amino-m-toluic acid; by reduction of the corresponding nitro-compound (Jacobsen; Findelee; Jürgens, *l.c.*). It melts at 172°.

Acetyl-derivative; glistening needles, m.p. 193°-194° (Miller and Meyer, Ber. 1891, 24, 1909).

Nitrile; m.p. 38° (Gabriel and Thieme).

Amide; m.p. 149° (Gabriel and Thieme; Jürgens).

Methyl-ester; oil with an odour of orange peel (Jürgens).

Ethyl-ester; large transparent prisms, m.p. 71°-72°. *Diethyl-ester*; long slender needles, m.p. 55°-57° (Wheeler and Hoffman).

4-Amino-m-toluic acid; by reduction of the corresponding nitro-compound (Jacobsen; Findelee, *l.c.*). It melts at 132° (Jacobsen), 175° (Findelee), or 172° (P.). B^*HCl , long needles (Panaotović, J. pr. Chem. 1886, (2) 33, 62).

Nitrile; glistening needles and plates, m.p. 60°-61° (Ehrlich, Ber. 1901, 34, 3366).

Amide; monoclinic prisms, m.p. 178° (P.) or 179° (F.).

Anilide; pearly rhombic tables, m.p. 240° (P.).

Acetyl-derivative; fibrous needles, m.p. 193°-194° (von Müller and Ohler, Ber. 1891, 24, 1910).

Methyl-ester, m.p. 62° (P.).

5-Amino-m-toluic acid; in a yield of 50 p.c. by reducing the corresponding nitro-compound with ferrous sulphate and ammonia (Müller, Ber. 1909, 42, 423). Small needles with a pink tint, m.p. 183° (M.).

Nitrile; needles, m.p. 75° (Gabriel and Thieme, Ber. 1919, 52, 1079).

6-Amino-m-toluic acid; by reducing 6-nitro-*m*-toluic acid with tin and hydrochloric acid (Beilstein and Kreusler, Ann. 1867, 144, 177; Kreusler, Zeit. f. Chem. 1866, (2) 2, 320) or with ferrous sulphate and ammonia (Müller). Long needles, m.p. 168°-169°. B^*HCl ; B^*HNO_2 ; $\text{B}^*\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$, long prisms.

Nitrile; long colourless needles, m.p. 95° (Gabriel and Thieme).

Amide; crystals $+ \text{H}_2\text{O}$, which when anhydrous melt at 115° (B. and K.).

Methyl-ester; prisms, m.p. 115° (Herre, Ber. 1895, 28, 598).

Ethyl-ester; colourless needles, m.p. 79° (H.).

ω-Amino-m-toluic acid; by heating *m*-cyanobenzylphthalimide with concentrated hydrochloric acid at 200° (Reinglass, Ber. 1891, 24, 2419). Scales, m.p. 215°-218°. *Platinochloride*, ochre-yellow crystalline precipitate; *aurochloride*; yellow prisms, m.p. 175°-177° (R.).

When *m*-toluic acid is sulphonated a mixture of the 5- and 6-monosulphonic acids is formed, which could not be separated. On alkaline fusion, 5-hydroxy-*m*-toluic acid and 6-hydroxy-*m*-toluic acid respectively are formed (Jacobsen, Ber. 1881, 14, 2355).

p-Toluic acid; by oxidising *p*-xylene (Beilstein and Yessel, Ann. 1866, 137, 302; Kekulé and Dittmar, Ann. 1871, 162, 339; Brückner, Ann. 1880, 205, 113), cymene (Noad, Ann. 1847, 63, 289; Phil. Mag. 1848 (3) 32, 19), or terpenes (Hirzel, Zeit. f. Chem. 1866, (2) 2, 205) with dilute acid; by heating *p*-bromotoluene with ethylchloroformate and sodium amalgam followed by hydrolysis of the product (Wurtz, Compt. rend. 1869, 68, 1293); from *p*-bromotoluene, carbon dioxide and sodium (Kekulé, Ann. 1866, 137, 184); by reducing bromo-*p*-toluic acid with sodium amalgam (Remsen and Morse, Amer. Chem. J. 1880, 1, 138); from the acid chloride, obtained by the action of phosgene on toluene in presence of aluminium chloride (Ador and Crafts, Ber. 1877, 10, 2176); from the amide, obtained by the action of aluminium chloride on a mixture of toluene, carbon disulphide and chloroformamide (Gattermann and Schmidt, Ann. 1888, 244, 51; Ber. 1887, 20, 858); by heating a mixture of toluene and acetic acid at 110° in presence of zinc chloride and phosphorus oxychloride, and treatment of the product with dilute sodium hydroxide (Frey and Horowitz, J. pr. Chem. 1891, (2) 43, 114); together with benzoic acid by fusing toluylbenzoic acid with potassium hydroxide (Friedel and Crafts, Bull. Soc. chim. 1881, (2) 35, 508); by passing gaseous cyanic acid and hydrogen chloride into toluene at 100° in presence of aluminium chloride (Gattermann and Rossolym, Ber. 1890, 23, 1195); by heating dinitro-*p*-tolylmethane at about 180° (Ponzo, Atti R. Acad. Lincei, 1906, [v.] 15, II, 42, 118).

Needles, m.p. 176°-177° (B. and Y.), 177°-

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186
Be
D₄
12

178° (A. and C.), or 180° (Fischli, Ber. 1879, 12, 615), b.p. 264° (Cannizzaro, Ann. 1862, 124, 254) or 274°-275° (F.), volatile with steam. When oxidised with chromic acid it yields terephthalic acid which is formed also when *p*-toluic acid is oxidised in presence of acetone and sulphuric acid at a lead peroxide anode (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). When treated with potassium persulphate it yields dibenzyl-4:4'-dicarboxylic acid (Fischer and Wolfenstein, Ber. 1904, 37, 3215). $\text{NH}_4\text{A}'$, plates (Lossen, Ann. 1897, 298, 72); KA' (B. and Y.); $\text{MgA}'_2 \cdot 3\text{H}_2\text{O}$ (B. and Y.); $\text{CaA}'_2 \cdot 3\text{H}_2\text{O}$, needles (B. and Y.); $\text{BaA}'_2 \cdot 2\text{H}_2\text{O}$, fine needles (Buchka and Irish, Ber. 1887, 20, 1764); CuA'_2 (N.); AgA' (N.); KHA' , large laminæ (Farmer, Chem. Soc. Trans. 1903, 83, 1443); $\text{NH}_4\text{HA}'$, long needles (Farmer).

Hydroxylamine salt; m.p. 128° (Vesper and Ballard, J. Amer. Chem. Soc. 1925, 47, 2424).

Methyl-ester; m.p. 32°; b.p. 217° (Fischli), or m.p. 34°-35° (Kellas, Zeitsch. physikal. Chem. 1897, 24, 245).

Ethyl-ester; liquid, b.p. 228° (N.) or 235.5° (Perkin, Chem. Soc. Trans. 1896, 69, 1238); D_4^{20} 1.0393; D_{15}^{20} 1.0306; D_{25}^{20} 1.024 (P.); magnetic rotatory power at 15° 14.74 (P.).

Chloride; liquid, b.p. 107°/8 mm. (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1311), 102° (or 108°)/15 mm. (Frankland and Aston, *ibid.* 1899, 75, 494), 224°-226°/720 mm. (Ador and Rilliet, Ber. 1879, 12, 2298), 214°-216° (Cahours, Ann. 1858, 108, 316), D 1.175 (C.).

Amide; m.p. 160-8° (Remsen and Reid, Amer. Chem. J. 1890, 21, 290), fine needles or large tables, m.p. 151° (Fischli), 156° (Gattermann and Schmidt, Ann. 1888, 244, 51; Ber. 1887, 20, 120), 158°-159° (Holleman, Rec. trav. chim. 1887, 6, 78; cf. Spica, Ber. 1878, 9, 82; Vollrath, Zeit. f. Chem. 1866, (2) 2, 489); *methylamide*, m.p. 143° (G. and S.), 144°-145.5° (Wheeler, and Atwater, Amer. Chem. J. 1900, 23, 146; van Scherpenzeel, Rec. trav. chim. 1901, 20, 149); *dimethylamide*, m.p. 41°, b.p. 150°/10 mm. (van S.); *ethylamide*, m.p. 90° (G. and S.).

The methyl-ester, amide, and methylamide when nitrated at 0° yield derivatives of the 2-nitro-acid (van S.).

Anhydride; plates, m.p. 95° (Frankland and Wharton, Chem. Soc. Trans. 1899, 75, 344).

Nitrile; by distilling potassium toluene *p*-sulphonate with potassium cyanide (Merz, Zeit. f. Chem. 1868, (2) 4, 33); by heating tri-*p*-tolyl phosphate with potassium cyanide (Heim, Ber. 1883, 16, 1775); by heating *p*-tolyl isocyanate with copper (Welth, Ber. 1873, 6, 421); from *p*-toluidine by the Sandmeyer reaction (Glock, Ber. 1888, 21, 2650; Herb, Ann. 1890, 258, 9); by the action of mercury fulminate on toluene in presence of aluminium chloride (Scholl, Ber. 1903, 36, 10).

Crystals, m.p. 38° (Pinner and Caro, Ber. 1894, 27, 3275), b.p. 217.8° (Spica and Paterno, Ber. 1875, 8, 441; cf. Vollrath, Zeit. f. Chem. 1866, (2) 2, 489) or m.p. 29.5°, b.p. 215° (Krüger, Ber. 1890, 23, 1030), or b.p. 217.8°, D_{20}^{20} 0.9805, D_{15}^{20} 0.9751; magnetic rotatory power at 31° 12.84° (Perkin, Chem. Soc. Trans. 1896, 69,

1244). When reduced with sodium and alcohol a small quantity of *p*-methylbenzylamine is formed, but the greater part is saponified (Bamberger and Lodter, Ber. 1887, 20, 1710), and on hydrogenation with hydrogen at 250° in presence of reduced nickel it yields *p*-methylbenzylamine and di-*p*-methylbenzylamine (Frebault, Compt. rend. 1905, 140, 1036; cf. Sabatier and Senderens, *l.c.* 482). On oxidation at a lead peroxide anode it readily yields *p*-cyanobenzoic acid (Fichter and Grisard, Helv. Chim. Acta, 1921, 4, 928). For its polymeride, see Glock (*l.c.*) and Piepes-Poratyski (Bull. Acad. Sci. Cracow, 1900. Cf. Chem. Soc. Absta. 1900, 78, 648).

Isocyanide; m.p. 21°, b.p. 99°/32 mm., D_{24}^{20} 0.96 (Nef, Ann. 1892, 270, 320; Smith, Amer. Chem. J. 1894, 16, 374).

Mercaptan; b.p. 105°/760 mm. (Bourgeois, Rec. trav. chim. 1899, 18, 426).

2-Chloro-p-toluic acid; by oxidising 2-chlorocymene with dilute nitric acid (Fleischer and Kekulé, Ber. 1873, 6, 1090; Gerichten, *ibid.* 1877, 10, 1249). Large plates, m.p. 194°-196° (199°-201° corr.) (Gerichten, *ibid.* 1878, 11, 366). $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, columns (Claus and Böcker, Ann. 1891, 265, 363); $\text{CaA}'_2 + 3\text{H}_2\text{O}$, nodules; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, needles (G.).

Nitrile; from 2-chloro-*p*-toluidine by the Sandmeyer reaction, small pillars or needles, m.p. 48°-48.5° (Claus and Davidsen, J. pr. Chem. 1889, (2) 39, 498).

Amide; glistening plates (C. and D.).

Ethyl-ester; b.p. 149°-150° (C. and D.).

3-Chloro-p-toluic acid; together with other acids by boiling 1 part of 3-chlorocymene with 15 parts of nitric acid (D 1.24-1.29) (Fileti and Crosa, Gazz. chim. ital. 1886, 16, 290). Needles, m.p. 155°-155.5°.

Salts, see Claus and Davidsen (*l.c.*). $\text{NaA}' + \text{H}_2\text{O}$ crusts; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, prisms; $\text{BaA}'_2 + 5\text{H}_2\text{O}$, prismatic needles; AgA' , silvery plates.

Nitrile; leaflets or flat needles, which sublime, m.p. 61°-62° (C. and D.).

Amide; glistening prismatic needles, m.p. 182° (C. and D.).

ω-Chloro-p-toluic acid; from the nitrile, obtained by passing chlorine into nearly boiling *p*-toluonitrile, by hydrolysis with 25 parts of boiling hydrochloric acid for 1½ hours (Mellinghoff, Ber. 1889, 22, 3208); from *ω*-chloro-*p*-toluoyl chloride by dissolving in 98 p.c. sulphuric acid and maintaining at 0°-5° until the evolution of hydrogen chloride ceases (B. A. S. F., D. R. P. 239311 of 1910). Silky microscopic needles or pillars, m.p. 199° (M.) or 190°-192° (B. A. S. F.).

Amide; thin plates, m.p. 173° (M.). *Nitrile*, rhombic prisms, m.p. 79.5°, b.p. 263° (Fock, Ber. 1889, 22, 3208).

Ethyl-ester; b.p. 260°-280° (Einhorn and Papastavros, Ann. 1900, 310, 205).

2:5-Dichloro-p-toluic acid; from 5-chloro-2-amino-*p*-toluic acid by the diazo-reaction (Claus and Davidsen, Ann. 1891, 265, 346) or from 3-chloro-0-nitro-*p*-toluic acid (Claus and Böcker, *l.c.* 359). Flat needles, m.p. 187°. $\text{BaA}'_2 + 4\text{H}_2\text{O}$, small needles.

2:6-Dichloro-p-toluic acid; from 6-chloro-2-nitro-*p*-toluic acid or 2:6-diamino-*p*-toluic acid (Claus and Böcker; Claus and Beynen,

Ann. 1891, 266, 239). Leaflets, m.p. 186°-188°. $\text{BaA}'_2 + 4\text{H}_2\text{O}$, small needles.

o-Dichloro-*p*-toluic acid, m.p. 151°-158°, has a chloride, m.p. 45°, and an ethyl ester, m.p. 46° (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2212).

o-Trichloro-*p*-toluic acid; prepared from its chloride, which is obtained by chlorinating *p*-toluoyl chloride (Davies and Perkin, Chem. Soc. Trans. 1922, 121, 2214). Minute plates, m.p. 197°.

Tetrachloro-*p*-toluic acid; by oxidising tetrachloro-*p*-xylene with nitric acid and potassium permanganate (Rupp, Ber. 1896, 29, 1628). Needles, m.p. 212°.

2-Bromo-*p*-toluic acid; by oxidising 2-bromocymene (Landolph, Ber. 1872, 5, 268), 2-bromo-*p*-xylene (Jannasch and Dieckmann, Ann. 1874, 171, 83), or bromo-*p*-ethyltoluene (Morse and Remsen, Ber. 1888, 11, 225) with chromic acid mixture; by keeping a mixture of *p*-toluic acid and excess of bromine for 12 hours in the cold (Brückner, Ber. 1876, 9, 407); from 2-bromo-*p*-toluidine via the nitrile (Claus and Kunath, J. pr. Chem. 1889, (2) 39, 487). Thin needles or laminae, m.p. 203°-204°. $\text{CaA}'_2 + 3\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, hair-like needles.

Nitrile; small needles, m.p. 44° (C. and K.). 3-Bromo-*p*-toluic acid; from 3-bromo-*p*-toluidine via the nitrile (C. and K.). Needles, m.p. 140° (C. and K.) or leaflets, m.p. 196°; by oxidation of bromocymene, obtained by the hydrolysis of β -bromocymene sulphonic acid (Kelbe and Koschnitzky, Ber. 1886, 19, 1731). $\text{NaA}' + 3\text{H}_2\text{O}$, needles; $\text{KA}' + 4\text{H}_2\text{O}$, nodules; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, needles; $\text{BaA}'_2 + 6\text{H}_2\text{O}$, small leaflets.

Chloride; needles, m.p. 120° (C. and K.).

Nitrile; needles, m.p. 47° (C. and K.).

Amide; sublimes in needles, m.p. 137° (C. and K.).

o-Bromo-*p*-toluic acid; by the action of bromine on a bromoform solution of *p*-toluic acid (Zalkind, J. Russ. Phys. Chem. Soc. 1914, 46, 508). Plates with a vitreous lustre, m.p. 223° (Z.).

Nitrile; by bromination of *p*-toluonitrile at 200°. Prisms with a pungent odour, m.p. 115°-116° (Banse, Ber. 1894, 27, 2169).

Methyl-ester; vitreous needles, m.p. 53°-53.5°, b.p. 160°-161°/17 mm. (Z.).

2:3-Dibromo-*p*-toluic acid; from 3-bromo-2-nitro-*p*-toluic acid (Claus and Herbabny, Ann. 1891, 265, 375). Needles, m.p. 194°(?)

2:5-Dibromo-*p*-toluic acid; by oxidising 3:6-dibromo-*p*-xylene with chromic acid in presence of acetic acid (Schultz, Ber. 1885, 18, 1762); from 5-bromo-2-amino-*p*-toluic acid (Fileti and Cross, Gazz. chim. ital. 1888, 18, 308). Needles m.p. 195° (S.), 200°-201° (F. and C.).

$\text{NaA}' + 7\frac{1}{2}\text{H}_2\text{O}$, large tables (C. and H.); $\text{CaA}'_2 + 4\text{H}_2\text{O}$, long needles; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, long thin needles.

Ethyl-ester; long needles, m.p. 49°, b.p. about 310° (S.).

Chloride; needles, m.p. 60° (Claus and Herbabny).

2:6-Dibromo-*p*-toluic acid; from 2:6-dibromo-*p*-toluidine via the nitrile (Claus and Seibert, Ann. 1891, 265, 378). Silky needles, m.p. 238°-236°. $\text{NaA}' + \text{H}_2\text{O}$, fine needles; $\text{KA}' + 1\frac{1}{2}\text{H}_2\text{O}$, silvery needles.

Nitrile; large glistening needles, m.p. 49° (C. and H.).

Amide; small needles, m.p. 117° (C. and S.).

Chloride; needles, m.p. 80° (C. and S.).

Ethyl-ester; vitreous needles, m.p. 79°-80° (C. and S.).

3:5-Dibromo-*p*-toluic acid; from 3:5-dibromo-*p*-toluidine via the nitrile (Claus and Herbabny, Ann. 1891, 265, 378). Needles, m.p. 182°.

Nitrile; large silky needles, m.p. 156° (C. and H.).

Amide; leaflets, m.p. 148° (C. and H.).

3-Chloro-6-bromo-*p*-toluic acid; together with 2-chloro-5-bromo-*p*-toluic acid by heating 3-chloro-6-bromocymene with dilute nitric acid (Plancher, Gazz. chim. ital. 1893, 23, ii. 73; cf. Willgerodt and Wolfien, J. pr. Chem. 1889, (2) 39, 409). The mixture is separated by crystallisation from ligroin. Fibrous crystals, m.p. 187°-188° (P.), 186° (W. and W.).

5-Chloro-2-bromo-*p*-toluic acid; from 5-chloro-2-amino-*p*-toluic acid (Claus and Davidson, Ann. 1891, 265, 347). Needles, m.p. 192°-193°. $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, needles.

2-Nitro-*p*-toluic acid; by treating cymene with concentrated nitric acid (Noad, Ann. 1847, 63, 297; cf. Fittica, *ibid.* 1874, 172, 309); by nitrating *p*-toluic acid at 0° (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; cf. Fittig and Ramsay, Ann. 1873, 168, 251).

Large monoclinic prisms, m.p. 189°-190° (Ahrens, Zeit. f. Chem. 1869, (2) 5, 104). Yields 6-amino-3-hydroxy-*p*-toluic acid on electrolysing its solution in sulphuric acid.

$\text{CaA}'_2 + 3\text{H}_2\text{O}$; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, needles (A.); $\text{CuA}'_2 + 7\frac{1}{2}\text{H}_2\text{O}$, blue needles (Noyes, Amer. Chem. J. 1888, 10, 483); $\text{Cu}_2\text{A}'_4(\text{OH})_2$; $\text{Cu}_3\text{A}'_6(\text{OH})_4$ aq. (Noyes, *ibid.* 472).

Nitrile; by nitrating *p*-toluonitrile (Banse, Ber. 1894, 27, 2162). Long yellow needles, which sublime, m.p. 107° (Noyes).

Amide; long needles, m.p. 165°-166° (Fileti and Cairoia, Gazz. chim. ital. 1892, 22, ii. 392); formed also by nitrating *p*-toluamide at 0° (van S.).

Chloride; b.p. 185°/36 mm. (Soderman and Johnson, J. Amer. Chem. Soc. 1925, 47, 1390).

Methyl-ester; crystals (Noad), formed also when methyl-*p*-toluate is nitrated at 0° or 20° (van S.); ethyl-ester, yellow crystals (Noad).

3-Nitro-*p*-toluic acid; by heating the nitrile with hydrochloric acid (D 1-17) for 8-10 hours (Niemientowski and Rozański, Ber. 1888, 21, 2993; Noyes, Amer. Chem. J. 1888, 10, 478); in small yield by oxidising 3-nitro-*p*-xylene with potassium ferricyanide and potassium hydroxide (Noyes).

Long needles or monoclinic pillars which sublime (Nimentowski, Rozański and Haushofer, Ber. 1888, 21, 1904), m.p. 161° (N. and R.), 164°-165° (corr.) (Noyes). When warmed with mixed acids it yields 2:3-and 2:5-dinitro-*p*-toluic acids.

$\text{NaA}' + 6\text{H}_2\text{O}$, large tables (Claus and Joachim, Ann. 1891, 266, 210); $\text{KA}' + 6\text{H}_2\text{O}$, large tables (C. and J.); CaA'_2 , anhydrous (N. and R.) + $2\text{H}_2\text{O}$ (Noyes); $\text{BaA}'_2 + 4\text{H}_2\text{O}$ (N. and R.), + $5\text{H}_2\text{O}$ (Noyes), glistening leaflets; $\text{CuA}'_2 + \text{H}_2\text{O}$, greenish-blue tables; AgA'_2 , needles.

Nitrile; from 3-nitro-*p*-toluidine by the

Sandmeyer reaction (Leuchart, Ber. 1888, 19, 175; Glock, *ibid.* 1888, 21, 2682; Weise, *ibid.* 1889, 22, 2429; Noyes, *l.c.*; Niemcewicz, J. pr. Chem. 1889, (2) 40, 4; Ber. 1888, 21, 1535, 1902). Needles, m.p. 99° (G; W.), 100° (Noyes), 99-8° (Bogert and Hoffman, J. Amer. Chem. Soc. 1905, 27, 1293). It does not form an imino-ether when treated with alcoholic hydrochloric acid (Pinner, Ber. 1890, 23, 2919).

Amide; long hair-like needles, m.p. 152°-153° (N. and R.; cf. Weise, Ber. 1889, 22, 2430).

Chloride; small needles, m.p. 157° (C. and J.). Some nitrotoluic acids of unknown orientation have been described by Ahrens (Zeit. f. Chem. 1869, (2) 5, 103); Fittica (Ber. 1874, 7, 1357); Ann. 1874, 172, 316); Landolph (Ber. 1872, 5, 937).

2:3-Dinitro-*p*-toluic acid; see below. Glistening rhombic prisms, m.p. 249°, more sparingly soluble than the 2:5-acid. With hydrochloric acid at 265° it yields 2:3-dinitrotoluene.

$\text{CaA}'_2 + \text{H}_2\text{O}$ (R.), or $+1\frac{1}{2}\text{H}_2\text{O}$ (C. and J.), long leaflets; $\text{BaA}'_2 + 3\text{H}_2\text{O}$ (C. and J.) or $+4\text{H}_2\text{O}$ (R.).

2:5-Dinitro-*p*-toluic acid; together with the 2:3-acid by treating 3-nitro-*p*-toluic acid with a mixture of 3 parts of sulphuric acid in 3 parts of nitric acid (D 1.51) (Rozafski, Ber. 1889, 22, 2675; Claus and Joachim, Ann. 1891, 266, 211). Fine needles, m.p. 188° (R.), or small glistening pillars, m.p. 194° (C. and J.). Hydrochloric acid at 250° yields 2:5-dinitrotoluene.

$\text{NaA}' + 3\text{H}_2\text{O}$, yellow glistening scales; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, reddish-brown glistening leaflets; $\text{BaA}'_2 + 2\frac{1}{2}\text{H}_2\text{O}$, fine yellow needles, or $+2\text{H}_2\text{O}$ (C. and J.).

2:6-Dinitro-*p*-toluic acid; by nitrating *p*-toluic acid or its methylamide at the ordinary temperature (van Scherpenzeel, Rec. trav. chim. 1901, 20, 149; cf. Brückner, Ber. 1875, 8, 1678); by nitrating 2-nitro-*p*-toluic acid with mixed acids (Cl. and J.); by oxidising 2:6-dinitro-*p*-tolualdehyde with potassium permanganate (Gattermann, Ann. 1906, 347, 347).

Yellow plates which sublime, m.p. 157°-158°. $\text{KA}' + 2\text{H}_2\text{O}$; $\text{CaA}'_2 + 2\text{H}_2\text{O}$, thick red prisms; $\text{BaA}'_2 + 2\text{H}_2\text{O}$, fine needles; AgA' .

3:5-Dinitro-*p*-toluic acid; by heating the corresponding amide with concentrated hydrochloric acid at 220°-230° for 8 hours (Claus and Beysen, Ann. 1891, 266, 226). Slender plates or prisms, m.p. 226°, subliming in needles. $\text{BaA}'_2 + \text{H}_2\text{O}$, yellow pillars.

Amide; by boiling the nitrile with 60 p.c. sulphuric acid. Thin yellow needles, m.p. 255°-257°.

Nitrile; from 3:5-dinitro-*p*-toluidine. Golden-yellow needles, m.p. 103° (C. and B.).

2:3:5-Trinitro-*p*-toluic acid; by oxidising 2:3:5-trinitro-*p*-xylene. Lustrous white lamellae, m.p. 230°-231°, giving a brownish-red coloration with alkali hydroxide.

Methyl-ester, white needles, m.p. 114°-115°; *ethyl-ester*, colourless prisms, m.p. 87°-88° (Gina, Gazz. chim. ital. 1922, 52, i. 183).

ω -Chloro-2-nitro-*p*-toluic acid; by nitration of ω -chloro-*p*-toluic acid (Einhorn and Papastavros, Ann. 1900, 310, 209). Yellow needles, m.p. 190°.

2-Chloro-3-nitro-*p*-toluic acid; in small

quantity together with two isomeric acids, by nitrating 2-chloro-*p*-toluic acid (Claus and Böcher, Ann. 1891, 265, 362). Plates, m.p. 211°. CaA'_2 , glistening needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, rosettes.

2-Chloro-5-nitro-*p*-toluic acid; by hydrolysis of the nitrile derived from 2-chloro-5-nitro-*p*-toluidine (Claus and Böcher); by nitration of 2-chloro-*p*-toluic acid (Claus and Böcher); from 2-nitro-5-amino-*p*-toluic acid (Claus and Beysen, Ann. 1891, 266, 234). Needles, m.p. 184°-185°. $\text{KA}' + \frac{1}{2}\text{H}_2\text{O}$, glistening leaflets; CaA'_2 , needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$; CuA'_2 , green precipitate.

Nitrile; tables or smooth pillars, m.p. 157° (Claus and Beysen).

2-Chloro-6-nitro-*p*-toluic acid; together with the 5-nitro- and 3-nitro-derivatives by nitrating 2-chloro-*p*-toluic acid (Claus and Böcher); from 2-nitro-6-amino-*p*-toluic acid (Claus and Beysen). Fine silky needles, m.p. 159°. CaA'_2 , needles; $\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$, pillars.

3-Chloro-2-nitro-*p*-toluic acid; by nitrating 3-chloro-*p*-toluic acid with nitric acid (D 1.48) in the cold (Claus and Davidsen, Ann. 1891, 265, 347). Needles, m.p. 192°. $\text{MgA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles.

3-Chloro-6-nitro-*p*-toluic acid; by boiling 3-chlorocymene or 3-chloro-6-nitrocymene with nitric acid (D 1.39) (Fileti and Cross, Gazz. chim. ital. 1888, 18, 312); by nitration of 3-chloro-*p*-toluic acid with nitric acid (D 1.5 (Claus and Davidsen, J. pr. Chem. 1888, (2) 39, 495; Ann. 1891, 265, 341). Needles, m.p. 180°-181°. $\text{MgA}'_2 + 8\text{H}_2\text{O}$, large triclinic tables (Claus, Davidson and Beckenkamp, Ann. 1891, 265, 342).

$\text{BaA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, needles, or $+3\text{H}_2\text{O}$ (C. and D.).

Ethyl-ester; tables or needles, m.p. 60°.

Nitrile; from the amine. Long needles, m.p. 93° (C. and D.).

ω -Chloro-2-nitro-*p*-toluic acid; by heating *p*-cyanobenzyl chloride with fuming nitric acid for $\frac{1}{2}$ hour at 100° (Banse, Ber. 1893, 27, 2168). It melts at 140°-141°. BaA'_2 , leaflets; AgA' , precipitate.

Amide; by keeping a mixture of *p*-cyanobenzyl chloride, potassium nitrate, and sulphuric acid for 24 hours. Microscopic needles, m.p. 125° (B.).

Nitrile; by treating a well-cooled solution of *p*-cyanobenzyl chloride in sulphuric acid with potassium nitrate. Prisms, m.p. 84° (B.).

3-Chloro-2:6-dinitro-*p*-toluic acid; by nitrating 3-chloro-2-nitro-*p*-toluic acid or 3-chloro-6-nitro-*p*-toluic acid (Claus and Davidsen, J. pr. Chem. 1889, (2) 39, 496; Ann. 1891, 265, 349). Small glistening needles, m.p. 233°. $\text{BaA}'_2 + \text{H}_2\text{O}$, large vitreous prisms.

Ethyl-ester, m.p. 71°.

2-Bromo-5-nitro-*p*-toluic acid; from 5-nitro-2-amino-*p*-toluic acid (Claus and Beysen, Ann. 1891, 266, 234). Needles, m.p. 181°.

2-Bromo-6-nitro-*p*-toluic acid; from 6-nitro-2-amino-*p*-toluic acid (C. and B.). Small needles, m.p. 181°. BaA'_2 , flat needles.

2-Bromonitro-*p*-toluic acid; by nitrating 2-bromo-*p*-toluic acid (Landolph, Ber. 1872, 5, 268). Needles, m.p. 170°-180° (decomp.). $\text{BaA}'_2 + \text{H}_2\text{O}$, needles.

3-Bromo-2-nitro-*p*-toluic acid; in small quantity, together with the 6-nitro-isomeride, by

nitration 3-bromo-*p*-toluic acid (Claus and Herbabny, Ann. 1891, 265, 368). The acids are separated by means of their magnesium salts. The free acid forms fine needles, m.p. 214°, not volatile with steam. $\text{MgA}'_2 + 3\frac{1}{2}\text{H}_2\text{O}$, leaflets; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, tables.

3-Bromo-5-nitro-*p*-toluic acid; by hydrolysis of the nitrile obtained from the corresponding amine (C. and H.). Small needles, m.p. 206°.

Nitrile; citron-yellow needles, m.p. 130°.

Amide; glistening needles, m.p. 171° (C. and H.).

3-Bromo-6-nitro-*p*-toluic acid; by boiling 3-bromocymene with nitric acid (D 1-29-1-39) (Fileti and Crosa, Gazz. chim. ital. 1886, 16, 297); or better, by boiling 3-bromo-6-nitrocymene with 15 times its weight of nitric acid (D 1-39) for 8 hours (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 300); by nitrating 3-bromo-*p*-toluic acid (C. and H.). Thin tables, m.p. 203°. When heated with alcoholic ammonia at 180°, it yields 6-nitro-3-amino-*p*-toluic acid.

$\text{NaA}'_2 + 4\frac{1}{2}\text{H}_2\text{O}$, plates; $\text{KA}'_2 + \text{H}_2\text{O}$, needles; $\text{MgA}'_2 + 8\text{H}_2\text{O}$, large tables; $\text{CaA}'_2 + 5\text{H}_2\text{O}$, needles or prisms; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, long needles (F. and C.), or $+ 5\text{H}_2\text{O}$ (C. and H.).

Ethyl-ester; glistening needles, m.p. 61° (C. and H.).

Chloride; leaflets, m.p. 60° (C. and H.).

Amide; needles, m.p. 191° (C. and H.).

Nitrile; needles, m.p. 132° (C. and H.).

Chlorobromonitro-*p*-toluic acid; by heating chlorobromo-*p*-toluic acid (m.p. 186°) with 5-6 parts of fuming nitric acid (Willgerodt and Wolfen, J. pr. Chem. 1889, (2) 39, 411). Needles which sublime, m.p. 220°. $\text{BaA}'_2 + \text{H}_2\text{O}$.

2-Amino-*p*-toluic acid; by reducing 2-nitro-*p*-toluic acid with tin and hydrochloric acid (Ahrens, Zeit. f. Chem. 1869, (2) 5, 104). Long hair-like needles, m.p. 164°-165°.

$\text{BaA}'_2 + 1\frac{1}{2}\text{H}_2\text{O}$; CuA'_2 , green crystalline precipitate; **hydrochloride**; **platinochloride** (Cahours, Ann. 1859, 109, 17).

Nitrile; by reducing ω -chloro-2-nitro-*p*-tolonitrile with tin and hydrochloric acid (Banse, Ber. 1894, 27, 2163). Prisms, m.p. 81°-82°.

Acetyl-derivative; m.p. 267°-270° (decomp. (Kunkell, Ber. deut. pharm. Ges. 1911, 21, 419).

Diethylaminoethyl ester (Soderman and Johnson, J. Amer. Chem. Soc. 1925, 47, 1390).

3-Amino-*p*-toluic acid; from the nitrile (Niementowski, J. pr. Chem. 1889, (2) 40, 15); by reduction of 3-nitro-*p*-toluic acid with tin and hydrochloric acid (Niementowski and Rozański, Ber. 1888, 21, 1997; Noyes, Amer. Chem. J. 1888, 10, 479). Needles, m.p. 177° (decomp.). $\text{CaA}'_2 + 2\text{H}_2\text{O}$, scales; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, leaflets (Noyes).

Formyl-derivative; long silky needles, m.p. 183°-187° (Niementowski).

Acetyl-derivative; needles, m.p. 183° (Niementowski).

Amide; by boiling the nitrile for 2-3 hours with dilute aqueous potassium hydroxide (Niementowski). Very thin plates, m.p. 146°-147°.

ω -Amino-*p*-toluic acid; by heating *p*-carboxybenzylphthalamic acid with concentrated hydrochloric acid for 3 hours at 200°

(Günther, Ber. 1890, 23, 1060). Yellow scales. **Hydrochloride**, long needles or trimetric prisms; **platinochloride**, yellow amorphous substance (G.).

2:3-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-acid with tin and hydrochloric acid (Claus and Joachim, Ann. 1891, 266, 216). Thin needles, m.p. 192°. It yields red flocks with ferric chloride (Kehrmann, Ber. 1889, 22, 1984). BaA'_2 , reddish-yellow plates.

2:5-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-compound with tin and hydrochloric acid (C. and J.). Glistening needles, m.p. 240° (decomp.).

2:6-Diamino-*p*-toluic acid; by reducing the corresponding dinitro-compound with tin and hydrochloric acid (C. and J.; Markwald, Ann. 1893, 274, 357). Silky needles, m.p. 212°. Nitrous acid yields an intense yellow coloration. BaA'_2 , glistening leaflets; **sulphate** $+ 3\text{H}_2\text{O}$, yellow needles (M.).

Methyl-ester; brown crystals with a peculiar fluorescence, m.p. 129° (Kauffmann and Weissel, Ann. 1912, 393, 1).

Diacetyl-derivative; colourless needles, m.p. above 280° (K. and W.).

5-Chloro-2-amino-*p*-toluic acid; by reducing the corresponding nitro-derivative (Claus and Davidsen, Ann. 1891, 265, 346). Needles, m.p. 220°.

5-Bromo-2-amino-*p*-toluic acid; tables, m.p. 186°-187° (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 307).

5-Nitro-2-amino-*p*-toluic acid; by reducing an ammoniacal solution of 2:5-dinitro-*p*-toluic acid with hydrogen sulphide (Claus and Beysen, Ann. 1891, 266, 232). Long yellowish-red pillars or needles, m.p. 220° (decomp.). BaA'_2 , yellowish-brown plates or prisms.

6-Nitro-2-amino-*p*-toluic acid; by reducing 2:6-dinitro-*p*-toluic acid with ammonium sulphide, or with stannous chloride and alcoholic hydrochloric acid (C. and H.). Citron-yellow needles which sublime, m.p. 214°.

$\text{NaA}'_2 + \frac{1}{2}\text{H}_2\text{O}$, yellow silky needles; $\text{MgA}'_2 + 5\text{H}_2\text{O}$, yellow crystals; CaA'_2 , deep yellow pillars; $\text{BaA}'_2 + 4\text{H}_2\text{O}$, golden-yellow leaflets.

6-Nitro-3-amino-*p*-toluic acid; by heating the corresponding bromonitro-*p*-toluic acid with alcoholic ammonia at 180° (Fileti and Crosa, Gazz. chim. ital. 1888, 18, 303; cf. Niementowski, J. pr. Chem. 1889, (2) 40, 27). Long silky needles, m.p. 235°-236°. When heated with hydrochloric acid at 150°, it yields 6-nitro-*m*-toluidine.

2-Nitro- ω -amino-*p*-toluic acid; by heating 2-nitrocyanobenzylphthalimide with hydrochloric acid and acetic acid for 3 hours at 150° (Banse, Ber. 1894, 27, 2166). Pearly leaflets, m.p. 243° (decomp.). **Hydrochloride**, needles, m.p. 249°-250° (decomp.).

***p*-Toluic sulphinate**, 'Methylsaccharin'; obtained similarly to saccharin (Randall, Amer. Chem. J. 1891, 13, 269); by heating 3-sulphonamino-*p*-toluic acid at 200°-220° for 2 to 4 hours (Weber, Ber. 1892, 25, 1737; B. A. S. F., D. R. P. 48583 of 1889); by hydrolysis of *p*-cyanotoluene *m*-sulphonamide with caustic alkalis (B. A. S. F., D. R. P. 48583 of 1889; cf. Basler Chem. Fabr., D. R. P. 122587 of 1900). Long fine needles $+ 1\frac{1}{2}\text{H}_2\text{O}$, which

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lose the water of crystallisation at 190°, and then sublimes gradually with decomposition. It melts at 240° (R.) or 246° (W.) and possesses an intensely sweet taste, but a bitter after-taste. On heating with a mixture of potassium hydroxide and potassium hypochlorite, followed by acidification of the product with acetic acid, *p*-toluidine 3-sulphonic acid is obtained. *Barium salt* + 5H₂O, triclinic crystals; *Calcium salt*, opaque white needles; *Silver salt* + 1½H₂O, colourless diamond-shaped crystals.

Ethyl imide: crystals, m.p. 106°; *methyl imide*, m.p. 153° (W.).

For the sulphonic acids, etc., of toluic acid, see Fleisch (Ber. 1873, 6, 480); Bechler (J. pr. Chem. 1873, (2) 8, 170); Fittig (Ann. 1874, 172, 329); Iles and Remsen (Ber. 1878, 11, 230); Fischli (Ber. 1879, 12, 616); Hall and Remsen (Ber. 1879, 12, 1433); Remsen and Burney (Amer. Chem. J. 1880-1, 2, 411); Meyer and Baur (Ann. 1883, 220, 18); Kelbe and Baur (Ber. 1883, 16, 2565); Remsen and Emerson (Amer. Chem. J. 1886, 8, 264); Weinreich (Ber. 1887, 20, 982); Randall (Amer. Chem. J. 1891, 13, 258); Holmes (*ibid.* 1891, 13, 380); Weber (Ber. 1892, 25, 1741); Lyman (Amer. Chem. J. 1894, 16, 513); Meldrum and W. H. Perkin (Chem. Soc. Trans. 1908, 93, 1419; B. A. S. F., D. R. P. 48583 of 1889; Basler Chem. Fabr., D. R. P. 122567 of 1900; Jacobsen (Ber. 1878, 11, 895; 1881, 14, 39, 2355); Iles and Remsen (Amer. Chem. J. 1880-1, 1, 41); Jacobsen and Wierss (Ber. 1883, 16, 1959).

F. M. R. and J. S. H. D.

o-TOLYGLYCINE. Formed by heating *o*-toluidine with an aqueous solution of sodium chloroacetate (Friswell, Eng. Pat. 18149 of 1907).

TOLYLENE-DIAMINES. *Diamino-toluenes v. AMINES.*

TOLYLENE RED v. AZINES.

p-TOLYL-α-NAPHTHYLAMINE

NH·C₆H₄·CH₃



obtained by heating *α*-naphthylamine with *p*-toluidine and iodine, or *α*-naphthol with *p*-toluidine, or *α*-naphthylamine hydrochloride with *p*-toluidine. M.p. 78·5°, b.p. 230°/10 mm. The tolylnaphthylamines are described in Vol. IV., pp. 437, 451.

1-p-TOLYNAPHTHYLAMINE 8-SULPHONIC ACID. Prepared by heating 1-naphthylamine 8-sulphonic acid with *p*-toluidine in an autoclave at 150°, with or without hydrochloric acid or benzoic acid (Farb. f. F. Bayer & Co., D. R. P. 71168; Kalle & Co., D. R. P. 170630).

TOLYPYRIN, TOLYSAL, v. SYNTHETIC DRUGS.

TOMATO, *Solanum Lycopersicum* (Linn.) or *Lycopersicon esculentum vulgare*. A Peruvian plant now largely cultivated in many parts of the world for its fruit, which is esteemed as a vegetable. Several species and many varieties are known, differing greatly in size, shape, and colour of fruit.

König gives as the average composition—

Water	Protein	Fat	Sugar	Other N-free	Crude
93·4	1·0	0·2	3·5	0·5	0·8
					Ash

About half the total nitrogen is present as true proteids.

Passerini (Staz. Sper. Agrar. 1891, 18, 545) found the fresh fruit to consist of skin 1·3 p.c., pulp and juice 96·2 p.c., and seeds 2·5 p.c., and the pulp to contain two colouring matters—a yellow amorphous substance and a red crystalline compound—both insoluble in water, but soluble in amyl alcohol or ether, and bleached by chlorine. He attributes the acidity to citric acid, which he estimates as forming about 9 p.c. of the total dry matter of the whole fruit. The ash he found to contain—

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₂	SiO ₂	Cl
59·5	6·0	1·3	3·1	0·2	12·9	3·5	0·3	19·1

Albahary (Compt. rend. 1907, 145, 131) found in the fresh fruit—

Water	Protein	Fat	Carbo- hydrates	Malic acid	Citric acid	Oxalic acid	Ash
93·5	1·0	0·2	3·6	0·49	0·15	0·001	0·74

Traces of tartaric and succinic acids were also detected.

Stüber (Zeitsch. Nahr. Genussm. 1906, 11, 578) obtained somewhat similar results, but states that citric acid was the chief cause of the acidity (amounting to about 0·5 p.c. citric acid), and that he could not detect malic, tartaric, or succinic acids. The presence of citric acid may be detected by the formation of its triphenacyl ester.

The juice of tomatoes was found by Passerini (*l.c.*) to have a sp.gr. 1·01833 at 15°, to contain 2·44 p.c. of dry matter, of which rather more than ½ was protein, ¼ ash, and a little more than half carbohydrates and acids.

Other analyses of the juice were made by Stüber (*l.c.*), who found water 96·1, nitrogen 0·093, ash 0·56, total sugars, after inversion, 2·15, acidity (as citric acid) 0·65 p.c. The red colouring matter of the tomato was investigated by Arnaud (Compt. rend. 1886, 102, 1119), who believed it to be identical with carotin C₄₀H₅₆; Montanari (Chem. Zentr. 1905, i. 544) concluded that it had the composition C₄₀H₇₄; Willstätter and Escher (Zeitsch. physiol. Chem. 1910, 64, 47), who name it *lycopene*, find that it had the molecular composition C₁₀H₁₂, the same as that which Willstätter and Mieg (Annalen, 1907, 355, 1) have ascribed to carotin. It, however, differs in its properties from that substance. It crystallises from light petroleum or a mixture of alcohol and carbon disulphide in dark, carmine-red, felted prisms; it melts at 168°–169° (corr.), but is less soluble in ether, alcohol, carbon disulphide, or light petroleum than carotin. It absorbs oxygen much more readily than does carotin, and forms a di-iodide C₄₀H₁₂I₂, a dark green, gelatinous, insoluble substance.

The leaves and stems of tomatoes were examined by Passerini (Staz. Sper. Agrar. 1893, 20, 471), who found in the fresh substance—

	Total dry matter	Ash
Stems	8·8-9·9	1·6-2·0
Leaves	11·6-14·6	1·6-3·2

The ash contained—

	K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	Mn ₂ O ₄	P ₂ O ₅	SO ₂	SiO ₂	Cl
Stems	25·0	11·1	22·2	7·9	0·3		2·2	4·7	6·0	14·1
Leaves	2·0	1·4	35·1	9·0	0·1	0·05	1·4	12·3	25·3	1·8

Lithium, boron, and copper were also present in the ash of the stems.

Salicylic acid occurs naturally in tomatoes, although in very small quantity. Pellet (Ann. Chim. anal. 1907, 12, 10) considers that the presence of 10 mgm. of salicylic acid in 1 kilog. of tomatoes should not be regarded as proof of adulteration.

Tomatoes are often canned. American analyses (Bill. 28, U.S. Dept. of Agric.) give, as the mean of 19 samples—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94.0	1.2	0.2	3.5	0.5	0.6

In the ash was included about 0.1 p.c. common salt. Tomatoes are largely used in the preparation of sauces and chutneys, in some of which the red colour is enhanced by the addition of eosin (König).

Air-dried tomato seeds give a yield of about 25 p.c. oil when extracted with ether, and about 18 p.c. when the seeds are pressed. Sp.gr. (average), 0.9190; refractive index at 25°, 1.4722; iodine No. (Hanūs), 122.5; sapon. No., 189.5; Reichert-Meißl No., 0.26; Polenski No., 0.55; acetyl value, 14.2; insol. fatty acids, p.c. 98.5; soluble fatty acids, 0.52; unsat. (liquid) acids, p.c. 78.5; sat. (solid) acids p.c. 16.4 (Jamieson and Bailey, J. Ind. Eng. Chem. 1919, 11, 850). The antiscorbutic value of fresh and canned tomatoes has been studied by Delf (Bio-Chem. J. 1924, 18, 674; Chem. Soc. Abstr. 1924, 126, i. 902).

H. I.

TONITE v. EXPLOSIVES.

TONKA BEAN. *Tonquin bean* (Fève tonka, Fr.; *Tonkabohnen*, Ger.). The seed of the fruit of the leguminous tree *Dipterix odorata* (Willd.) which inhabits Guiana and Venezuela. Each pod contains a single seed, which is about 2 ins. long and $\frac{1}{2}$ in. wide. It has a dark-brown colour, is deeply wrinkled externally, and characterised by an agreeable odour and bitter aromatic taste. The tree flourishes in the forests of the Caracas district of Venezuela. The first crop of beans is gathered when the tree is three years old, but a full crop is not obtained until two years later. The fruit bears some resemblance to a small mango, and contains the odorous bean in its centre. The seed of *D. oppositifolia* (Willd.), the so-called English Tonka bean, has similar properties to that of *D. odorata*, but it is smaller and darker in colour.

Besides sugar, gum, malic acid, and woody fibre, tonka bean contains fixed oil and about 1.5 p.c. of coumarin (Boullay and Boutron-Charlard, J. Pharm. Chim. 11, 480). It is to the presence of coumarin that the odour and taste of the seed are due, and crystals of this compound often occur as an efflorescence on commercial specimens. To extract the coumarin, the finely-chopped beans, according to Gössmann, are heated for some time nearly to boiling with an equal bulk of 80 p.c. alcohol; the whole is then filtered and the residue again heated in the same manner; the extracts are mixed together, and the alcohol removed by distillation until the residue becomes turbid, when it is mixed with four times its volume of water, which precipitates the coumarin in somewhat impure crystals. Adhering fat may be removed by heating the mixture to boiling, and filtering through a

moistened filter. On cooling, the crystals which re-dissolve in the hot liquid again separate, and they may be further purified, if necessary, by treatment with animal charcoal (Annalen, 98, 86), v. COUMARIN.

Tonka bean is used to flavour tobacco, and especially snuff, as an ingredient of sachet powder, and in alcoholic solution as a flavouring essence.

TOPAZ (*Topaze*, Fr.; *Topas*, Ger.). A gemstone composed of aluminium fluo-silicate (AlF_2SiO_3) crystallised in the orthorhombic system. As shown by S. L. Penfield and J. C. Minor (Amer. J. Sci. 1894, 47, 387) the fluorine (15.48-20.37 p.c.) is replaced isomorphously by hydroxyl (0.18-2.50 p.c., as shown by analyses), so that the formula becomes $[\text{Al}(\text{F},\text{OH})]_2\text{SiO}_3$; and, chemically, a fluor-topaz and a hydro-fluor-topaz may be distinguished. Although these two varieties show slight differences in sp.gr. (3.574 in the former, and 3.523 in the latter), and in optical constants, the distinction is of no practical importance. The mineral is very resistant to acids, and water is expelled only at an intense heat. Topaz usually occurs as crystals in granitic and gneissose rocks, and is often associated with tin-ore. An important character is the presence of a perfect cleavage in one direction, perpendicular to the prism. The crystals may be dull and opaque, or more often clear and transparent, and colourless, bluish, greenish, yellow, or pink. The sherry-yellow crystals from Brazil become pink when heated ('burnt topaz'). Most of the gem material comes from Brazil and Russia, but it is also found in many other countries. Colourless topaz, when faceted, is sometimes mistaken for diamond, and much yellow quartz ('Spanish topaz', 'Scotch topaz', 'occidental topaz') is passed off as topaz. The more valuable yellow corundum, on the other hand, is known as 'oriental topaz.' The distinguishing characters of these are shown in the following table:—

	Topaz	Quartz 'Occidental topaz'	Corundum 'Oriental topaz'
Comp.	$(\text{AlF}_2)_2\text{SiO}_3$	SiO_2	Al_2O_3
Cryst.	Orthorhombic	Rhombohedral	Rhombohedral
Sp.gr.	3.55	2.65	4.0
H.	8	7	9
Refr.			
Indices	1.61-1.63	1.54-1.55	1.76-1.77

L. J. S.

TOPAZ, ORIENTAL, v. CORUNDUM.

TOPAZ, SCOTCH, v. CAIRNGORM.

TOPAZ, SPANISH, v. CAIRNGORM.

TOPE-LIVER OIL. According to Chapman (Analyst, 1922, 203), the oil obtained by steaming the livers of the tope (*Galeus galeus*, family *Carchariidae*), found on all the coasts of the British Isles, has the following characteristics:—

Specific gravity (15°/15°)	0.9249
Iodine value (Wijs)	152.2
Saponification value	185.1
Unsaponifiable matters	1.14 p.c.
Refractive index at 15°	1.4803
" " at 20°	1.4778
Specific dispersion ($n_D^{20} - n_H^{20}$)	0.0101
Brominated glycerides insoluble in ether	42.5 p.c.

It is a pale-coloured oil, having a strong but not unpleasant odour, and is very similar to cod-liver oil. It is used medicinally by local fishermen and in the dressing of leather.

TORBANITE or **TORBANEHILL MINERAL** v. PARAFFIN.

TORBERNITE or **CUPRO-URANITE** (*Kupferuranit*, Ger.). A mineral consisting of hydrated phosphate of uranium and copper



It crystallises as square (tetragonal) plates, which possess a perfect micaceous cleavage, with pearly lustre, parallel to their surface. The colour is bright grass-green, which distinguishes cupro-uranite at a glance from the closely-allied mineral autunite (*q.v.*) or calco-uranite. Sp.gr. 3.5; H. 2½. It is a mineral of secondary origin, occurring in the upper portions of lodes containing pitchblende and copper ores, and sometimes as an incrustation on the joint faces in granite. Fine specimens have been found at Gunnislake, Grampound Road, and Redruth in Cornwall. Other localities are Joachimsthal in Bohemia, Johanneergegenstadt in Saxony, Sabugal in Portugal, Mount Painter in South Australia, Katanga in Belgian Congo, &c. To a limited extent the mineral has been mined, together with autunite, as a source of uranium and radium. L. J. S.

TORMENTILLA. The underground stems of *Potentilla tormentilla* (Neck.) have been occasionally substituted for those of rhatany in medicine. They contain from 5 to 6 p.c. of a tannin, giving a dark-green precipitate with ferrous sulphate, bluish-red with ferric acetate; is also precipitated by gelatin and by tartar-emetic (Stenhouse) (v. TANNINS).

TORREFACTION. Roasting ores in order to expel volatile substances, *e.g.* sulphur, arsenic, &c.

TOSCA. v. TUFF.

TOULOUOUNA or **TULUCANA OIL.** An oil obtained by pressing the kernels of *Carapa tucanensis* (Aubl.) v. CARAPA OIL.

TOULOURON OIL. A brown oil obtained from *Pagrus Latro*. Used in Senegal as a remedy for rheumatism.

TOURMALINE (*Turmalin*, Ger.; from the Anglès *turamali*). A complex boro-silicate of aluminium, together with variable and mutually-replaceable amounts of ferrous oxide, magnesia, and alkalis. As chemical types there may thus be distinguished iron-tourmaline, magnesium-tourmaline, and alkali-tourmaline. Analyses how: SiO_2 , 35-38; TiO_2 , 0-1; B_2O_3 , 9-11; Al_2O_3 , 30-42; Cr_2O_3 , 0-10 (rarely); Fe_2O_3 , 1-8; FeO , 0-17; MnO , 0-2; MgO , 0-14; Na_2O , 0-2; Na_2O , 0-3; K_2O , 0-2; Li_2O , 0-1.7; I_2O , 1-4; F, 0-1 p.c. Many different formulæ have been suggested. Penfield and Foote (1899) regard the several varieties as salts of a hypothetical aluminoboro-silicic acid



With these wide differences in chemical composition, the sp.gr. ranges from 3.0 to 3.2, and the refractive indices (Na) $n = 1.6123$ - 1.6515 , $n = 1.6315$ - 1.6354 (E. A. Wülfing, 1900), but there are only very slight variations in the crystallographic constants (this being attributed

by Penfield and Foote to the mass effect of the large acid radical). The crystals are rhombohedral-hemimorphic, there being a different development of faces at the two ends. The habit is almost invariably prismatic, with deeply-grooved prism faces, the striations being parallel to the edges of the prism; the cross-section of the prism is triangular with straight or curved outlines. These peculiarities of form render tourmaline a mineral readily recognisable. As a consequence of the hemimorphism the crystals are pyroelectric. The material ranges from colourless to jet-black in colour, and may be any shade of red, yellow, green, or blue. In one and the same crystal there are often striking contrasts in the differently coloured zones. The more darkly coloured crystals are strongly dichroic, the ordinary ray vibrating perpendicular to the principal axis being almost completely absorbed. On this property depends the use in polarising apparatus (*e.g.* the well-known tourmaline-tongs) of tourmaline plates cut parallel to the principal axis of a crystal.

Common black tourmaline (*schorl*) is of abundant occurrence in granite and metamorphic rocks, and is a frequent associate of tin ores. Coloured tourmalines are much used in jewellery, either as clear faceted stones or, when cloudy, as beads (H. 7½). The red is often called *rubellite*, and the blue *indicolite*, whilst fanciful names such as 'Brazilian emerald,' 'Siberian ruby,' &c., are also sometimes used. Within recent years large quantities of gem material have been quarried from the pegmatites of California, Madagascar, and the Usakos district, South-West Africa.

L. J. S.

TOUS-LES-MOIS is a species of arrowroot procured from the tubers of *Canna edulis* (Ker-Gawl.) nat. ord. *Marantaceæ*. The starch is obtained in the same manner as other descriptions of arrowroot. Under the microscope the granules show themselves to be unusually large, measuring from 0.0015 to 0.0037 inch in length and from 0.001 to 0.0027 in breadth; broad, flat, ovate. The hilum is situated at the narrow extremity, and the rings are very close, firm, and regular.

Tous-les-mois is used in admixture with cocoa preparations and as a food for infants, for which latter purpose it is bleached. V. STARCH.

TOXICODENDROL. The active principle of the 'Poison Ivy' (*Rhus Toxicodendron* Linn. and *R. venenata* [DC.]), is an oily substance possessing intensely irritating properties, found in all parts of the plant, the fruits giving 3.6, the leaves 3.3, and the stem 1.6 p.c. The degree of activity varies in the case of different persons; in some cases 1 mgm. produced hundreds of vesicles, and even 100 mgm. proved active in one case. The vesicant action was not immediate, a period of 24 hours to 7 or 9 days elapsing before the eruption appeared (Pfaff, J. Soc. Chem. Ind. 1897, 1037).

The poisonous substance is probably a glucoside; it is decomposed by acids yielding gallic acid, fisetin, and rhamnose. Cases of poisoning are said to be best treated with potassium permanganate* (Acree and Syme, Amer. Chem. J. 1906, 301).

The 'poison oak' (*Rhus diversiloba*, T. & G.), which is very similar in appearance to *R. toxicodendron*, has been examined chemically

by McNair (J. Amer. Chem. Soc. 1916, 38, 1417), who finds that the leaves and branches contain a substance of which the alcoholic extract is poisonous. The poisonous material is not, however, a glucoside of fisetin, rhamnose, and gallic acid, since none of these substances is produced on hydrolysis. Fisetin, rhamnose, and gallic acid are found in non-poisonous species of *Rhus*, and the natural glucoside of these substances is non-toxic.

TOXINS and ANTITOXINS.

TOXINS.

Infective diseases of man and animals, that is diseases which are contagious, infectious, or transmissible by inoculation, are caused by pathogenic (i.e. disease-producing) living organisms which are parasitic on or in the individual attacked. The parasitic organisms may be minute vegetable ones, principally bacteria, minute animal protozoa, or higher and larger forms such as moulds, insects, and worms. The bacteria, and presumably also the protozoa, as a rule produce their deleterious effects principally by means of substances which are poisonous to the host, and which are elaborated by, or are derived from, the parasitic organisms. Even the larger parasites, such as worms, though acting mechanically and in other ways, may also elaborate poisonous substances.

In the early days of bacteriology, under the influence of the work of Panum, Selmi, Nencki, and others on the products of putrefaction, attempts were made to isolate from the cultures of the pathogenic organisms and from the tissues of the disease-stricken patients nitrogenous bodies of a basic and alkaloidal nature similar to the ptomaines of putrefaction, and Brieger in particular isolated such substances as typhotoxine from cultures of the typhoid bacillus and tetanine from the tissues of a case of tetanus (see art. PTOMAINES). It was soon found, however, that such basic substances are not, as a rule, the essential or specific toxic agents of the pathogenic bacteria, and some of those described by Brieger are quite likely artifacts, due to the methods of extraction employed.

The specific toxic agents of the bacteria, or *toxins*, as they may conveniently be termed, are substances of complex composition, which, so far as they have been investigated, seem occasionally to be protein in nature, or to be allied to the proteins or to the enzymes. The whole subject of the nature of toxins is still in a very indeterminate condition, so that any views expressed here must be regarded as tentative. In some instances the toxin appears to be a substance *vis generis*, in others it may be proteose in nature (tox-albumose), and in others it may be albuminous (tox-albumin). Of late, the conception has been gaining ground that toxins and other 'antigens' (v. *infra*, under *Antitoxins*) may be lipid substances or lipid-protein complexes. The toxin may be an excretory product, as it were, of the micro-organism, e.g. tetanus toxin (S. Martin), or may be formed by the action of enzymes, excreted by the micro-organism, on the constituents of the culture medium or of the tissues, e.g. anthrax toxin, or it may be a mixture of these two, e.g. diphtheria toxin (S. Martin), or it may be a protein or other con-

stituent of the bacterial cells themselves, e.g. typhoid toxin. Toxins which are excretory products, or are formed by the action of the organism on the culture medium, are termed *exo-toxins* or simply *toxins*, e.g. diphtheria, tetanus, and botulismus toxins; those which are intimately associated with the bacterial cells are termed *endo-toxins*; the toxins of the majority of pathogenic bacteria belong to the latter class. The term toxin has also been extended so as to include various toxic bacterial extracts, such as tuberculin, the toxic proteins, &c., which are found in the higher plants and animals, e.g. abrin and ricin of the jequirity and castor-oil beans respectively, substances like eel serum, which is toxic on injection into other animals, and snake venom.

The bacterial *exo-toxins* may be prepared by cultivating the organisms in a suitable fluid culture medium under appropriate conditions for 1-4 weeks, and then filtering the fluid culture through a Pasteur-Chamberland porcelain, or a Berkefeld, filter. The filtrate is more or less toxic, and may be termed the toxin broth, the actual toxin contained in it may be concentrated in various ways, but extraction in a pure condition is at present impossible, owing to the difficulty of separating it from the constituents of the culture medium. Bacterial *endo-toxins* may be obtained by growing the organisms on a solid culture medium and extracting the bacterial mass with weak alkalis, &c., or by grinding up the bacterial paste in a mechanical disintegrator, such as Macfayden and Rowland's or Barnard's, and subsequent filtration through a porcelain filter (Proc. Roy. Soc. 1912 and 1911).

The bacterial toxins generally are unstable bodies, disappearing, or being converted into non-toxic modifications, on keeping, and destroyed by light, warming to 60°-70°, by acids, alkalis, and oxidising agents, and by digestive enzymes; owing to the last-named fact, the toxins usually are not toxic when taken by the mouth, but only on inoculation. They are much more stable in the dry condition than when in solution. They are insoluble in and are precipitated by strong alcohol, and are precipitated on saturation of their solutions with ammonium sulphate. Diphtheria and tetanus toxins dialyse very slightly through parchment, and they will pass through a gelatin-coated porcelain filter, which does not permit of the passage of serum albumin, suggesting that their molecules are smaller than those of the latter (Brodie, Journ. Path. and Bacter. 1897). They are probably *lavorotatory*. The 'toxin,' in some instances at least, may contain more than one toxic constituent.

Diphtheria toxin was first investigated by Löffler. By precipitating broth cultures of the diphtheria bacillus with alcohol, he obtained a white toxic powder which he classed among the enzymes (Deut. med. Woch. 1890, Nos. 5 and 6). Roux and Yersin, by the cautious addition of calcium chloride, obtained the toxin entangled with the precipitate of calcium phosphate which comes down, and similarly regarded it as an enzyme (Ann. Inst. Pasteur, iii.). Brieger and Fränkel concluded that the toxin is a protein ('tox-albumin'); they found that it is precipitated by ammonium sulphate, but not by magnesium

sulphate, contains a relatively high percentage of sulphur and gives the biuret and Millon's reactions (Berl. klin. Woch. 1890, 241, 1133).

Brieger and Fränkel's method of preparing the diphtheria toxin was to saturate broth cultures with magnesium sulphate at 30°, filter from the precipitated globulin, &c., saturate the filtrate with ammonium sulphate at 30°, wash and dissolve the precipitate, dialyse to remove as much adherent salts as possible, and remove remaining traces of ammonium sulphate by the cautious addition of barium chloride; evaporate the filtrate to half the volume *in vacuo* at 40°, and precipitate with absolute alcohol. The precipitate was collected, redissolved, and precipitated with alcohol 6-8 times. Ultimate analysis gave the following figures: C 45.35, H 7.13, N 16.33, S 1.39, O 29.80.

Brieger and Boer subsequently prepared the diphtheria toxin in as pure a form as it has yet been obtained by precipitating broth cultures with a 1 p.c. solution of zinc sulphate or chloride. The precipitate of the zinc double salt is washed with feebly alkaline water and decomposed with carbon dioxide. The purified product gave the xanthoproteic, biuret, Adamkiewicz's, and Millon's reactions. A litre of broth culture gave about 3 grm. of the zinc double compound (Zeitsch. Hygiene, xxii. 267).

Sidney Martin isolated from diphtheritic membrane and from the spleen and other organs of diphtheria cadavers proteoses, chiefly deutero-albumose, and from the membrane alone an organic acid which was not identified. The latter is a yellowish amorphous body, becoming deep brown with alkalis, and is soluble in water and absolute alcohol, but not in ether, chloroform, or benzene. The proteoses were extracted by placing the minced tissues in absolute alcohol until the ordinary proteins were coagulated and rendered insoluble, extracting with water, and precipitating this extract with alcohol many times. Similar proteoses were obtained from cultures in alkali-albumin of the diphtheria bacillus (Brit. Med. Jour. 1892, i.).

Ehrlich concluded that the diphtheria 'toxin' contains two or more toxic constituents, as well as non-toxic bodies, 'toxoids,' derivatives, or degradation-products, of the toxin (*v. infra*, under *Antitoxins*).

Warden, Connell and Holly regard diphtheria toxin as a fat complex derived from dead and disintegrating bacilli in an emulsified or colloidal form which then becomes adsorbed upon colloidal particles in the broth culture medium, forming, with electrolyte, an adsorption entity constituting toxin (Journ. of Bacteriology, vi. 1921, p. 103).

Tetanus toxin was obtained in a somewhat concentrated form by Kitasato from anaerobic broth cultures of the tetanus bacillus (which produces lock-jaw), and he gave a detailed account of the action of heat and of a number of chemical reagents on the toxin broth (Zeitsch. Hygiene, x. 267). Brieger and Cohn precipitated veal-broth cultures by saturation with ammonium sulphate (*ibid.* xv. 1). The toxin formed a flocculent precipitate which floated; it was purified by redissolving, precipitating the protein with basic lead acetate, removing other soluble impurities by dialysis, and finally pre-

cipitating the dialysed solution with alcohol. Thus prepared, the tetanus toxin formed pale yellow, odourless, easily soluble scales, having a gummy taste; the solution was feebly leucorotatory. It contained only a trace of ash, did not give the Millon's and xanthoproteic reactions, and gave no precipitate with potassium ferrocyanide and acetic acid, nitric acid, or mercuric chloride. Boiled with ferric chloride it gave no red colour. With copper sulphate and sodium hydroxide it gave a slight violet colour. It contained no phosphorus and only a trace of sulphur, and ultimate analysis gave the following figures: C 52.06, H 8.1, N 15.71 (Brieger, Zeitsch. Hygiene, xix. 101). Subsequently, Brieger and Boer obtained the toxin by the method employed by them for isolating the diphtheria toxin (*vide ante*). On these facts Brieger considered that the tetanus toxin is not a true protein.

Hayashi, however, employing the Brieger-Boer method, or a modification of it, came to the conclusion that the tetanus toxin is a protein, and is a primary proteose (Arch. f. exper. Pathol. xlvii. 9). S. Martin also isolated proteoses, chiefly deutero-albumose, from the spleen of a cadaver, but they did not induce tetanic convulsions on inoculation. Tetanus cultures contain methyl-mercaptan and other sulphur compounds (Nencki, Monatsh. x.); but Fermi and Pernossi were unable to extract any basic substance from them (Zeitsch. Hygiene, xvi. 385). Besides the convulsive constituent, 'tetano-spasmin,' the toxin broth also contains a substance, 'tetano-lysin,' which is a solvent for red-blood corpuscles. The purified tetanus toxin is probably the most toxic substance known, less than 0.5 mgrm. being a fatal dose for a man.

Anthrax toxin. Hankin obtained proteoses from cultures of the anthrax bacillus, and Brieger and Fränkel a tox-albumin from animals dead of anthrax. Marmier, by precipitating cultures with ammonium sulphate, isolated a toxic substance which he considered to be neither protein nor basic (Ann. Inst. Pasteur, ix. 533). S. Martin (*loc.*) obtained both from cultures in alkali albumin, and from animals dead of anthrax, proteoses, chiefly deutero-albumose, and a nitrogenous basic substance, both of which were toxic. The toxins are formed mainly by the action on the culture medium of enzymes excreted by the bacillus. Endo-toxins may also be formed.

The toxins of the majority of other pathogenic bacteria are endo-toxins. That is to say, if the organisms be grown in a fluid medium, the filtrate is almost non-toxic, but the dead and disintegrated bacterial cells yield toxic substances. Toxins of protozoan organisms are not known with certainty.

Tuberculin. The original or old tuberculin of Koch is obtained by boiling, concentrating over a water-bath and filtering glycerin broth cultures of the tubercle bacillus. It is toxic to healthy animals only in large doses, but minute doses cause considerable disturbance in tuberculous patients and animals, and this reaction is made use of for the detection of tuberculous infection. It contains small quantities of proteoses, extractives, and salts, and traces of basic bodies. Small quantities of an acid

substance, probably teraonic acid, possibly derived from the bacillar cells, are also present in cultures of the tubercle bacillus. Other tuberculin and bacterial extracts have been prepared.

It must be clearly recognised that in those cases in which the toxin is supposed to be a protease or other protein, the latter may be merely constituents of the culture medium by which the toxin is entangled or adsorbed.

[On toxins, &c., see Oppenheimer in Kolle and Wassermann's *Handbuch der Pathogenen Mikroorganismen*, vol. i. (Bibliog.); Vaughan and Novy, *Cellular Toxins*, 1902 (Bibliog.); S. Martin, *Man. of Gen. Pathology*, 1904, and *Reps. Med. Off. Loc. Gov. Bd.* 1889-1900; also various papers in the *Ann. Inst. Pasteur*; *Zeitsch. Hygiene, Centr. Bakteriol.* Abstracts also in chemical journals.]

Snake venom. Poisonous snakes are divided into two groups, the colubrine and viperine. The venom, which is secreted by glands in connection with the mouth, may be limpid or syrupy, pale yellow, orange or greenish in colour, odourless and tasteless, sp.gr. 1.04 (rattlesnake), 1.11 (cobra), 1.08 (Russell's viper). Microscopically, it contains few elements, and when dry resembles dry albumin. The reaction of the pure venom is acid; it contains C, H, O, N, and S in the proportions found in proteins, gives the protein reactions, is precipitated with alcohol, ammonium sulphate, sodium chloride, and coagulates on heating. Viperine venoms lose their toxicity on heating to 80°-85°, but colubrine venoms require to be heated to 120° to destroy their toxicity. The active toxic substances of venom are coagulable proteins (globulin), proteoses, toxins allied to bacterial toxins, and Faust has separated a non-nitrogenous toxic substance, *ophiotoxin*. The proteoses are chiefly proto- and hetero-proteose. The venoms are complex mixtures containing some, but not in any venom all, of the following active substances: 1. *Neurotoxins* acting on (a) respiration, (b) heart, (c) muscle, particularly the diaphragm; 2. *Cytolysins*, solvents for (a) blood corpuscles, (b) vascular endothelium, (c) other cells; 3. *Fibrin ferment* inducing blood-clotting, and others. The venoms thus produce paralysis of voluntary muscles and of the heart and respiration, solution of the red and white-blood corpuscles and hemorrhages, and the blood may be either fluid or coagulated in the vessels, and the bodies of the dead putrefy rapidly owing to the destruction of the anti-bacterial properties of the blood. The venom is most active when injected into a blood-vessel, whereas in the subcutaneous tissues it may take some time to act: it is also readily absorbed from the eye. Taken by the mouth, provided there are no cracks or abrasions, colubrine venom is harmless, but viperine venom may cause gastritis, &c., and even death. The hemolysins which cause solution of the red corpuscles are of the nature of 'amboceptors,' requiring a 'complement' (c. *infra* under *Bactericidal sera*) to activate them. In some cases the venom alone can hemolyse washed red corpuscles *in vitro*, e.g. man, dog, &c., in others it has no action on washed corpuscles but becomes active on the addition of serum. Some corpuscles, therefore, contain the activating 'complement,' others do

not, and, hence, are not hemolysed when washed. Kyes, Sachs, Flexner, and Noguchi have shown that lecithin and lecithides in the corpuscles are the complement-like activators of the hemolytic amboceptors. A venom which is inactive on washed corpuscles becomes active on the addition of lecithin or even of oleic acid or other fatty acids and soaps.

By the cautious treatment of an animal with increasing doses of venom an antitoxin ('antivenin') is formed which has the power of neutralising the particular venom.

The venom of scorpions (against which an antitoxin can be prepared) and spiders is probably protein in nature; of mosquitos and gnats it may be the products of certain bacteria or moulds present in the oesophageal sacs; of bees a protein-free organic base. The formic acid present in the 'venom' of ants, bees, &c., is probably not the active toxin. Many fish are also poisonous by their bites or by spines connected with special glands. Toads and salamanders have acid and basic poisons in the skin glands. Jelly-fish and sea-anemones have stinging glands. Extracts of intestinal worms may be toxic.

[On snake venom, see Martin and Lamb in Allbutt and Rolleston's *System of Med.* vol. ii. pt. ii. (Bibliog.); *Sc. Memoirs of the Gov. of India*, Nos. 1, 3, 4, 5, 7, 10, 16, 17; Faust, *Die Tierischen Gifte* (Braunschweig, 1906, Bibliog.); Noguchi, *Journ. Exper. Med.* viii. and ix.; and *Snake Venoms* (Smithsonian Inst. Publication); Calmette, *Venoms and Venomous Animals* (Bale). On other animal toxins, see Castellani and Chalmers, *Manual of Tropical Med.* (Bibliog.).]

ANTITOXINS.

It is a remarkable fact that proteins on injection into a suitable animal (the domestic mammals generally) give rise to the formation of 'anti-bodies'—substances having properties in some way opposed to those of the proteins injected—which accumulate in the blood of the treated animal. This property of generating anti-bodies, according to Abderhalden, is characteristic of the animal body and is most active against injected cells, proteins, and allied substances. The substance which generates the anti-body is termed the 'antigen.' Antigens, with certain doubtful exceptions, seem to be proteins or substances related to proteins, or possibly lipoids or lipid-protein complexes. Hence mineral poisons, alkaloids, carbohydrates, &c., form no anti-bodies. If a protein such as human serum is injected into a rabbit, the serum of the treated rabbit gives a white precipitate when mixed with human serum, and to a less extent with apes' serum, but with no other sera—a specific 'precipitin' for human serum has been formed. By this means bloodstains, flesh, &c., can be identified with great certainty. By injecting an enzyme, such as rennin, anti-enzyme is formed which inhibits the action of the enzyme; by injecting red-blood corpuscles 'hemolysin,' solvent for red-blood corpuscles, is formed. If a poisonous protein is injected (in properly graduated doses so as to avoid killing the animal), such as ricin or snake venom, an anti-body is generated which completely neutralises the poisonous

action of the substance injected. The same is the case with toxins like diphtheria and tetanus toxins. By repeated injections of a horse with increasing doses of the toxin, the animal becomes less and less susceptible, so that it can finally tolerate huge doses of the toxin without harm, and coincident with the development of this insusceptibility antidotal substances appear in its blood, and may be obtained in the blood-serum by bleeding the animal and allowing the blood to clot. The antidotal or neutralising substance to toxin is termed antitoxin; it is a fairly stable substance, and by obtaining and bottling the serum aseptically it may be preserved, and is employed to treat the respective disease in man.

The antitoxic serum contains a variable amount of the antitoxic constituent and for therapeutic use must be standardised.

The antitoxic constituent is probably protein (globulin) in nature, or at least is associated with the globulin constituent of the serum. The globulin content of the blood of antitoxin-yielding horses is frequently higher than normal, and the antitoxin may be precipitated by saturation of the serum with magnesium sulphate, or by partial saturation with ammonium sulphate; it comes down with the eu-globulin fraction of the serum globulin.

Brieger and Boer (*loc.*) separated the antitoxic constituent by the following methods: (a) 4 grms. of potassium iodide or chloride are added to 10 c.c. of the antitoxic serum diluted with an equal quantity of distilled water. After solution, 4-5 grms. of finely-powdered sodium chloride are added, the mixture is kept at 30°-37° for 18-20 hours, and the precipitate (0.4 grm.) is collected; it is the antitoxic portion of the serum with a slight admixture of protein and salts.

(b) The proteins of the antitoxic serum are precipitated with basic lead acetate containing a trace of ammonia, the precipitate is filtered off and the filtrate is saturated with ammonium sulphate. The precipitate is collected and redissolved, the solution is dialysed, and evaporated to dryness. A light powder is obtained (0.06 grm. from 10 c.c. serum) which contains the antitoxic constituent.

(c) 10 c.c. of the serum are diluted with 50 c.c. of distilled water, and 20 c.c. of a 1 p.c. solution of zinc sulphate or chloride are added. The precipitate is collected, dissolved in feebly alkaline water, and the zinc compound is decomposed with carbon dioxide. The antitoxic constituent is present in solution when the precipitant is zinc chloride, but is entangled in the zinc carbonate precipitate when the precipitant is zinc sulphate.

Homer has elaborated a very exact method by partial saturation of the serum with sodium chloride and ammonium sulphate, whereby practically the whole of the antitoxin may be concentrated and recovered from a weak antitoxic serum (*Journ. of Hygiene*, 1918, 22, 51); also MacConkey, *ibid.* 1924, 22, 413.

Anti-venia, the antidotal serum for snake-bites, is a truly antitoxic serum.

In the case of pathogenic micro-organisms which do not form an exo-toxin, an antidotal anti-serum can also be prepared by the injection of the bacterial cells, first killed cultures, and sub-

sequently the living organisms, but such serums are not nearly so potent as the antitoxic serums produced by exo-toxins, and many are practically useless for treating the respective diseases, e.g. typhoid and cholera serums. The principal action of such an anti-serum is bacteriolytic, i.e. it brings about solution of the micro-organism.

In this bacteriolytic reaction (and similarly in the solution of red-blood-corpuscles by a 'haemolytic' serum) two protein substances seem to be concerned. The fresh anti-serum is solvent for bacteria, but not the old, nor the heated (to 56°C.) anti-serum. The two latter may be rendered active again by the addition of fresh normal serum. That is to say, by injection of the bacteria (or blood corpuscles), a new and relatively stable substance is formed, which reacts with an unstable normal constituent of the serum, the two together bringing about bacteriolysis (or haemolysis). To the former, the name of 'immune body' or 'amboceptor,' to the latter, 'alexin' or 'complement,' is given.

Specificity is the distinguishing feature of the anti-bodies; the anti-body produced by an antigen always reacts most actively with this particular antigen.

The formation of anti-bodies is usually explained by Ehrlich's 'side-chain theory.' This supposes that the protoplasmic molecules of the cells of the animal have an affinity for the substance injected (the 'antigen') which gives rise to the anti-body, so that the antigen becomes incorporated with the protoplasm. The union of the antigen with the protoplasm is assumed to be brought about by the combination of atomic groups comparable to the side-chains of a ring nucleus, those of the protoplasmic molecule being termed 'receptor groups,' those of the antigen 'haptophore' (=binding) groups. The poisoning caused by a toxin is thus due to the union of the toxin with the protoplasm by the combination of the haptophore groups of the toxin with the receptor groups of the protoplasm. Should the animal's protoplasm not possess receptor groups having an affinity for the haptophore groups of the toxin, the toxin would not be poisonous to this animal. This is often the case—a toxin is never poisonous to all animals. Now Ehrlich assumed that the protoplasmic receptor groups fulfil physiological functions in the animal, e.g. nutrition, &c., so that when a toxin becomes united with the protoplasm a defect is created, whereby the latter cannot properly fulfil its physiological functions. Provided the dose of toxin be not too large, recovery ensues, due to the regeneration by the protoplasm of the particular receptor groups involved. This process is repeated again and again, and as a result of the continued stimulation by the numerous doses of toxin, the protoplasm ultimately forms the receptor groups in question in large excess—much more than is necessary simply to repair the damage done. A considerable proportion of the now very numerous receptor groups then becomes detached from the protoplasm, accumulates in the blood, and constitutes the anti-body. The antidotal property of antitoxin is, therefore, due to the fact that it saturates the haptophore groups of

the toxin so that the latter is then unable to combine with the protoplasm.

[On antitoxins, &c., see Ehrlich, *Die Wertbemessung des Diphtherieserums*, 1897; *Trans. Jenner Inst. of Prov. Med.* ii.; Croonian Lect. Roy. Soc. Lond. 1900; and *Collected Papers on Immunity*, 1909; Hewlett, *Serum and Vaccine Therapy*, Churchill, 1910 (Bibliog.); Kolmer, *Infection, Immunity and Biologic Therapy* (Saunders, 3rd ed. 1923, Bibliog.)]

Toxin-antitoxin reaction.—The neutralisation of toxin by antitoxin is approximately quantitative, and the toxin and antitoxin unite. This is shown by the fact that if a recently-made mixture of toxin and antitoxin be filtered through a gelatin-coated porcelain filter, the toxin passes through into the filtrate, but not the antitoxin (*see ante*). If, however, the mixture be allowed to stand so that interaction may occur, the toxin can no longer be separated from the antitoxin by this method. The interaction between the two is slow, is retarded by cold, and is hastened by warming (Brodie, *l.c.*; Martin and Cherry, *Proc. Roy. Soc. Lond.* lxi.).

The exact nature of the union of toxin with antitoxin, 'the toxin-antitoxin reaction,' has been the subject of much controversy, and three principal hypotheses have been formulated to explain it. Ehrlich held that the union is comparable to the combination of a strong acid with a strong base, i.e. the reaction is a complete one, and there cannot be at the same time in a mixture of toxin and antitoxin, free toxin and antitoxin, together with neutralised toxin. The strictly quantitative relation of toxin and antitoxin supported this view, viz. if 10 equivalents of antitoxin exactly neutralise 10 equivalents of toxin, then 100 equivalents of antitoxin will exactly neutralise 100 equivalents of toxin. But it is found that if 100 fatal doses of toxin (for the guinea-pig) are just neutralised by 100 equivalents of antitoxin, 101 fatal doses of toxin+100 equivalents of antitoxin is not a fatal mixture, and generally 108-116 (sometimes many more) fatal doses of toxin must be added to the 100 equivalents of antitoxin to render the mixture a fatal one (the Ehrlich phenomenon). Ehrlich explained this by supposing that the 'toxin broth' contains not one toxic substance only, but is a mixture of toxin and toxone, the latter being much less toxic than toxin, though requiring as much antitoxin to neutralise it as toxin does. Toxin has, however, a greater affinity for antitoxin than toxone has, so that when more toxin is added to a neutral mixture of toxin broth (containing toxin and toxone) and antitoxin, the toxone-antitoxin complex present is dissociated, and the antitoxin set free then combines with the added toxin, and it is not until the added toxin is more than can be neutralised by the freed antitoxin that the mixture becomes fatal. Ehrlich, in fact, was forced to conclude that toxin broth contains diverse toxic bodies. The second hypothesis, that of Arrhenius and Madsen, while admitting that the union of toxin with antitoxin takes place in definite proportions, regards it as comparable to the neutralisation of a weak base by a weak acid, e.g. ammonia and boric acid, the reaction is incomplete, though resulting in equilibrium, so that free toxin and antitoxin exist in the mixture, together with the toxin-

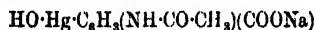
antitoxin complex. The quantity of free toxin would be a function of the relation existing between the initial quantities of the two substances. The Ehrlich phenomenon is quite explicable on this hypothesis, and there is no need to postulate the existence of toxone or other toxic constituents in toxin broth. But other phenomena concerning the neutralisation of toxin by antitoxin do not seem explicable by either of these hypotheses. One of these is what is known as the 'Danysz effect,' which is obtained with many different toxins and their corresponding antitoxins. If a mixture consisting of *a* parts of toxin and *b* parts of antitoxin is exactly neutral, when the whole of the toxin *a* is mixed with the antitoxin; a similar mixture of *a* parts of toxin and *b* parts of antitoxin, prepared by adding the toxin in several fractions to the antitoxin is *still toxic*. This is explained according to Arrhenius and Madsen as being analogous to the neutralisation of chloracetic acid by sodium hydroxide. If equivalent quantities of the acid and base are taken, and only half the acid is added in the first instance to the whole of the hydroxide, the acid is wholly neutralised, leaving half the base free. This then slowly reacts upon the sodium chloracetate forming sodium chloride and glycolate, and the solution ultimately becomes neutral. (Communications from the Nobel Institute, 1, iii. 1906). The Danysz effect has its counterpart in the neutralisation of arsenious acid with ferric hydroxide. Bordet maintains that the union of toxin with antitoxin takes place in variable proportions, and resembles the phenomenon of adsorption, similar to the colouring of filter-paper with a dye. Thus, if pieces of filter-paper be placed in a dilute solution of a dye at sufficiently long intervals, the first pieces become distinctly coloured, but the last pieces remain colourless through lack of free dye in the solution. On the other hand, if all the pieces of paper are simultaneously placed in the solution, they all become similarly coloured. Likewise, a mixture of toxin and antitoxin, in which the latter is in insufficient quantity to render the mixture completely innocuous, does not contain, according to Bordet, a certain quantity of free toxin, together with neutralised toxin, but contains only molecules of toxin insufficiently neutralised, because the antitoxin is diffused over all the molecules of toxin, each of which, therefore, fixes an amount of antitoxin too small completely to inactivate it. In a series of mixtures containing increasing quantities of antitoxin for a uniform amount of toxin, each molecule of the latter will, therefore, be united to increasing quantities of antitoxin. The toxicity of the poison will thus become weaker and weaker, and such a series of mixtures will possess all degrees of toxicity. From this conception, reversibility of the toxin-antitoxin combination should exist, and toxin can sometimes be recovered from the toxin-antitoxin complex, showing that it is not destroyed in the interaction. Reversibility can be demonstrated in the case of some antigen-antibody systems, a reversibility which is variable and generally incomplete. On the whole, almost every phenomenon of the toxin-antitoxin reaction seems to be explicable on Bordet's adsorption hypothesis, which is not the case with other hypotheses. Specificity is not explained by

it, nor is it explained by other hypotheses; it may be due to secondary interactions.

[On the toxin-antitoxin reaction, see Ehrlich, Deutsch. med. Woch. 1898; Arrhenius, Immuno-Chemistry (Macmillan Co., 1907), and Quantitative Laws of Biological Chemistry (Bell, 1915), Ergebnisse der Physiol. vii. Jahr., 1908, and Jour. of Hygiene, viii.; Bordet, Ann. Inst. Pasteur. 1899, 1900, 1903; Craw, Jour. of Hygiene, vii., ix.; McKendrick, Proc. Roy. Soc. Lond. B. 1911; Gengou, Jour. State Med. 1912, xx. (Summary and full Bibliog.). Many abstracts in J. Chem. Soc.]

Anaphylaxis. Under certain conditions, an antigen on injection instead of conferring in-susceptibility gives rise to increased susceptibility, and this may occur not only with definite toxins but also with proteins, such as egg-white and blood-serum, which are ordinarily innocuous. Thus, if a minute dose of horse-serum be injected into a guinea-pig and three weeks later a second somewhat larger dose be injected, the animal will collapse and probably die in a few minutes. This state of increased susceptibility is known as 'anaphylaxis.' If a course of serum injections be given at intervals not exceeding 14 days, anaphylaxis does not occur. The production of anaphylaxis has been explained as follows: the first serum injection is followed by the formation of an anti-body. This anti-body then reacts with the second dose of serum and in the presence of complement generating a substance, 'anaphylatoxin,' which causes spasm of the bronchial muscles and suffocation. R. T. H.

TOXYNONE. Trade name for sodium m-acetyl amino-mercuribenzoate



TRACHYTE. A volcanic rock composed mainly of alkali-felspar with usually only small amounts of ferro-magnesian minerals. The presence of the latter give the varieties hornblende-trachyte, augite-trachyte, and mica-trachyte. In mineral and chemical composition they correspond to the coarse-grained plutonic syenites; whilst in appearance they are very like the rhyolites, differing from these in having little or no free silica (when present this is often tridymite rather than quartz). The rock is fine-grained and usually light-greyish in colour. Owing to its more or less cellular structure, it is harsh and rough to the touch, hence the name, from *τραχύς*, rough. Sp.gr. 2.2-2.7; porosity 3-6 p.c.; crushing strength 455-730 tons per square foot. In the normal potash-trachyte the felspar is orthoclase of the sanidine variety, which, besides being present in the groundmass, may form porphyritic crystals sometimes of large size (e.g. on the Drachenfels on the Rhine). In the soda-trachytes anorthoclase and albite are also present. With increasing alkalis there is a passage to phonolite (*q.v.*). The following analyses are of trachyte from: I, Plateau de l'Angle, Auvergne. II, mica-hypersthene-trachyte, from Monte Amiata, Tuscany (also SiO_2 0.08, Cl 0.01, α 0.33, Li_2O , trace). III, Algersdorf, Midland Mountains of Bohemia (also BaO 0.06, Cl, F, traces; contains sanidine 60, plagioclase 30, augite 5, magnetite 2, sphene 0.8, apatite 0.5 p.c.). IV, 'Piperno' from Arecco quarries, Pianura, Naples (also NaCl 0.19). V, Whittin Hill, Jedburgh, Scotland (Old Red

Sandstone age). VI, Garleton Hills, Haddington-shire (Carboniferous age).

	I.	II.	II.	IV.	V.	VI.
SiO ₂	63.53	64.76	64.69	61.74	62.44	62.61
TiO ₂	—	0.42	0.31	—	—	—
Al ₂ O ₃	17.81	18.48	18.34	19.24	18.99	18.17
Fe ₂ O ₃	3.92	0.74	—	4.12	3.35	0.82
FeO	—	2.74	3.44	—	1.80	4.25
MnO	—	trace	trace	—	0.25	0.20
CaO	2.31	3.24	1.72	1.14	1.84	2.58
MgO	1.10	1.74	0.50	0.39	1.37	0.74
K ₂ O	5.21	5.49	6.46	5.50	5.02	4.02
Na ₂ O	4.76	2.67	4.61	6.68	2.65	6.49
P ₂ O ₅	—	trace	0.18	—	—	—
H ₂ O	1.16	1.62	0.24	1.12	2.48	0.80
	99.80	100.32	100.57	100.12	100.19	100.18
Sp.gr.	2.64	2.56	2.57	2.59	2.55	2.6

Recent and Tertiary trachytes are found in the Rhenish and Eifel district, Auvergne, central Italy, Canary Islands, &c. These are used on the Continent for building stones, and occasionally for millstones. A variety called locally *piperno* is distinguished by dark flame-like streaks parallel to the lines of flow in a lighter ground; this is from Pianura and Soccavo near Naples, where it is used as a building stone. In the British Isles the trachytes of the Exeter district are of Permian age, and those of the central valley of Scotland of Carboniferous age; these are quarried for road-stones. L. J. S.

TRAGACANTH. *Tragacanthin v. GUMS.*

TRASS v. TUFF.

TRAUMATOL v. SYNTHETIC DRUGS.

TRAVERTINE, Calc-sinter, or Calcareous Tufa (*Tuf calcaire*, Fr.; *Kalktuff*, *Tuffstein*, Ger.). A porous, cellular variety of limestone formed by the direct chemical precipitation of calcium carbonate, as the mineral calcite, from calcareous springs. It is of common occurrence in limestone districts, more particularly in those of declining volcanic activity. The liberation of carbon dioxide, on which the precipitation depends, is assisted by the agitation of the water in rapidly-running streams and cascades, and also to a considerable extent by water plants and algae, the material being often deposited around and encrusting reeds, twigs, and mosses. Even in the hot springs at Karlsbad in Bohemia microscopic plants have been found to be important agents in determining the deposition of the calcareous tufa or *Sprudelstein*, which here consists of the mineral aragonite.

The typical locality is at Tivoli, the ancient Tibur, near Rome; hence the name, from the Latin *lapis tiburtinus*, through the Italian *tiburtino* and its corrupted form *travertino*. Here the most important deposit, with a thickness of 500 feet, occupies the site of an ancient crater lake into which issued the sulphuro-calcareous waters of the Acque Albule thermal springs. The material is being deposited under the same conditions at the present day in the Lago di Zolfo in the Roman Campagna. It is also seen in process of formation at the cataracts of the Anio at Tivoli. Travertine is the principal building stone of ancient and modern Rome. The quarries of Barco, on the Anio, furnished the stone for the Colosseum, and those of Fosse the material for St. Peter's church. To supply modern Rome new quarries have been opened at the Villa Adriana below Tivoli. Roman travertine has also been exported, being used,

for instance, for the columns supporting the arched roof of the new (1910) railway station in New York. The stone is whitish or light cream-coloured, porous, and with wavy lines of lamination; sp.gr. 2.35. When freshly quarried it is soft enough to be cut with a saw, but it hardens on exposure (N. Pelati, I Travertini della Campagna Romana, Rome, 1882; P. Zezi, in H. J. Johnston-Lavis's *South Italian Volcanoes*, Naples, 1891, 83).

Similar deposits of travertine are formed by the thermal springs at Clermont and Vichy in the Auvergne, Hieropolis in Asia Minor, &c. Analyses of travertine from Vichy (C. Girard and F. Bordas, C.R., 1891, 132, 1423) show CaCO_3 91.71-97.17, MgCO_3 1.01-2.10 p.c., with small amounts of carbonates of sodium, potassium, manganese, and iron, sodium phosphate, aluminium sulphate, ferric arsenate (trace to 0.342 p.c.), alumina, silica, insoluble residue, and traces of copper, barium, lithium, and chlorine. In the British Isles small deposits are found in limestone districts, e.g. at Matlock Bath in Derbyshire, Knaresborough in Yorkshire, and it was formerly quarried at Dursley in Gloucestershire and elsewhere as a building stone, but now it is employed only for rock-gardens and aquaria. In all these instances the travertine is of recent formation, but material of the same mode of origin, though now more compacted, is met with in the geological series of sedimentary rocks

L. J. S.

TREACLE *v.* SUGAR.

TREE WAX *v.* *Insect wax*, art. WAXES.

TREHALOSE *v.* CARBOHYDRATES.

TREMOLITE *v.* ASBESTOS AND HORNBLÉNDE.

TRENT SAND. A sand found in the Trent, Severn, and in other rivers; used for polishing.

TRICALCOL. Trade name for a combination of tricalcium phosphate and albumen.

TRICARBIN (*Glycarbin*). Glyceryl carbonate.

TRIDECAIC or **TRIDECYLIC ACID** $\text{C}_{13}\text{H}_{27}\text{COOH}$ is obtained by the oxidation of methyl tridecyl ketone; it crystallises in thin plates; m.p. 40.5° ; b.p. 236° (100 mm.) (Krafft, Ber. 1879, 1668).

TRIDYMITE. One of the three crystalline modifications of native silica, SiO_2 , of much less common occurrence than quartz (*q.v.*) but more frequent than cristobalite (*q.v.*). The crystals have the form of thin hexagonal plates or scales, which are often grouped with a fan-like arrangement or in rosettes. These crystals are, however, pseudo-hexagonal, since, when examined under the polarising microscope, they are seen to be built up of two or more optically biaxial individuals, the symmetry of which is probably orthorhombic. At a temperature of 117° these optical anomalies disappear, and the crystals are then optically uniaxial and truly hexagonal. The hexagonal plates themselves are also twinned together, often in radial groups of three; hence the name of this mineral, from *τρίδυμος*, threefold. Other more complex types of twinning also exist, producing at times pseudocubic forms. The crystals are dull and of a white or greyish colour. They are quite small, usually 1 or 2 mm. across, and only exceptionally as much as $\frac{1}{2}$ cm. Sp.gr. 2.28-2.3; H. 7; mean refractive index (Na) 1.477. In addition

to the much lower sp.gr., the mineral also differs from quartz in being soluble in a boiling solution of sodium carbonate. The crystals are, however, often altered to an aggregate of differently orientated grains of quartz, being, in fact, paramorphs of quartz after tridymite.

Tridymite occurs principally in acid volcanic rocks—rhyolite, andesite, and especially trachyte—the crystals being attached to the sides of cavities in the rock. It is also found in blocks of sandstone and quartzite that have been caught up and baked by lavas. Well-known localities are in trachytes at the Euganean Hills near Padua, the Drachenfels on the Rhine, Mont Dore in Auvergne, &c. At the Cerro San Cristobal, near Pachuca in Mexico, it occurs together with cristobalite in andesite. Other modes of occurrence are: as crystals embedded in opal; in zeolitised Roman tiles at the hot springs of Plombières in France; in fulgurites produced by the fusing of siliceous rocks by lightning; and rarely (as 'asmanite') in meteoric stones and irons. It has also been observed as a furnace product, e.g. in the vitrified walls of zinc muffles, and as fibrous concretionary masses in blast furnaces; and it has been formed by the burning of stacks of straw. It has been produced artificially by a variety of methods, both by wet methods (hot solutions under pressure) and by dry fusion. The silica skeleton obtained by dissolving silicates in blowpipe beads of microcosmic salt consists of tridymite. The best crystals are obtained from quartz in a sodium tungstate fusion. The products are only to be distinguished by their optical characters under the microscope. But the very frequent formation by artificial means unintentionally has only recently been recognised. As noted below, quartz is converted into tridymite at 870° with a considerable increase in volume (16.2 p.c. corresponding to the change in sp.gr. from 2.65 to 2.28). This has an important bearing on the siliceous refractory materials used for furnace linings and silica-bricks. Coarsely powdered quartzite quickly heated to 1400° in presence of a small quantity of a catalyst is converted after five or six hours into almost pure tridymite (Rebuffat, Trans. Ceram. Soc. 1923-24, 23, 14; J. Soc. Chem. Ind. 1924, 43, B. 514).

In addition to the reversible inversion of α -tridymite to β -tridymite at 117° noted above, the heating curve shows a second break at 163° , indicating another inversion β -tridymite \rightarrow β' -tridymite. Here there is no observable change in the optical characters, and the change is perhaps one of degree of symmetry, analogous to α -quartz \rightarrow β -quartz at 575° . At ordinary temperatures quartz is the only stable crystalline modification of silica, but at 870° it passes over into tridymite with an accompanying increase in volume. At 1470° this tridymite is changed into cristobalite, which melts at 1626° .¹ Tridymite is therefore the stable form between the temperatures 870° and 1470° , but the velocity of transformation being slow it can also exist at lower temperatures. In this connection we

¹ C. N. Fenner, *The Stability Relations of the Silica Minerals*, Amer. J. Sci. 1913, 24, 231, 77, also Shepherd, Rankin, and Wright, 1922, 1900, 28, 232; C. Johns, *Geol. Mag.* 1906, 2, 118. Ferguson and Merwin, Amer. J. Sci. 1918, 46, 417 give the melting-point of tridymite as 1670° and of cristobalite as 1710° .

may recall the frequent occurrence in nature of paramorphs of quartz after tridymite; and also the fact that tridymite is not found in older (pre-Tertiary) volcanic rocks. L. J. S.

TRIFOLIN v. GLUCOSIDES.

TRIGEMIN, TRIPHENIN, v. SYNTHETIC DRUGS.

TRIGONELLINE (*Methyl betaine of nicotinic acid*) $C_8H_{10}NO_2$ is an alkaloid which occurs in the seeds of *Trigonella Foenum-graecum* (Linn.); in ordinary peas (*Pisum sativum* [Linn.]); in hemp seeds (*Cannabis sativa* [Linn.]) (Jahns, Ber. 1885, 18, 2518; Schulze and Frankfurt, *ibid.* 1894, 27, 769; Schulze and Winterstein, Landw. Versuchs. Stats. 1895, 46, 23); in commercial strophanthine and in the seeds of *Strophanthus hispidus* (DC.) and *S. Kombé* (Oliver) (Thoms, Ber. 1898, 31, 271, 404; Karsten, Chem. Zentr. 1902, ii. 1514). Trigonelline has also been found in an animal, the sea-urchin (*Arbacia pustulosa*) (Holtz, Kutscher and Thielmann, Z. Biol. 1924, 81, 57; Chem. Soc. Abstr. 1924, 126, i. 907).

Preparation.—The powdered seeds are extracted with alcohol; after distilling off the latter, lead acetate and caustic soda are added, and the alkaloid is separated by means of potassium bismuth iodide and sulphuric acid. The precipitate is then treated with caustic soda to separate albuminoids, the filtered solution is neutralised with sulphuric acid and precipitated with mercuric chloride. The choline so precipitated is removed by filtration, the filtrate acidified with sulphuric acid, and the trigonelline in the form of its mercury iodide salt is then precipitated. The free base is obtained by decomposing the double salt with a sulphide (see Schulze, Zeitsch. physiol. Chem. 1909, 60, 155).

Trigonelline has also been obtained by treating nicotinic acid with methyl iodide, and the product of the reaction with silver hydroxide (Hantzsch, Ber. 1886, 19, 31); or by the oxidation of nicotine *iso*-methoxyhydroxide, with potassium permanganate (Pictet and Genequand, Ber. 1897, 30, 2117, 2122).

Trigonelline crystallises with one molecule of water, forming colourless, flat prisms of feeble saline taste and neutral reaction. It is hygroscopic, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether, benzene, and chloroform. When heated, it loses its water of crystallisation and dissolves or melts in the latter at 130°. The anhydrous alkaloid darkens when heated at 200°, and melts at 218° (decomp.). When heated with barium hydroxide at 120° trigonelline evolves all its nitrogen as dimethylamine, and when heated with excess of hydrochloric acid, it yields nicotinic acid and a gas, probably methy chloride (Jahns, Ber. 1887, 20, 2840). It gives the usual reactions of an alkaloid with reagents.

On reduction of trigonelline with hydrogen in presence of platinum black it forms products resembling, but apparently not identical with, those of arecolidine (Winterstein and Weinhegen, Zeitsch. physiol. Chem. 1917, 100, 170).

A *hydrochloride*, *platinochloride*, and two *aurochlorides* $C_8H_{10}NO_2 \cdot HCl \cdot AuCl_3$, m.p. 198°, and $4(C_8H_{10}NO_2) \cdot 3HCl \cdot 3AuCl_3$, m.p. 186° (Jahns, l.c.; Schulze and Frankfurt, l.c.), are known. The ferrocyanide and ferriocyanide crystallise in red and yellow prisms respectively (Roeder, Ber.

1913, 46, 3724). For the physiological action of trigonelline, see Kohlrausch, Chem. Zentr. 1909, ii. 465; Zeitsch. Biol. 1911, 57, 273; for its origin, see Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 46 (v. BETAINES).

TRIHYDROXYBENZENE v. PHENOL AND ITS HOMOLOGUES.

TRIKETOHYDRINDENE v. KETONES, INDENE.

TRIKETONES v. KETONES.

TRIMETHOL. Trimethylmethoxyphenol.

TRIMETHYLACETIC ACID v. VALERIC ACIDS.

TRIMETHYLBENZENES v. CUMENES.

TRIMETHYLENE v. PROPYL.

TRIMETHYLHISTIDINE v. BETAINES.

TRIMETHYLHYDROXYBENZENE v. PHENOL AND ITS HOMOLOGUES.

TRIMYRISTIN. Piettre and Roeland (Compt. rend. 1924, 278, 2283; Analyst, 1924, 49, 437) obtained 2 grms. of trimyristin (see Vol. IV., p. 405) by dissolving the fat from one litre of milk in a mixture of ether and alcohol and allowing the solution to cool slowly.

TRINITRIN. Syn. for nitroglycerin.

TRINITROPHENOL v. PICRIC ACID.

TRIONAL (*diethylsulphonemethylethylmethane* or *methyl sulphonal*) $CH_3(C_2H_5)_2C(SO_2C_2H_5)_2$ is prepared, like sulphonal and tetronal, from methyl ethyl ketone and ethyl mercaptan (Fromm, Annalen, 1889, 253, 150; D. R. P. 49073; Frdl. 1887-1890, ii. 521). It forms colourless, odourless, lustrous square tablets, m.p. 76°, soluble in 320 parts of cold water, but more readily so in boiling water, in ether, and in alcohol. It is employed in medicine for the same purposes as sulphonal and tetronal, v. SYNTHETIC DRUGS. For its detection, v. SULPHONAL AND TETRONAL.

TRIPHANE v. SPODUMENE.

TRIPHENIN. *p*-Propionyl-phenetidine, used as an antipyretic.

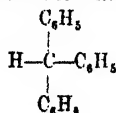
TRIPHENYLMETHANE COLOURING MAT-

TTERS. This is the generic name of a very large and varied class of artificial dye-stuffs which have been obtained by very different methods. Some of the oldest artificial dye-stuffs belong to this group. Their generic connection was, in many instances, not known until their constitution was fully ascertained. When this had been done, a large number of new dye-stuffs belonging to the same class was prepared by direct synthesis. The members of this group vary more than those of any other in their physical properties; they represent almost every possible shade, and include dye-stuffs suitable for almost every kind of dyeing and printing process. They are applicable to silk, wool, and cotton dyeing; as a rule, they are of very pure and brilliant shades—in fact, the most brilliant of all colouring matters are found amongst them. Many are rather fugitive, especially the older ones—magenta-red and its congeners. It is for this reason that aniline dyes generally have been declared fugitive and unstable by people of hasty judgment. This want of stability is, however, not characteristic of the triphenylmethane group; some of the best and most permanent dye-stuffs belong to it. It may be well to remark at once that resistance to light and other influences seems not to be directly related to the chemical constitution of these substances, as it is frequently observed that of two

dye-stuffs of very similar constitution one may be very fugitive, whilst the other is remarkable for its fastness. The fastness of these and other dye-stuffs also depends to some extent on the manner in which they are applied to the textile fibre.

The members of this family are not, like those of the azo-group, connected by one generic method, by which all of them might be produced from various materials. Nor is it possible to enumerate a number of general synthetic methods which result in their production. The methods applicable are so numerous that no generalisation is possible. The only connecting link between all these dyes is their chemical constitution, which is now well established in almost every case; it is also in this constitution that we find the necessary criteria for the subdivision of the group. Some introductory remarks about the constitution of these dyes are therefore necessary for a complete revision of the subject.

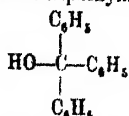
If we consider the constitution of these colouring matters, we observe that there is but one characteristic feature common to them all. This is the presence of an atom of carbon connected by three of its valencies to three aromatic radicles. The compound of the simplest constitutional formula in which this 'central carbon' (as we will henceforth call it) is observed is the hydrocarbon triphenylmethane, the formula of which is $C_{19}H_{15}$:



Triphenylmethane thus becomes the prototype of all the members of this group; it is for this reason that the name of *triphenylmethane colouring matters* was chosen.

Triphenylmethane was first prepared by Kekulé and Franchimont, in 1872, by heating benzylidene chloride with mercury diphenide to 150° (Ber. 5, 907). Its formation has since been observed in numerous reactions. The best method for preparing it consists in treating a mixture of two parts of chloroform and seven parts of benzene with aluminium chloride, until no more hydrogen chloride is given off. The resulting liquid is washed with water and dried. On distillation it yields benzene, diphenylmethane, and triphenylmethane. The last may be purified by crystallisation. This method was indicated by Friedel and Crafts (Ann. Chim. Phys. [vi.] 1, 489). Triphenylmethane is obtained in colourless crystals; m.p. 92° ; b.p. 358° – 359° . It is capable of forming a molecular compound with benzene. Of its derivatives the following three are important on account of their relations to the colouring matters under consideration.

Triphenyl-carbinol $C_{19}H_{15}O$ is the tertiary alcohol derived from triphenylmethane:



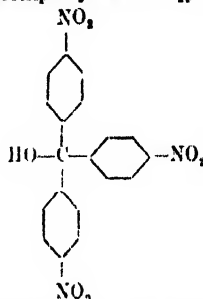
It is easily obtained by oxidising the hydrocarbon by means of chromic acid. It forms

colourless crystals, melting at 159° and boiling at 360° (E. and O. Fischer, Annalen, 194, 271).

In boiling glacial acetic acid it is readily reconverted to triphenylmethane either by hydriodic acid (Tschitschibabin, Ber. 1911, 44, 441) or by trioxymethylene in presence of a small quantity of conc. sulphuric acid (Bauds, Anal. Fis. Quim. 1913, 11, 599; cf. J. Chem. Soc. 1914, i. 279). For the use of formic acid for this purpose, see Guyot and Korache (Comp. rend. 1912, 154, 121, and 1913, 156, 1324).

Trinitrotriphenylmethane $C_{19}H_{13}N_3O_6$ is obtained by treating the hydrocarbon with strong nitric acid. Crystals, melting at 203° . Chromic acid transforms it into trinitrotriphenylcarbinol (E. and O. Fischer, *ibid.* 194, 256).

Tri-*p*-nitrotriphenylcarbinol $C_{19}H_{13}N_3O_7$:



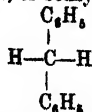
is best crystallised from glacial acetic acid and forms small crystals, melting at 171° – 172° and soluble in alcoholic potash solution with a beautiful reddish-blue colour.

None of the above substances is a colouring matter, nor are they even coloured. But if we reduce trinitrotriphenylcarbinol by adding zinc-dust to its solution in acetic acid, we obtain triaminotriphenylcarbinol, which is identical with pararosaniline. By showing this identity, E. and O. Fischer solved the problem of the constitution of this very important colouring matter. Leucaniline, the reduction product of rosaniline, was shown to be identical with triaminotriphenylmethane. This discovery became the starting-point for very important theoretical and practical work. All the congeners of rosaniline were shown to be derivatives of triphenylmethane or analogous hydrocarbons, and new synthetic methods were devised by which such derivatives could be obtained.

It is quite obvious that not only triphenylmethane, but also all its homologues and analogous hydrocarbons, are parent substances of dye-stuffs. The number of such hydrocarbons indicated by theory is very large, since every one of the three phenyl radicles connected with the central carbon may be replaced by any other aromatic radicle. Every one of the hydrocarbons thus formed is capable of yielding, like triphenylmethane itself, a very large number of colouring matters, as will be seen from subsequent considerations. It thus becomes evident that the theoretical number of possible triphenylmethane colouring matters is almost unlimited. It has, however, been shown that the variation of the aromatic radicles connected with the central carbon is not the only point of importance as regards the variation of the shades and properties of the resulting

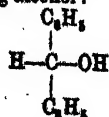
dye-stuffs. The triphenylmethane colouring matters in actual use are the derivatives of a very few hydrocarbons, of which triphenylmethane itself is by far the most important. Tolyldiphenylmethane, ditolyldiphenylmethane, tritolyldiphenylmethane, and naphthylidiphenylmethane are the principal parent substances of a large number of colouring matters, which at present form the object of regular and extensive manufacture, and of several hundred more which have been prepared and patented without coming into general use. The extensive range of shade and general applicability, so characteristic of the colouring matters of this class, and unequalled by any other class of dye-stuffs known, is not so much a result of the variation of the hydrocarbons forming their parent substances, as of the extremely large number of coloured derivatives which may be produced from every one of these hydrocarbons. No other branch of the chemistry of dye-stuffs is so extremely fertile in the synthetical methods at its disposal as this, and every one of these methods forms an easy way for the production of a considerable number of dye-stuffs, which can generally be produced by this one method alone. Many of these methods, both empirical and synthetical, have been patented, and some of these patents are of great value and importance. They are generally 'process' patents, claiming new methods of manufacture; in this respect they form the exact counterpart of the still more numerous 'substance' patents for azo-colouring matters, which, being all based on the same method of work, only claim the novelty of the product obtained by varying the ingredients of the process.

Before entering into the details of the constitution of triphenylmethane dye-stuffs, and the connection of this constitution with the properties of the dyes, we have to describe another substance closely related to triphenylmethane, some of the derivatives of which are dye-stuffs similar to those derived from triphenylmethane itself, whilst others play an important part in the process for the production of triphenylmethane colouring matters. This substance is also a hydrocarbon, derived from methane by replacing only two of its hydrogen atoms by the aromatic radicle phenyl. This hydrocarbon is *diphenylmethane*, or benzylbenzene $C_{13}H_{12}$:



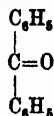
It was discovered by Zincke in 1873 (Annalen, 159, 374), and is best prepared by the method indicated by Friedel and Baisohn (Bull. Soc. chim. [ii.] 33, 337), by adding aluminium chloride to a mixture of 1 part benzyl chloride with 5 parts of benzene. It melts at $26^{\circ}-27^{\circ}$, and boils at $261^{\circ}-262^{\circ}$. It forms white crystals, possessing an agreeable odour of oranges. Of its derivatives the following are of practical importance:—

Diphenylcarbinol or benzhydrol $C_{15}H_{14}O$ is the corresponding alcohol:



It is prepared by boiling benzophenone with alcoholic potash solution and zinc-dust. It forms white crystals, melting at $87^{\circ}5'-68^{\circ}$, boiling at $297^{\circ}-298^{\circ}$ (Linnemann, Annalen, 133, 6; Zagumenny, *ibid.* 184, 174).

Benzophenone $C_{15}H_{10}O$ is the second product of oxidation of diphenylmethane, to which it stands in the same relation as that which exists between propane and acetone. Benzophenone is the typical ketone of the aromatic series



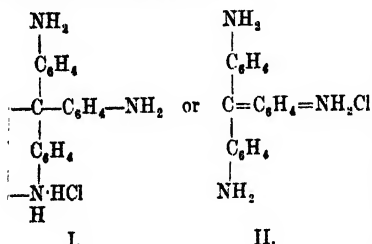
It is prepared by the process which led to its original discovery, by distilling calcium benzoate, or, better still, by distilling a mixture of calcium and zinc benzoate. Another process consists in adding aluminium chloride to a solution of carbonyl chloride $COCl_2$ (phosgene) in pure benzene, or to a mixture of benzene with benzoyl chloride. Benzophenone forms beautiful prismatic crystals, melting at $48^{\circ}-48^{\circ}5'$, distilling at 305° (Péligot, Annalen, 12, 41; Chancel, *ibid.* 72, 279; Friedel, Crafts and Ador, Ber. 10, 1854) (v. QUINONES).

The amino derivatives of diphenylmethane diphenylcarbinol, and benzophenone, which are of special importance in the chemistry of the triphenylmethane dye-stuffs, will be described subsequently in connection with the dye-stuffs to which they give rise.

The substances mentioned so far, although the parent substances of so many beautiful dyes, are all perfectly colourless. Even triaminotriphenylcarbinol, which is identical with *p*-rosaniline, is perfectly colourless; it only becomes a dye-stuff by being dissolved in an acid, a reaction from which one might infer that *p*-fuchsin, the typical magenta colour, is merely a salt of *p*-rosaniline. This is, however, not the case, although colour-makers are apt to call, for simplicity's sake, the rosanilines 'magenta bases.' In this connection a decision of the U.S.A. Customs Authorities is of interest, in that they upheld the claim of an importer, that rosaniline, not being itself a dye, should be subject to duty (20 p.c. ad. val.) as 'a coal-tar product not being a colour or dye,' and not to the duty (30 p.c. ad. val.) levied upon coal-tar colours or dyes (U.S.A. Cust. decision, Oil Paint and Drug Rep. Nov. 3, 1913, cf. J. Soc. Chem. Ind. 1913, 1060). The dissolution of any or either of the aminocarbinols in an acid is invariably accompanied by a condensation in the molecule, and a loss of one molecule of water. The basic triphenylmethane colouring matters are therefore free from oxygen (unless they contain it in the shape of water of crystallisation); if we decompose the salts, by the addition of an alkali, coloured bases are formed, which, however, are very unstable. They take up, at once, one molecule of water, and re-form the original colourless or faintly-coloured carbinol base. If the precipitation is carried out by means of ammonia instead of sodium hydroxide or carbonate, or if ammonia be present in the liquid, the carbinol base is partly or wholly transformed into the corresponding amino compound.

as has been shown by Villiger and Kopetschni, Ber. 45, 2910, and by Nölting and Saas, *ibid.* 48, 952. By this observation it is clearly shown that something more than the presence of the 'central carbon' is necessary for the formation of a triphenylmethane colouring matter. We have, therefore, to consider the constitution of the colouring matters themselves to obtain a knowledge of the chromophoric group of these dye-stuffs. This consideration leads at the same time to an easy and useful classification, to a subdivision into a series of small groups, the members of which show a closer connection in their methods of formation, their physical properties, and their manner of application.

The constitution of parafuchsin is now established beyond any doubt. It may be represented by the following formulae :



which are practically identical, II. corresponding to the modern way of expressing 'quinonoid' structure. This formulation will therefore be used exclusively in this article to explain the constitution of the dyestuffs to which it refers, whilst formulae corresponding to I. have been used in the first edition of this work. For alternative formulae more recently suggested by Kauffmann, see Ber. 1912, 45, 781. For consideration of the salts of triphenylmethane bases which are formed in strongly acid solutions, see Kehrman, Ber. 1918, 51, 468. The formulae chosen show also the typical constitution of all the congeners of magenta, every one of which may be represented by similar formulae, in which either one or more of the phenyl radicles is replaced by other aromatic radicles, or one of the amino groups replaced by hydrogen, or one of the six available hydrogen atoms of the amino groups replaced by radicles of the fatty or aromatic series, or several of these changes introduced at the same time. It will at once be obvious that several thousand different combinations may thus be produced, all colouring matters of different shades, but showing in their properties a general resemblance to parafuchsin. The constitutional formulae of all these colouring matters have but one thing in common besides the 'central carbon' (which is, as has been said, characteristic not only of these, but also of all the other triphenylmethane colouring matters); this one essential feature is the quinonoid nature of the substance, expressed in the structural formula either by the connection between the central carbon atom and the pentavalent nitrogen (as shown in formula I.), or, as it has become customary of late, by shifting the double valencies in the benzene hexagon and connecting it accordingly with the other parts of the molecule, as shown in formula II. We

have, therefore, a perfect right to claim this invariably present quinonoid configuration as the essential feature of the whole molecule, and as the cause of its being a colouring matter. It forms a part of the chromophoric group of the fuchsin family.

It is, however, important to notice that, no matter how we write the structural formula of *p*-fuchsin or any of its congeners, whether we use the older or the more modern way of expressing the quinonoid nature of the substance, one of the amino groups present is always taking part in the quinonoid chromophoric group and therefore is no longer available as an auxochromic group. To supply this, at least one more amino-group must be present, and this is the reason why only di- or poly-amino derivatives of triphenylmethane can become mother-substances of dye-stuffs belonging to this group. On the other hand, both the amino groups of auxochromic nature, as well as the one entering into the chromophoric part of the molecule, may be replaced by other suitable groups. The hydroxyl group with its tendency to form salts by combining with metallic ions is as important an auxochromic group in the series of triphenylmethane dye-stuffs as in any other. And the quinonoid imino group contained in the chromophore, may, as in other dye-stuffs, be replaced by an oxygen atom acting in similar capacity. Thus we obtain two separate groups of dye-stuffs, the first of which, generally called the *fuchsin group*, is characterised by the presence of nitrogen and the basic nature of its members; the second, called the *aurin group*, by the absence of nitrogen and the phenolic character of the dyestuffs it embraces. In addition to these two groups, a third one, the *phthalein group*, has been established by the common consent of all authors on the subject. This group contains a large number of important dye-stuffs of both basic and acid nature, which have this in common, that they are all derived from phthalic acid and take their 'central carbon' from one of the carboxyl groups of this acid, whilst the other, remaining available, enters the molecule of the dye-stuff and thus renders the latter a true organic acid, which is not necessarily the case amongst the members of the fuchsin and aurin group. Moreover almost all the phthalein dye-stuffs of any practical importance contain, in addition to the typical chromophore of the triphenylmethane colouring matters, an additional one in the shape of the 'pyrone' ring, formed by the elimination of water from certain suitably placed hydroxyl groups of the molecule. This pyrone ring will be easily recognised in the formulae of the members of the phthalein group to be given subsequently. The fact that only those phthaleins, which contain this pyrone ring, are colouring matters of any practical value, greatly diminishes the number of possibilities for the synthesis of such dye-stuffs, which might be made to form a class of their own, if it had not become customary to treat them as a special division of the triphenylmethane group of colouring-matters.

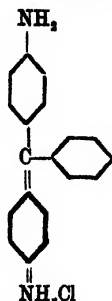
We now proceed to give a detailed account of these three groups and their various members, of which, however, we shall enumerate only those which are, either scientifically or practically, important. For a complete list we refer the

reader to the well-known tables of Schultze and Julius,¹ or the more recent "Colour Index."²

I. THE FUCHSIN GROUP.

(A) *Diaminotriphenylmethane derivatives.*—The simplest type of these colouring matters is

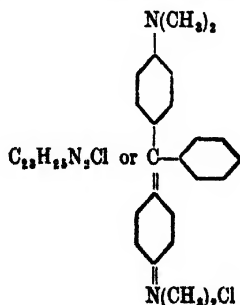
1. Benzaldehyde violet $C_{11}H_{11}N_2Cl$ or



which may be prepared from diaminotriphenylmethane by oxidation. The yields are, however, very poor, and the colour itself is of no great value. Its manufacture has, therefore, never been taken up.

The derivatives of this substance, however, in which the hydrogen of its two amino groups is replaced by various radicles of either the fatty or aromatic series, are of great value and importance. Of these, the oldest, best known, and simplest in its constitution, is

2. Benzaldehyde green. (Syn. *Malachite green*, *New green*, *Victoria green*, *Fast green*, *Diamond green*, *Benzoyl green*, *Benzal green*.)



This product was discovered almost simultaneously by Otto Fischer (1877; Ber. 10, 1625) and O. Döbner (1878; *ibid.* 11, 1236), who prepared it by different methods. For some time it was believed that Döbner's product was different from Fischer's until their identity was finally established. Döbner's process was patented (D. R. P. 4322). Fischer's process found, however, more favour with the majority of manufacturers, and has mostly been adopted.

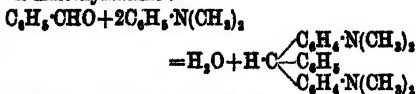
Fischer's process gave bad yields and a poor product at first, until the best method for its manufacture was worked out. It consists in the following operations:—

(a) Manufacture of tetramethyldiaminotri-

¹ Gustav Schultze und Paul Julius. *Tabellarische Uebersicht der künstlichen organischen Farbstoffe*. Berlin (Fifth edition, 1914.)

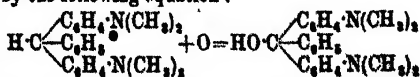
² "Colour Index," published by the Society of Dyes and Colourists, Bradford, 1934-5.

phenylmethane by the action of benzaldehyde on dimethylaniline:



The base obtained in this reaction is generally called 'green leuco base' by the manufacturers. For preparing it one molecule of benzaldehyde is mixed with very little more than two molecules of absolutely pure dimethylaniline, a substance capable of absorbing the water formed in the reaction being added. Dry zinc chloride was originally employed, and is still used by many manufacturers. In quantity it should be equal in weight to the aldehyde employed. Hydrochloric, sulphuric, or anhydrous oxalic acid, or acid sodium sulphate may be used instead of the zinc salt. The mixture is heated in a jacketed still to 100°–110° for about forty-five to forty-eight hours. The product is then transferred to a still, a sufficient quantity of caustic soda is added to make the mixture alkaline to test-paper, and a current of steam is blown through the liquid in order to remove every trace of dimethylaniline and benzaldehyde. The leuco base is not volatile; it remains in the still in the shape of a viscid mass, which solidifies into white crystals after a while. This base is now subjected to the second operation.

(b) Oxidation into green. It is here that great difficulties were encountered in the beginning of the manufacture. Special conditions are required to obtain a good crystallisable dye-stuff. If these are not strictly adhered to, a non-crystallisable green is the result. The latter is different from the crystallisable substance in composition, containing one methyl group less, which is lost in the shape of formaldehyde by a too powerful action of the oxidising agents. The following conditions give excellent results: 33 kilos of leuco base are dissolved in 25 kilos of ordinary hydrochloric acid, and diluted with 200 litres of water; 30 kilos of ordinary acetic acid of 45–50 p.c. are then added. It is necessary that these two acids should be present; neither of them can be replaced by another acid of equal strength. The solution is then oxidised in the cold (in the summer it is advisable to add some ice) with a paste of lead peroxide of known strength. The peroxide should be tested by the oxalic acid method (determination of the CO_2 evolved from an excess of oxalic acid by the peroxide in question), and not by the iodometric method, as the latter gives too high results. Every kind of lead peroxide contains a certain amount of crystalline peroxide, which neither acts on the leuco base, and is therefore quite irrelevant in its oxidation into green, nor on oxalic acid, whilst the iodometric method gives values for both modifications indiscriminately. For oxidising the leuco base the exact quantity of peroxide should be taken, which is indicated by the following equation:

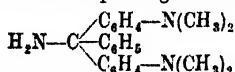


One molecule of active peroxide is, therefore, required for every molecule of the base.

As soon as the peroxide has been added

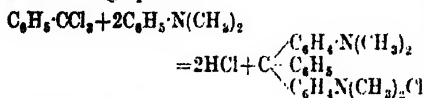
with constant stirring, the liquid turns a deep green. From this liquid the dye-stuff may be separated by various methods; an addition of zinc chloride solution is generally recommended. This, however, precipitates both the crystalline green and the tarry modification which is never quite absent. The following process has given excellent results in the hands of the writer.

The green liquid obtained by oxidation is saturated with common salt. On standing small glittering scales of the lead double chloride of the crystallisable green very soon make their appearance, and are collected on a filter. From the mother-liquor an inferior quality of green may be obtained by adding a solution of sodium sulphate, filtering, and precipitating with zinc chloride and common salt. The crystals of the lead double chloride are dissolved in hot water, and sufficient sodium sulphate is added to precipitate the lead. The liquid is then filtered and precipitated with ammonia. The 'green base' (a mixture of tetramethyl-diaminotriphenyl-carbinol with the corresponding amino derivative



discovered by Villiger and Kopetschni) settles out in the shape of a pink precipitate, which is filtered off and washed. From it the 'green crystals' of commerce may be prepared, either by dissolving it in a hot solution of oxalic acid and allowing the liquid to cool very slowly, or by dissolving it in dilute hydrochloric acid and adding a solution of zinc chloride. Besides these two the iron double salt is also occasionally met with in commerce. The picrate is also sold under the name of 'spirit green.'

Döbner's process.—This consists in heating dimethylaniline with benzotrichloride in presence of metallic chlorides. This process has certain advantages if benzotrichloride is available at a low price. It may be represented by the following equation:



The following proportions are recommended in the patent:

3 parts dimethylaniline,
2 „ benzotrichloride,
1.5 „ zinc chloride.

These are to be heated for three hours to 110° in an enamelled iron vessel with constant stirring. The resulting melt is transferred to a still, and steam is blown through it to remove all excess of trichloride. It is then thoroughly extracted by boiling water. The filtrate is now precipitated by salt, and the precipitate recrystallized from water. The dye-stuff is always obtained in the shape of the zinc double chloride.

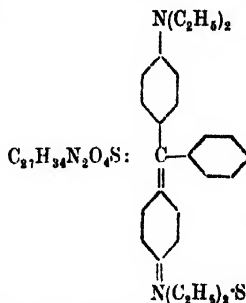
The oxalate of benzaldehyde green forms large plates of an intense grass-green colour, which dissolve easily in hot water. It contains three molecules of oxalic acid to every two of green base.

The zinc double chloride, which has the composition $3(\text{C}_{22}\text{H}_{22}\text{N}_2\text{Cl}) \cdot 2\text{Zn}(\text{I} \cdot 2\text{H}_2\text{O})$, forms green crystals with a fine yellow metallic lustre. It is not quite so easily soluble as the oxalate.

The application of these salts is similar to

that of all the basic dye-stuffs, and need not here be described.

3. Brilliant green. (Syn. *Ethyl green*, *Emerald green*; also all the other names given for the preceding compound, with the addition of the letters G, J, or Y (meaning *gelb*, *jaune*, or *yellow*).



is prepared from diethylaniline by exactly the same process as described for benzaldehyde green. After precipitating the free green base, it is transformed into its sulphate by mixing it with the theoretical quantity of sulphuric acid diluted with its own weight of alcohol. The mixture forms a thick tar at first, but suddenly solidifies into a mass of well-defined crystals.

The shade of this green is considerably yellower than that of the ordinary benzaldehyde green.

4. Victoria green 3 B. $\text{C}_{22}\text{H}_{22}\text{N}_2\text{Cl}_3$. This is a colouring matter prepared from dichlorobenzaldehyde instead of the ordinary benzaldehyde. It is considerably bluer in shade than the ordinary benzaldehyde green. A large number of similarly constituted bluish-greens and greenish-blues is manufactured and sold, especially by the Swiss colour-works.

Acid greens. Considerable importance has always been attached by dyers to the sulpho derivatives of basic colouring matters, because these are more easily and evenly dyed on wool than the hydrochlorides and other salts of the bases themselves. Many attempts have, therefore, been made to obtain acid greens. They were at first only partly successful; at present there are, however, several acid greens in commerce, ranging in shade from a yellowish-green to a clear greenish indigo blue. They are very largely used in wool dyeing, especially for mixed shades.

The oldest of these acid greens, which appeared in the market in 1878, was called

5. Helvetia green or Acid green C. It was the sodium salt of the mono-sulpho derivative of the ordinary benzaldehyde green, prepared either by sulphonating the green itself by means of chlorosulphonic acid, or by sulphonating tetramethyldiaminotriphenylmethane and oxidizing the resulting colourless acid by means of lead peroxide. Neither of these two methods works satisfactorily. For this reason the product has gradually been abandoned, and replaced by the benzyl derivatives, which are more easily prepared, and at the same time much more brilliant in shade.

6. Benzyl acid greens. In the various attempts to prepare acid greens it was found that the phenyl groups, combined with the central carbon, show little tendency to permit of the introduction

$$\begin{array}{c} \text{C}_{27}\text{H}_{36}\text{N}_2\text{O}_7\text{S}_2\text{Na}_2 \text{ or} \\ \text{C}_6\text{H}_5 \diagup \text{C} \begin{array}{l} \text{C}_6\text{H}_4\text{N} \begin{array}{l} \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2\text{Na} \\ \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2\text{Na} \end{array} \\ \text{C}_6\text{H}_4\text{N} \begin{array}{l} \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2\text{Na} \\ \text{CH}_2\text{C}_6\text{H}_4\text{SO}_2\text{Na} \end{array} \end{array} \\ \text{HO} \diagdown \end{array}$$

8. Patentblau, Patent blue, a product of the Farbwerke vorm. Meister, Lucius and Brüning, in Höchst-am-Main. This is a dye-stuff closely allied to the acid greens. It was discovered by Hermann, and patented by the Farbwerke (D. R. P. 46384, 1888, and many additional patents; see also Fritzsche, Ber. 1890, 29, 2291, and Erdmann, Annalen, 1897, 294, 376). It is prepared by a somewhat complicated method.

CN(C)C1=CC=CC=C1C(=C2C=CC(=C(C=C2)N(C)C)S(=O)(=O)C3C(O)C(S(=O)(=O)[Ca+2])C=C3Nc1ccccc1C(=C2C=CC=CC=C2N)N

This is the dye-stuff which was used by O. and E. Fischer for the elucidation of the chemistry of this class of substances (O. and E. Fischer, *Annalen*, 1878, 194, 242; *Ber.* 11, 1079; 13, 2204). It is one of the oldest artificial dye-stuffs; it was discovered in 1858 by A. W. Hofmann (*J.* 1858, 351); and re-discovered by Rosenstiehl in 1869 (*Bull. Soc. Ind. Mulhouse*, 36, 264). For a long time it was considered a substance of merely theoretical interest, because its shade is almost identical

with that of ordinary fuchsin or magenta (see under 2), which is much more easily prepared. At present, however, it is manufactured on a large scale, not as a dye-stuff for sale, but as a raw material for certain blues, which will be mentioned later on.

A large number of reactions have been observed and described which result in the formation of pararosaniline. Of these the following may be mentioned:

(a) Pure aniline heated with carbon tetrachloride yields parafuchsin. This method was used on a manufacturing scale by Monnet and Dury in Lyons.

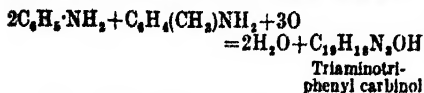
(b) Pure aniline, heated with iodoform, gives a fair yield of parafuchsin hydriodide.

(c) Pure aniline, heated with *p*-nitrobenzyl chloride in the presence of iron filings or iron salts gives a good yield of parafuchsin. This method, or modifications of it, form the substance of Greiff's and Baum's patents (D. R. PP. 15120 and 19304 Greiff, and 14929 Baum).

(d) Pure aurin (rosolic acid), which will be described subsequently, yields parafuchsin if strong ammonia be allowed to act on it for a long time at a high temperature.

(e) It has been shown (v. introduction) that the reduction-product of parafuchsin is paraleuco-aniline, and that the latter is identical with triaminotriphenylmethane. The latter may easily be prepared from triphenylmethane by nitration and reduction, and by various other methods. Attempts have not been wanting to work out a method for the production of parafuchsin from synthetical leucaniline. No good method, however, has hitherto been discovered for this purpose, and all the patents based on this reaction have proved failures. It is very easy to produce a trace of fuchsin in a solution of leucaniline; but no method is known for finishing the reaction.

(f) Mixtures of pure aniline with pure *p*-toluidine yield parafuchsin if subjected to oxidation. This is the usual practical way for the production of parafuchsin. The oxidation may be effected either by arsenic acid or by nitrobenzene. Other oxidising agents—such as mercuric chloride, stannic chloride, &c.—produce the same result, but at a higher cost. The arsenic acid process (which will be described later on) was for some time almost exclusively used for the production of parafuchsin. The chemical reaction which takes place is very simple. Arsenic acid is reduced to arsenious acid. The oxygen which is thus obtained combines with hydrogen of the aromatic bases:



The methyl group of *p*-toluidine is used up for yielding the central carbon around which the other radicles are grouped.

(g) Diaminodiphenylurethane, mixed with aniline and heated with oxidising agents, yields parafuchsin. This synthesis forms the basis of a more modern manufacturing process.

It has already been said that parafuchsin has no advantages over ordinary magenta red for dyeing purposes. It is, therefore, rarely to be met with as a dye-stuff in the market. As a

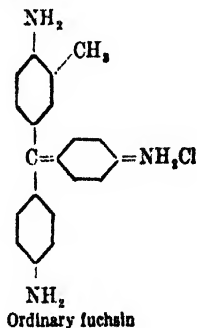
rule the melts are worked up in the same manner as ordinary magenta melts, but the resulting crystals of the pure hydrochloride are redissolved and precipitated in the shape of pararosaniline base by the addition of soda or milk of lime. The base is then used for the production of blues.

Parafuchsin hydrochloride forms small glistening crystals having a metallic green lustre. As a rule, they are very small, much smaller than the crystals of ordinary magenta. Parafuchsin acetate is similar in appearance and crystallises much more easily than the ordinary magenta acetate.

Pararosaniline is important because it is the parent substance of all the various violets, and of some of the blues, which will be described subsequently.

2. Ordinary fuchsin, magenta red, rosein (*rubesine*, *harmaline*, *aniline red*, *azalein*, *solferino*, *erythrobenzine*) $C_{21}H_{19}N_3Cl$, is an article of great importance and of very general application. The latter is due to the fact that it was one of the first artificial dye-stuffs, although not one of the best. A great demand for it has gradually been established, which forces the manufacturers to carry on its production on a large scale, even now, when much better dye-stuffs may be prepared by other methods.

Chemically, this colouring matter may be defined as the higher homologue of parafuchsin, in which one of the phenyl groups has been replaced by a tolyl group:



The product of commerce, though chiefly composed of this substance, invariably contains an admixture of parafuchsin as well as of the higher homologues ($C_{22}H_{21}N_3Cl$ and $C_{23}H_{23}N_3Cl$). Like parafuchsin, it contains four molecules of water of crystallisation.

Fuchsin is invariably prepared by oxidising a mixture of aniline with *p*-toluidine and *o*-toluidine. This mixture is generally known as 'aniline for red,' and was originally produced by the nitration and subsequent reduction of a certain fraction of crude benzene, which consisted of benzene and toluene. Sometimes it even contained some xylene; in this case xylidine entered into the composition of 'aniline for red.' At present most of the 'aniline for red' is a mixture of pure aniline with crude toluidine. By the latter we mean the mixture of *o*- and *p*-toluidine which is obtained by the nitration and subsequent reduction of pure toluene. Crude toluidine consists as a rule of 55 p.c. *o*-toluidine and 45 p.c. *p*-toluidine. The quantity of aniline added to crude toluidine

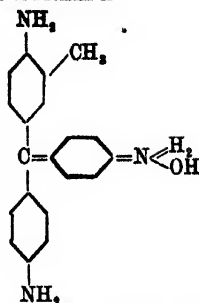
in order to produce the 'aniline oil for red' varies according to the recipes of various manufacturers. As a rule, half of the weight of the toluidine is added. A certain boiling-point (for instance, 188°-200°) and a certain specific gravity (for instance 1.010) are prescribed, and should be strictly adhered to by the aniline oil manufacturer. In some cases an addition of xylydine is necessary in order to produce a product of the desired boiling-point and density. Theoretically, an oil containing equal molecules of the three bases would be required; but for practical work an excess of aniline and *o*-toluidine is used, because a part of these two compounds escapes the reaction, whilst the *p*-toluidine is entirely used up.

Of all the methods which in the course of time have been proposed for oxidising this mixture, only two have survived, one of which is also rapidly disappearing. They are known under the names of the *arsenic acid melt* and the *nitrobenzene process*. From a practical point of view they are of equal value, but the arsenic acid melt is being abandoned on account of the poisonous nature of the arsenic compounds required.

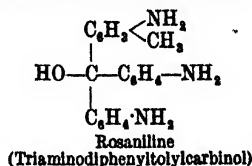
Magenta was originally prepared by Natanson, in 1856, by heating aniline with ethylene chloride. In 1858 Hofmann observed its formation when allowing carbon tetrachloride to act on aniline. In 1859 Verguin prepared it by the action of stannic chloride on aniline. Verguin's employers, the dyers Renard Frères and Franc, in Lyons, took up its manufacture on a large scale, and invented the name *fuchsin*. Later on a company was formed, under the name of 'La Fuchsin,' for working Verguin's patent. Gerber-Keller invented a process for oxidising aniline by means of mercuric nitrate. The dye-stuff thus obtained was believed to be different from fuchsin, and received the name *azalein*. In 1860 Medlock invented the arsenic acid process, which for a long time was considered the only practical method of manufacturing magenta. His patent was invalidated owing to a clerical error contained in the description. In 1869 Couplier described his process for producing fuchsin by the nitrobenzene process. This method, which did not give good results at first, was gradually worked out by various manufacturers, and is now equivalent, if not superior, to the best forms of the arsenic acid process.

Various salts of rosaniline were formerly in commerce. The original fuchsin was the hydrochloride, azalein was the nitrate; whilst magenta and rosein were the names applied to the acetate, produced by Nicholson, the first to manufacture this colouring matter in a practical and rational manner. Gradually the nitrate and acetate disappeared from the market. At present the hydrochloride is the only salt produced, to which, therefore, the original name of fuchsin should be applied. English manufacturers still use the names magenta and rosein for the hydrochloride. A large quantity of the fuchsin manufactured is transformed into rosaniline, which is delivered into the market either under this name or as 'magenta base,' 'red base,' or 'rosein base.' These names are not quite correct, because rosaniline may not strictly be considered as the true base of the hydrochloride of fuchsin.

The true base of fuchsin is



which, in the moment of its formation, undergoes a molecular transformation into



Manufacture of Fuchsin.

1. *Arsenic acid process*.—The properties of the 'aniline oil for red' have already been discussed. The mixture of bases known under this name is transformed into the dye-stuff by heating it with arsenic acid. The latter is prepared by oxidising arsenious acid (white arsenic) by means of nitric acid in closed earthenware pots. The escaping nitrous fumes are condensed in a tower, in which they meet an opposing current of water and air. The nitric acid is thus regenerated, and may be used again. Practically, therefore, the formation of the arsenic acid is accomplished by the oxygen of the air. The arsenic acid solution obtained has a sp.gr. of 1.85-2.3, and contains from 60-75 p.c. of arsenic acid H_3AsO_4 . 1,500-1,700 kilos of this solution are required in order to oxidise 1,000 kilos of 'aniline oil for red.' These quantities of the reagents are introduced into enamelled cast-iron pots, closed by lids; a mechanical stirrer and a tube for the escape of the vapours should be provided. The mixture is then gradually heated to 180°. This temperature should be strictly maintained during the whole operation. If the temperature rise above 190°, the dye-stuff already formed is decomposed. From eight to ten hours are required in order to complete the reaction. During the whole time vapours escape, which should be condensed in a leaden coil connected with the escape tube, and cooled by a current of water. At first the distillate consists chiefly of the water introduced with the arsenic acid. Later on, the water formed in the reaction distills; at the same time some aniline oil goes over. The total quantity of the aniline escaping the reaction is one-third, or even one-half, of the quantity originally used. The melt, which is very thin at first, gradually becomes viscid; at the same time it assumes a brown, metallic lustre. Samples should be taken from time to time. When the melt becomes brittle on cooling, the reaction is finished, and the fire should be drawn. The melt is then at once removed from the pot. In some factories an opening is provided for this purpose in the

lowest part of the pot, which is closed by a lid and screw whilst the heating lasts. As a rule, however, it is preferred to remove the cover of the pot, and to ladle out the melt. The latter is spread on trays made of sheet iron. On cooling, it solidifies into cakes, which are very brittle, and break up into small lumps on being handled.

The crude melt contains the colouring matter in the shape of arsenite, together with an excess of arsenious and arsenic acids, some coloured by-products (*v. infra*), and a large quantity of tarry impurities. In order to obtain the pure dye-stuff, the crude melt is introduced into horizontal wrought-iron boilers, in which an eccentric horizontal stirrer is made to rotate. Water is added, the lid of the boiler is closed, and steam is introduced at a pressure of from four to five atmospheres. After several hours' vigorous stirring, the greater part of the rosaniline arsenite has been dissolved by the water. The liquid is then forced through felt into iron tanks, where it is allowed to cool down to 50°. A sufficient quantity of salt is then added to precipitate the whole of the colouring matter. By the addition of the salt a mutual decomposition takes place. Sodium arsenite is formed, and remains in the liquid, whilst the colouring matter is precipitated in the shape of chloride. It settles out as a thick green tar of metallic lustre, which solidifies into a brittle substance on cooling. The supernatant aqueous liquid is then drawn off, the crude fuchsin is chipped out, and introduced into another extractor, similar to the one used for treating the melt. A very small quantity of soda ash or chalk (about $\frac{1}{2}$ p.c. of the weight of the crude dye-stuff) is added, and a second extraction takes place. The liquid is again forced through felt into large wooden vats, in which some wooden boards are suspended. When the vats are filled, a small quantity of hydrochloric acid and clean butter-salt is added to each vat. In these vats the dye-stuff separates out, in the shape of fine glistening green crystals. The largest crystals are generally deposited near the surface of the liquid. When the crystallisation is finished, the mother-liquor is drawn off, and the crystals are collected and sorted according to their shape and size. The largest crystals are sold under the name of 'diamond fuchsin.'

By-products.—The residues of the first boiling may be subjected to a second extraction; as a rule, some hydrochloric acid is added in this case. A deeply-coloured solution is thus obtained, from which an impure colouring matter may be precipitated by the addition of salt. This colouring matter is sold under various names (*magenta cake, cerise, granadine, maroon*), and finds a ready market. It dyes a magenta colour, which is less brilliant than the shade obtained with the crystals. A third boiling is sometimes necessary. The colouring matter obtained from this is very impure. It is, therefore, dissolved in weak hydrochloric acid, and some zinc-dust is added, which reduces the magenta contained in the liquid. On precipitating with salt, a colouring matter of a brown shade is obtained, which is sold as 'Nanking,' or 'leather brown.' The black insoluble residue of the third boiling still contains some dark-blue colouring matters of the induline series, which are, however, not worth the trouble of extracting.

The mother-liquors from the crystals contain a yellow colouring matter of great fastness and purity. This substance, known under the name of *phosphine*, belongs to another group of dye-stuffs, being a salt of diaminophenylacridine. For extracting it from these mother-liquors, the latter should be acidified with hydrochloric acid, and some zinc-dust added until all the fuchsin present in the liquid is reduced. The phosphine, which is not so easily reduced by zinc-dust, may then be precipitated by the addition of sodium nitrate. The amount of phosphine formed varies according to the composition of the aniline oil and the temperature of the melt. It is never considerable, and very often the quantity present is so small that it is not worth while to separate it (*v. CHRYSANILINE*, vol. ii. 246).

Recovery of the arsenious acid.—Formerly the residues of the manufacture of magenta were left in the factory yards or thrown into the sea. At present this is not allowed, and the manufacturers are invariably forced to recover their arsenious acid, so as to prevent the poisoning of wells and streams. The recovery, as it is now carried out, is so economical that the value of the arsenious acid obtained covers the cost of working the process. The process, which was worked out by A. Leonhardt, consists in burning the solid residues and using the heat for evaporating the arsenical liquids. The dry residue of the evaporation is introduced into the furnace, and burned along with the solid residues. Care is taken to introduce no more air than is necessary for burning the organic matter. By this precaution a complete volatilisation of the arsenic in the metallic state is obtained. The vapours of arsenic are led into a highly-heated combustion-chamber. Here they are mixed with the necessary quantity of hot air to completely burn the metallic arsenic into arsenious oxide As_2O_3 . The vapours of the latter are then led through condensing chambers similar to those used in the manufacture of white arsenic. In these chambers the arsenious acid is deposited in the shape of a white powder. From time to time the chambers are opened, the arsenic is removed, and used again for the manufacture of syrupy arsenic acid by the aid of nitric acid. A certain stock of arsenic is thus sufficient to carry on the manufacture of fuchsin for an indefinite period.

2. *The nitrobenzene process.*—This process was originally invented by Couper, of Paris; but it was for the first time successfully worked on a large scale by the firm of Meister, Lucius und Brünig, of Höchst-am-Main. Other firms followed in the course of time, and at present this process has practically superseded the one with arsenic acid.

It was originally supposed that the nitrobenzene used in this process enters into the rosaniline formed, after having served as an oxidiser. At present it is generally recognised that the nitrobenzene merely acts as an oxidising agent, and that, in so doing, it is transformed into tarry matters, which are useless and remain in the residues. The nature of the nitro compound used is, therefore, of no influence on the composition of the dye-stuffs obtained. Pure nitrobenzene, or a mixture of nitrobenzene with nitrotoluene, may be used. *o*-Nitrotoluenes acts

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more easily than any other nitro compound; it has, therefore, been used with advantage by the writer. *p*-Nitrotoluene has little tendency to act as an oxidiser. If, therefore, a mixture of nitrobenzene with the two nitrotoluenes (the so-called 'nitrobenzol for red') be used, the *p*-nitrotoluene escapes with the distillate.

The advantage of the nitrobenzene process consists, therefore, not in an economy of ingredients, but in the fact that by its application magenta free from arsenic may more easily be obtained. The yield in good crystallised fuchsin is slightly larger (if only the aniline used be taken as basis of the calculation) than in the arsenic acid process. This increase of yield pays for the increased price of the oxidising agent. In times when commercial benzene is cheap the process compares favourably with the arsenic acid process, whilst it was at a disadvantage when the prices of benzene were high. At the present time, benzene is so cheap and plentiful that the nitric acid consumed in this process is perhaps a more important item in the calculation of its cost than the benzene. For working this process it is a condition that the manufacture of aniline be carried on in the same works; the distillates are a mixture of aniline and nitrobenzene, which must be returned into the reduction process before they can be used again.

The process is worked with different proportions and in a different manner in different works. It is based on the following facts: aniline and nitrobenzene do not react upon each other; nor does a reaction take place if aniline hydrochloride be added. But if a small quantity of iron chloride be present, a reaction sets in, at a temperature of 160°. If the aniline and aniline salt used are pure, a dyo-stuff of the induline group is obtained; but if *p*-toluidine and *o*-toluidine be present in the necessary proportions ordinary fuchsin is the result of the reaction. The nitro compound, however, attacks the fuchsin already formed, and part of it is therefore decomposed again. For this reason, quantitative yields cannot be obtained. At 190° the action of the nitrobenzene becomes so violent that all the colouring matter is destroyed. The greatest care is, therefore, required in this process, and the temperature should never be allowed to rise over 175°. Cold-air flues, and even arrangements for cooling with water or ice, are therefore invariably provided in connection with the melting-pots. The size of the latter has been constantly increased, because it is easier to keep large vessels at a constant temperature than small ones. Enormous pots, capable of working one or two tons of melt, have been used. Excellent arrangements for stirring should be provided. It is a good plan to make the melting-pots of spherical shape, and to give the stirrer an oblique position in this spherical pot. No water should be present in the mixture, as in this case the nitro compound is simply reduced into aniline by the ferrous chloride, and the reaction stops. The hydrochloric acid used should, therefore, be mixed with the necessary quantity of the aniline and the mixture evaporated until it solidifies into 'aniline salt cake' on cooling. Sometimes the iron chloride solution is added, so that the cake obtained is intimately mixed with the iron salt. This cake is then dissolved

in the rest of the aniline, the nitro compound added, and the mixture heated until the reaction sets in. Other manufacturers prefer to add iron filings or dry ferrous chloride to the mixture of aniline with aniline cake and nitrobenzene. An ingenious patent, taken out by Herran and Chaudé, proposed the use of certain double salts of the general formula $R_2Cl_2 \cdot 2RCl_3$, such as ferric ferrous chloride, ferric zinc chloride, aluminium zinc chloride, and others. The addition of iron filings, originally proposed by Coupier is not customary at present. Anhydrous zinc chloride, which has also been proposed as a means of starting the oxidising action of the nitro compound, has not proved satisfactory.

The following proportions have been proposed:

100 parts aniline for red,
50 " nitrobenzene,
3-5 " iron filings,

and a sufficient quantity of hydrochloric acid to neutralise two-thirds of the aniline (Häussermann). The quantity of nitrobenzene is too large; it may very well be reduced to 40 parts, or even less.

Wurtz gives the following proportions:

38 parts aniline,
17-20 " nitrobenzene,
18-22 " hydrochloric acid,
2 " iron filings.

The following is Coupier's mixture:

67 parts toluidine,
95 " nitrotoluene,
65 " hydrochloric acid,
7 " ferrous chloride.

The large quantity of nitrotoluene proposed in this prescription is due to the fact that only the *o*-nitrotoluene, of which about 50 parts are present in the mixture, acts as an oxidiser. The *p*-nitro compound is recovered in the distillate.

The following proportions were used by the writer in regular factory work:

400 kilos aniline for red,
222 " hydrochloric acid, 20° Bé.,
247 " *o*-nitrotoluene,
and the ferrous chloride prepared from
9 kilos iron borings, and
41 " hydrochloric acid.

Half of the aniline is dissolved in the 222 kilos of hydrochloric acid, the solution of the ferrous chloride is added, and the whole evaporated in a stone still before being mixed with the remainder of the aniline and the nitrotoluene.

The nitrobenzene melt cannot be pushed so far as the arsenic acid melt. When finished it should not solidify into a brittle mass on cooling. It should be still soft, owing to a proportion of uncombined aniline which it still contains. This aniline must be extracted by boiling with a small quantity of dilute hydrochloric acid. After its removal, the melt becomes brittle on cooling. It is worked up in the Leonhardt extractors, in exactly the same manner as described for the arsenic acid melt.

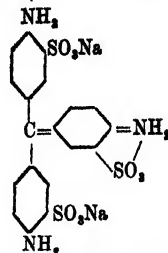
Later improvements.—It has already been said that several synthetical methods have been

proposed for the manufacture of magenta, which met, however, with no success. Gradually, however, improvements have been introduced into the old melting processes, which, being based on theoretical considerations, have given favourable results. The most important of these improvements is the one described in the German patent 53937 (and additional patent) of the Farbwerke vorm. Meister, Lucius und Brüning in Höchst-am-Main, dated November 27, 1889. It consists in replacing, in the nitrobenzene process, the 'aniline for red' by a mixture of diamino-diphenylmethane and aniline. The patents refer only to the production of the diamino-diphenylmethane, which is prepared by first acting with formaldehyde (the well-known 'formalin' of commerce) upon aniline. The methylene-aniline obtained is heated with aniline and aniline hydrochloride, by which means diamino-diphenylmethane is easily formed. If instead of $C_6H_5N:CH_2$, methylene-aniline, any of its higher homologues be heated with the corresponding bases, the homologues of diamino-diphenylmethane are produced. By introducing these bases instead of *p*-toluidine into the magenta melt, very large yields of the dye-stuff are said to be obtained. The dye-stuff prepared by this method is sold under the name of 'Neu-Fuchsin' (new magenta).

Later on a patent was obtained by Cassella & Co., of Frankfurt-am-Main, the essence of which is probably the same. It consists in introducing methyl alcohol into the arsenic acid melt. Formaldehyde is probably thus produced, which is at once transformed into diamino-diphenylmethane. By introducing chlorinated anilines into the pararosaniline melt the chlorine substitution products of rosaniline have been obtained, which are remarkable by being much more bluish in shade than either pararosaniline or ordinary magenta (Cassella & Co., D. R. P. 21923, 1913).

Acid magenta.—The ordinary fuchsin or magenta has been used for dyeing cotton, wool, and silk. But its properties make it necessary to use neutral or very slightly acid baths. This is a considerable drawback to its use on silk or wool, especially in combination with other dye-stuffs which require distinctly acid dyebaths for their successful application. It was, therefore, a decided advance to introduce a sulpho derivative of magenta into the market. This step was realised by H. Caro in 1877 (Eng. Pat. 3731, 1877; D. R. P. 2096, Badische Anilin- & Soda-Fabrik). Caro proved that magenta, which shows a marked resistance to ordinary sulphuric acid, may easily be converted into a trisulpho derivative by treatment with fuming sulphuric acid. The ordinary crystallised hydrochloride of magenta is used. It is introduced in a finely-powdered condition into fuming sulphuric acid; the mixture is then heated to a temperature not below 120° and not above 170° . Hydrogen chloride is given off, and the sulpho derivative is formed. When the operation is finished, it is diluted with water and worked up in the usual manner, by first preparing the lime-salt and then converting it into the sodium salt. The *para* derivative has the composition $C_{12}H_{10}N_2O_3S_3Na_3$, the higher homologue $C_{18}H_{14}N_2O_3S_3Na_3$; the ordinary acid magenta is a mixture of the two. The constitution of

the *para* derivative may be represented by the following formula:



from which it will be seen that the sulpho-groups occupy the *ortho* positions relative to the amino groups. It forms a metallic green powder, very soluble in water with magenta colour, which disappears completely on addition of caustic alkali, the sulpho derivative of the colourless triamino-triphenyl carbinol being formed.

Acid magenta may also be obtained by acting with chlorosulphonic acid upon dry magenta base (E. Jacobsen, D. R. P. 8764, 1879; Eng. Pat. 2828, 1879).

By using the various by-products of magenta instead of the pure dye-stuff, acid derivatives of these may be obtained which prove particularly valuable for dyeing mixed shades.

Magenta base (red base, rosein base). A large proportion of the fuchsin produced is transformed into the corresponding base, the composition of which has already been discussed. For the production of a good base, crystallised fuchsin only should be used. This is dissolved in a large volume of boiling water, and made alkaline either with milk of lime or with ammonia. In the latter case, the product obtained consists partly of the amino derivative already mentioned. No caustic alkali should be used. From the filtered solution the base settles out on cooling in crystals, which have the shape of a fern-leaf of pale-pink colour. In the air they generally become darker, because a certain amount of magenta carbonate is formed on their surface. The base thus prepared is sold for conversion into violets and blues (q.v.).

COLOURING MATTERS DERIVED FROM ROSANILINE.

The brilliant researches of A. W. Hofmann proved, at an early period, that rosaniline is capable of having the hydrogen atoms of its amino groups replaced by alkyl groups, and that the substances so formed are remarkable not only for the brilliancy, but also for the great variety, of their shades. Hofmann himself introduced the alkyl radicals of the fatty series into the molecule of rosaniline, and thus obtained the colouring matters which for a long time played an important part under the name of Hofmann's violets. Girard and De Laire discovered a method of introducing the phenyl and other aromatic groups into the molecule of rosaniline, and thus inaugurated the manufacture of aniline blues. It was then attempted, first by Lauth, to produce alkylated rosanilines by direct oxidation of alkylated aniline, and this method proved of great practical importance in the hands of Bardsy, although the theory of this

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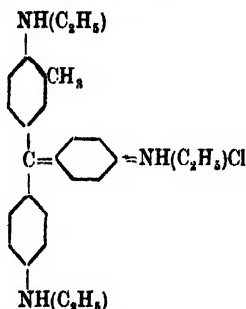
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process was only understood at a much later period. Finally, a synthetical method for the production of certain alkylated rosaniline derivatives which cannot be produced by direct alkylation of rosaniline itself, was discovered by Kern, whose processes are based on the theoretical researches of Michler.

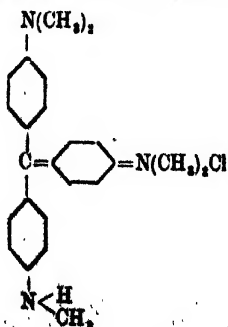
All these colouring matters will now be described, and the methods of their formation discussed.

1. **Hofmann's violet** $C_{26}H_{22}N_2Cl$, hydrochloride of triethyl-rosaniline



is obtained by heating magenta base with ethyl iodide, bromide, or chloride, and a sufficient quantity of alcoholic soda solution to neutralise the acid formed in the reaction. The magenta base is prepared by decomposing a very weak fuchsin solution with milk of lime or ammonia. From the filtered solution the base crystallises in small leaflets of a pink colour. The alkylation is effected in closed vessels of copper or cast-iron, which are heated to 80° – 100° by steam or in a water-bath. The trimethyl-rosaniline hydrochloride, which is slightly bluer in shade, was formerly also prepared. This is no longer employed. By using less of the alkyl haloids than is necessary for completing the reaction, redder shades were obtained, which were mixtures of the mono- and di-ethyl- or methyl-rosanilines. In commerce, the more or less reddish tinge of their shade is marked by the addition of the letter R, thus: Violet R, RR, up to 5 R.

2. **Methyl violet B.** C. Lauth, wishing to find a new method for the production of Hofmann's violets, tried to oxidise methylated aniline. He obtained a violet of much bluer shade. Bardy worked out the method, which was patented by Poirrier and Chappat (Fr. Pat. 71970, dated June 16, 1866). The product obtained was proved to be the hydrochloride of pentamethyl para-rosaniline $C_{24}H_{28}N_2Cl$ —



This dye-stuff, which became of great importance, was for a long time known under the name of *Violet de Paris*. At present it is sold by the various colour works under the name Methyl Violet B to 3 B.

The mode of formation of this colouring matter is very interesting. Many researches have shown that it is best prepared from pure dimethyl-aniline, which should be as free as possible from every trace of monomethyl-aniline. If three molecules of dimethylaniline be oxidised into one molecule of the dye-stuff, one of the six methyl groups present serves to form the central carbon atom, whilst the other five remain combined with the amino groups of the dye-stuff formed.

The process of oxidation employed is totally different from those resorted to in the manufacture of magenta or fuchsin. Cupric chloride is used as an oxidiser at a temperature which is little above that of the atmosphere. The cuprous chloride formed is again transformed into cupric salt by the oxygen of the air. The air should, therefore, have ready access to the mixture. To fulfil this condition, a porous condition is given to the melt by the admixture of sand or other indifferent materials. Cakes are formed of the mass, and these are left on trays in a hot chamber. The following proportions have been recommended:

100	parts sand,
10	„ dimethylaniline,
3	„ cupric nitrate,
2	„ sodium chloride,
1	„ weak acetic acid.

The cakes, which show a dull greenish colour at first, gradually assume a bronze lustre and become hard and brittle. They now contain the violet formed as an insoluble compound with cuprous chloride. To obtain the violet the cakes should be powdered, and all soluble substances extracted with water. The double salt of violet and cuprous chloride should then be decomposed. Various means have been adopted for this purpose.

The original process consists in treating the material with a weak solution of sodium sulphide. Insoluble copper sulphide is formed, and the free violet is dissolved. From the filtered solution it may be precipitated by the addition of salt. It comes out in the shape of a gold-coloured tar of metallic appearance, which is collected and dried in jacketed pans. When dry it forms a brittle mass of metallic aspect, showing no tendency whatever to crystallise. It is sold under the name of 'Methyl violet B' or 'direct violet.'

The use of sodium sulphide has this inconvenience, that any excess of the reagent acts as a reducing agent on the violet, transforming it into its leuco compound, which cannot be separated from the violet, and impairs its strength, besides producing other complications. To remedy this drawback, several factories used gaseous hydrogen sulphide instead of the 'sodium' compound. Hydrogen sulphide has no reducing action on the violet in neutral or slightly acid solutions. The use of this gas on a large scale is, however, extremely dangerous, and accidents, which happened

repeatedly, have led to the abandonment of its use.

The following methods admit of the extraction of the violet without the use of sulphides.

The first is based on the fact that, although the violet combines with cuprous chloride in the shape of its hydrochloride, this is not the case if the two be present as sulphates. If, therefore, the crude insoluble melt is boiled with dilute sulphuric acid, the violet goes into the solution together with the copper. The solution is then filtered off from the sand. If now salt were added in order to precipitate the violet, the insoluble compound ~~would rise from chloride~~ for precipitating the violet, which comes out as sulphate, whilst the copper remains in the solution. The violet sulphate is now carefully washed, re-dissolved, and re-precipitated in the shape of chloride by the addition of common salt.

Another process, which gives equally good results, is based upon the fact that the insoluble compound becomes soluble if the cuprous chloride contained in it be oxidised into cupric salt. For this purpose the crude cake is triturated with a solution of ferric chloride. It is then filtered off and washed. The violet, which has become soluble, may now be extracted with water, and precipitated by the addition of salt.

Great improvements have been effected in the melt itself. First of all, it was recognised that the cakes, if left to themselves, were apt to lose too much dimethylaniline by evaporation; they also remained insufficiently oxidised in their interior. To obviate this, the use of bread-kneading machines was resorted to, through which a current of air was blown. This current was made to pass through a vessel containing sulphuric acid, after leaving the machine. Complete oxidation was thus obtained, whilst the base which distilled over was recovered in the acid.

Later on, the quantities of the copper salt were reduced, and some potassium chlorate was added to the mixture. This yielded the necessary oxygen, the presence of a current of air became superfluous, and the evaporation of the base could be stopped by using closed vessels or kneading machines.

Another great inconvenience is the sand. It is necessary as a diluting agent, but in the after-operations it is very troublesome, being very heavy and producing great wear of the apparatus. It was, therefore, a great improvement to use clean salt instead of sand. The salt is quite as indifferent as the sand, but after having done its duty, it may be easily removed by solution, leaving the insoluble compound of the violet and cuprous chloride in the shape of a fine dark powder, which is admirably fitted for being worked up into soluble product.

By such improvements it was possible to raise the yield of colouring matter, which at first hardly reached 45 or 50 p.c. of the dimethylaniline used, to 80 p.c. and more. If we remember that 30 p.c. of pure colouring matter is a fair yield in the manufacture of magenta, we may well understand that methyl violet, although manufactured from a much more

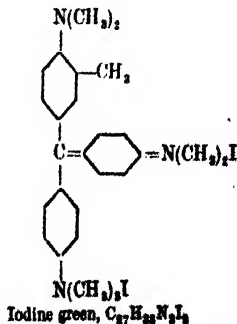
expensive raw material than fuchsin, soon became much cheaper than its parent substance.

The yields of violet have been further increased by a curious procedure. It consists in adding some phenol to the mixture. The action of the phenol, which may be recovered, is that of a solvent; by its use the yield of violet becomes very nearly theoretical.

In the manufacture of violet, especially by the older methods, there is always some tri- and tetra-methylrosaniline formed along with the penta-methyl derivative, because the methyl groups are attacked, and transformed into sulfoxide, ~~and~~ ^{the} violet is, therefore, slightly redder than it ought to be. To compensate for this loss, Bardy treated his direct violet with benzyl chloride, and thus introduced benzyl groups wherever methyl was wanting. The violet of very blue shade thus obtained was brought into commerce under the name of *Methyl violet 5 B* or *Benzyl violet*. It has now lost its importance, having been to a great extent replaced by the very beautiful crystallised violets obtained by the synthetical method of Kern.

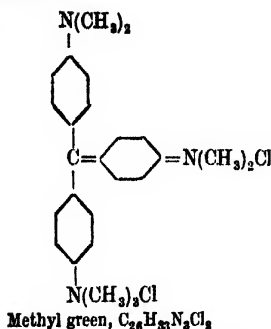
3. Iodine green and Methyl green. It has already been said that Hofmann's process of direct alkylation of rosaniline does not go beyond the tri-alkyl derivatives. If the action of alkyl halides be still continued, ammonium bases are formed. Thus by heating Hofmann's violet with methyl iodide in a methyl alcohol solution, Keisser obtained (1866) a green colouring matter, which was manufactured and sold for many years under the name of *iodine green*. A very similar dye-stuff was prepared from methyl-violet in a like manner by Bardy, who used, however, methyl nitrate instead of the iodide. After several explosions, the use of the nitrate was abandoned, and methyl chloride or bromide, also ethyl bromide, were used instead. The dye-stuff thus obtained was sold under the name of *methyl green*. It did not contain any iodine, and was therefore much cheaper than the iodine green, which it quickly replaced.

Chemically, the two may be considered as homologues of similar constitution, viz. as methyl ammonium derivatives of hexamethyl-rosaniline and hexamethyl-pararosaniline. Iodine green, being a derivative of ordinary rosaniline, contains one tolyl group:



The methyl groups in this formula may also partly be replaced by ethyl groups if ordinary Hofmann's violet were used as a raw material.

Methyl green is the corresponding derivative of pararosaniline :

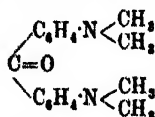


Both these dye-stuffs were brought into commerce in the shape of their zinc double chlorides. The iodine green formed a dark powder, whilst the methyl green formed pretty green needles or leaflets.

To prepare these dye-stuffs the violets were simply heated with the alkyl halides in closed enamelled iron vessels to 120° . Some wood spirit, or common alcohol, was added as a solvent. A pressure of 10–12 atmospheres was observed, which decreased when the reaction was finished. The crude product was dissolved in water. This solution was of dark-blue colour, because there was always some violet which remained unattacked. To separate this, the solution was shaken up with amyl alcohol, which dissolved out the violet. The green remained in the aqueous solution, from which it could be precipitated by the addition of zinc chloride and common salt. To obtain crystals, the crude green was re-crystallised from spirit.

These greens have now almost entirely been replaced by the diaminotriphenylmethane derivatives already described, which are not only more brilliant in shade, but also much more stable and at the same time very much cheaper. Iodine green and methyl green are decomposed and turn a dirty violet even by the action of a gentle heat, as produced in the process of cylindering fabrics, and on many other occasions.

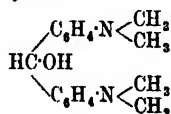
Pararosaniline derivatives prepared by Kern's method.—Another way of preparing alkylated pararosanilines was indicated by Kern, who started from the observations published by W. Michler (Ber. 1876, 9, 716). This chemist had shown that by acting with carbonyl chloride COCl_2 upon dimethylaniline, dimethylaminobenzoyl chloride is formed, which acts again on dimethylaniline, yielding tetramethyldiaminobenzophenone :



At the same time, as Michler observed, an intense blue colouring matter is formed. A. Kern (1883) followed up Michler's observations, and discovered not only the nature of the blue colouring matter, but also the conditions under which it may be obtained as the sole product of the reaction. The colouring matter proved to be pure hexamethylpararosaniline, the formula

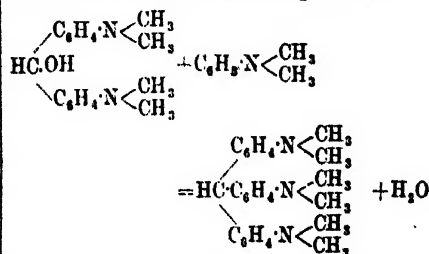
of which is due to the action of another molecule of dimethylaniline upon tetramethyldiaminobenzophenone. This action is, however, not very energetic, and must be intensified by the addition of certain substances, or by substituting for the ketone certain of its more active derivatives. A number of different processes have thus been worked out, the more important of which will now be described.

A. Kern's original modification of Michler's experiment is based upon the fact that tetramethyldiaminobenzhydrol, the secondary alcohol derived from the ketone tetramethyldiaminobenzophenone, acts readily upon aromatic bases, forming triphenylmethane derivatives. This process is described in Kern's Eng. Pat. 5450 (1883), and the corresponding D.R.P. 27032, Bad. Anilin- und Soda-Fabrik. Tetramethyldiaminobenzhydrol :



which had already been obtained by Michler by the action of sodium-amalgam upon the ketone may, according to this patent, be prepared industrially by boiling a solution of the ketone in amyl alcohol with caustic soda and zinc-dust. When the reduction is finished, the alcohol is blown off with steam, the residue dissolved in hydrochloric acid, and purified by fractional precipitation with caustic soda.

The product thus obtained may be condensed with primary, secondary, and tertiary aromatic bases, yielding in every case alkylated derivatives of pararosaniline; thus, for instance, with dimethylaniline the leuco base of hexamethylrosaniline is formed, if the two be brought together in a solution in weak sulphuric acid

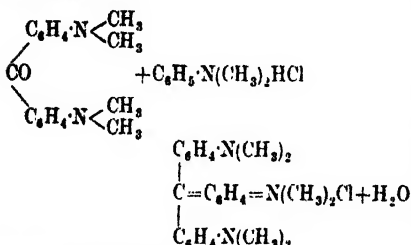


This leuco base may be oxidised into the corresponding dye-stuff by the method indicated for the production of benzaldehyde green—viz. by the action of lead peroxide upon the hydrochloride of the leuco base. The *hexamethylrosaniline hydrochloride* thus obtained is a beautifully crystalline substance, which forms green crystals if anhydrous, $\text{C}_{22}\text{H}_{23}\text{N}_3\text{Cl}$, or bronze-coloured prisms if containing water of crystallisation. In the latter case, its composition is $\text{C}_{22}\text{H}_{23}\text{N}_3\text{Cl} \cdot 8\text{H}_2\text{O}$. The power of crystallisation of this substance is very remarkable if we compare it with the ordinary violet obtained by direct oxidation of dimethylaniline; this, being a mixture of the tetra-, penta- and hexamethyl-rosanilines, shows no tendency whatever to crystallise.

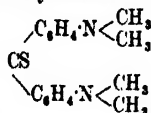
If in the process described diethyl-aniline be substituted for dimethyl-aniline, both for the

production of the hydrol base and its subsequent transformation, the result is, of course, hexaethylrosaniline, which cannot be prepared by any other process. This product is manufactured and sold under the name of 'Ethyl purple, 6 B' (ethyl violet). It is a very beautiful colouring matter, dyeing fine bluish-purple shades.

Very soon a simpler method than the one described was discovered by Kern and Caro (D. R. PP. 26016 and 29943; Eng. Pat. 4428, 1883). It was based upon the fact that the action of tetramethyldiaminobenzophenone upon dimethylaniline, which, in Michler's experiment, already had yielded a small amount of colouring matter, may be modified by the addition of certain substances, such as aluminium chloride, zinc chloride, and others. If these be present, the reaction of phosgene gas (carbonyl chloride COCl_2) upon dimethylaniline does not result in the formation of tetramethyldiaminobenzophenone; this is only formed as an intermediate product, which reacts at once upon another molecule of the base, forming hexamethyl-parosaniline:

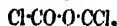


Many modifications of the processes here described have also been indicated and patented. Thus, instead of the carbonyl chloride, thiocarbonyl chloride CSCl_2 may be used, which yields with dimethylaniline the thioketone



The latter may replace the oxygen compound in all its applications.

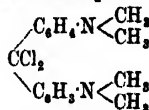
Again, trichloromethyl chloroformate



and similar substances have been proposed as substitutes for the carbonyl chloride.

The following is the method used at present for preparing *Crystal violet* and *Ethyl purple 6B*: 100 kilos of dimethylaniline (or diethylaniline) are acted upon in a high-pressure pot at a temperature of 20° with 19-20 kilos of carbonyl chloride; after 24 hours' standing another 50 kilos of the base and 30 kilos powdered zinc chloride are added. The mixture is now heated to 40° - 50° , and 20 kilos more of the carbonyl chloride are introduced. After 6 hours' heating to 50° , the reaction is finished. The mixture is now introduced into a still, made alkaline with caustic soda, and the excess of dimethylaniline driven off with steam. The base of the colouring matter is then dissolved in weak sulphuric acid, and precipitated in the shape of its chloride by the addition of common salt. It is then recrystallised from water.

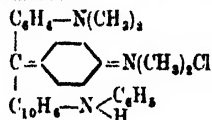
This process leads, of course, only to para-rosaniline derivatives in which the three amino-groups are substituted in the same manner. Besides the hexamethyl- and hexaethyl derivatives, the trimethyltriphenyl derivative has been obtained from methyldiphenylamine (Amer. Pat. 327953, Kern and C. Müller). It was, therefore, a great improvement when a method was found for effecting the condensation of tetramethyldiaminobenzophenone with all kinds of primary, secondary, and tertiary bases. This method, which was worked out by Kern and H. Caro, consists in the intermediate formation of the tetramethyldiaminobenzophenone chloride:



which, being more active than the ketone itself, reacts most easily upon bases of every description. For the manufacture of colouring matters it is not necessary to isolate the chloride, an extremely unstable substance. It is sufficient to react with phosphorus trichloride upon a mixture of the ketone with the base which is to be introduced into the triphenylmethane derivative.

This process is described in the D. R. P. 277891, the Eng. Pats. 4850 and 5038, 1884, and a large number of corresponding American patents, which contain many examples of its application to the production of dye-stuffs. Of these, however, only few have obtained lasting importance. These are basic colouring matters of a beautiful blue shade, and interesting because they are the only members of the triphenylmethane group which contain the naphthyl radicle.

Victoria Blue B $\text{C}_{23}\text{H}_{21}\text{N}_3\text{Cl}$ has the constitutional formula:



It is prepared by mixing together

10 kilos tetramethyldiaminobenzophenone and

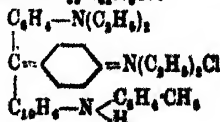
9 kilos α -naphthylphenylamine, and adding

7 kilos phosphorus trichloride to the mixture.

The reaction, which sets in at once, is finished by heating to 110° . The product is dissolved in water, and the solution precipitated with salt.

A similar dye-stuff, analogous in its constitution, but of a somewhat more reddish shade, is obtained if instead of α -naphthylphenylamine, monoethyl- α -naphthylamine be used. It is known under the name *New Victoria blue R*.

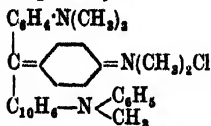
If α -naphthyl-*p*-tolylamine be taken instead of the naphthylphenylamine, and condensed with tetra-ethyl-diaminobenzophenone, a blue of a very greenish shade is obtained. It is sold under the name *Night blue (Nachtblau)* and has the composition $\text{C}_{28}\text{H}_{25}\text{N}_3\text{Cl}$:



Another blue of very red shade is the one sold under the name *Victoria blue 4 R*



It is prepared from tetramethyldiaminobenzophenone and α -naphthylmethylphenylamine. Its constitution is probably



In describing both the green dye-stuffs derived from diaminotriphenylmethane and the old and important magenta group, it has been mentioned how much the dyer values the possibility of dyeing the useful shades which these colouring matters supply from an acid bath and of thus being enabled to combine them with all the other wool dyes capable of such application, especially the azo colouring matters. The same necessity exists for the various shades of violet here described.

This want was at first supplied by the means which had proved successful in the case of magenta, viz. by the direct sulphonation with fuming sulphuric acid of the various violets, especially the redder shades obtained by the reaction of alkyl halides upon magenta base. The colouring matters thus produced were introduced at the end of the seventies under the name of *Acid violets* to which letters denoting the shade (R and B) were added. But they did not meet with the same ready reception that had been offered to acid magenta. It is now known that the sulphuric anhydride of the fuming acid is very apt to attack the alkyl groups and thus to tarnish the shade of the violets.

The new synthetical method which had produced *Crystal violet* and its many congeners and which is apparently analogous to the synthesis of *Victoria green* and its numerous homologues, could not fail also to indicate rational methods for the production of acid violets of every conceivable shade.

Some of these methods consisted—in strict analogy to what had been done in the group of the *greens*—in introducing the benzyl group into the molecule of the dye-stuff and utilising the capacity of this radicle for sulphonation. All the variations of this method given in the description of the acid greens are admissible in the violet group. In this way the following dye-stuffs have been obtained, the structural formulæ of which need not be given:—

Acid violet 4BN, 6B, 7B and *N*, prepared by the sulphonation of pentamethylbenzyl-pararosaniline or by the oxidation of the mono-sulpho derivative of pentamethylbenzyl-leucaniline.

Acid violet 6B or *Guinea violet 4B*. This is a disulpho derivative, obtained by oxidising the acid, which may be obtained by the condensation of dimethyl-*p*-aminobenzaldehyde with ethylbenzylamine sulphonic acid. The corresponding derivative of diethyl-*p*-aminobenzaldehyde is also manufactured.

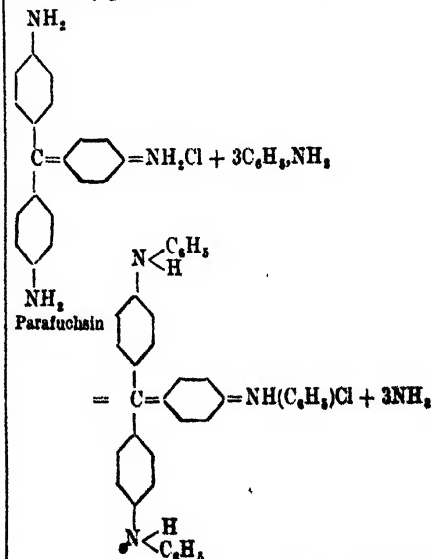
Another class of acid violets is derived from methyl-diphenylamine, which may be introduced instead of dimethylaniline by all the synthetical processes described. The additional

phenyl group entering into the molecule of the leuco base of the dye-stuff derived from it by oxidation is capable of carrying a sulpho group which may be introduced into it by the usual means. Thus *Alkali violet 6B* and *Acid violet 7B* can be prepared, whilst in *Acid violet 7BN* ready formed methyl-diphenylsulphonic acid is condensed with dimethyl-*p*-aminobenzic acid.

The process of introducing elements capable of being sulphonated into the synthesis of rosaniline derivatives may be carried still farther. Thus a useful dye-stuff, called *Wool green*, is manufactured by several firms by condensing tetramethyldiaminobenzophenone (Michler's ketone) with β -naphthol and subsequently sulphonating the insoluble dye-stuff so obtained.

Rosaniline blues or phenylated rosanilines. These are of great importance, forming by far the majority of blue aniline dyes in the market. The chemistry of these compounds is, however, extremely complicated. The blues sent into commerce are not chemically pure substances, but mixtures of various isomerides; it is very difficult to classify them. Moreover, they are known under a great variety of fancy names, many of which are applied to products of different composition by different firms. The following is an attempt to classify the various blues.

The method of phenylation is very remarkable, and quite different from the methods of substituting fatty radicles for hydrogen in the amino groups of rosaniline. The general method in this case consisted in treating rosaniline base with the halogen derivatives of these radicles. Owing to the great stability of chlorobenzene C_6H_5Cl , the same process cannot be applied to the phenylation of rosaniline. This takes place, however, with great facility if we allow aniline to act upon rosaniline, ammonia being given off as a by-product:



Triphenyl-pararosaniline hydrochloride (Rosaniline blue).

It has already been shown that a consider-

able difference exists between pararosaniline hydrochloride or parafuchsin and the ordinary fuchsin of commerce. The former is a uniform compound $C_{11}H_{11}N_3Cl_4H_2O$, whilst the latter is a mixture of parafuchsin with at least two isomeric homologues. Both these substances may be phenylated; their phenyl derivatives are blue colouring matters of great intensity and beauty. But a greater difference is found to exist between the phenyl derivatives of pararosaniline and those of ordinary magenta than even between the two kinds of fuchsin themselves.

This method of phenylation, which has been indicated by Ch. Girard and G. de Laire, is invariably resorted to. It cannot, however, be applied on a practical scale to the hydrochloride, as assumed for simplicity's sake in our equation. Experience has shown that organic acids must be used in order to get good results. The majority of organic acids have been tried for the purpose; at present, however, only two are used, which give distinctly different results, viz. acetic and benzoic acids. The reason for this difference has not been definitely ascertained, but it is a fact known to every manufacturer that blues of a greenish shade can only be obtained with benzoic acid, whereas acetic acid yields more reddish compounds.

The phenylation of rosaniline cannot be pushed further than the formation of triphenylrosaniline. The tetra-, penta-, and hexaphenyl derivatives are not known. But even the formation of triphenylrosaniline, such as it is indicated by our equation, takes place in three successive stages, the phenyl groups entering the molecule one after another. It is, however, practically impossible to separate these stages. If, in the beginning of a blue melt, a certain amount of mono-phenylrosaniline be formed, the reaction proceeds simultaneously on this and on rosaniline, which has not yet been attacked; thus, in a second phase, monophenyl and diphenyl rosaniline, and rosaniline (which has not yet been attacked) will be present together. To these the triphenyl compound will presently be added, a very complex mixture being the result. By a more prolonged action it is possible to eliminate rosaniline itself and its monophenyl derivatives completely from the mixture. But some diphenylrosaniline will always remain present. Moreover, all these compounds seem to exist in various isomeric modifications. It is a mixture of these which forms the ordinary *crude* or *Opal blue*.

If, instead of pararosaniline, the ordinary rosaniline of commerce be used for the production of the blue (as is the case in most instances) the product becomes even more complicated by the presence of the homologous compounds. Some process of separation which splits up the crude product into fractions of different shades and reactions must be resorted to; and although some of these are crystallised, it cannot be said with certainty that they represent chemically pure individuals.

Mon- and di-phenylpararoslaniline have hitherto not been prepared in a pure state. Nothing can, therefore, be said of their properties.

Triphenylpararoslaniline hydrochloride



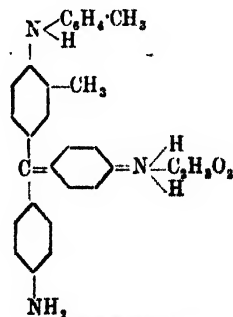
is the purest and brightest blue known. It is now invariably prepared by the phenylation of pararosaniline, but it may also be obtained by melting together diphenylamine and oxalic acid. The formic acid evolved in the decomposition of oxalic acid serves to link together three molecules of diphenylamine into one of triphenyl leuco aniline, which is then slowly oxidised into the rosaniline compound. It was this method which was formerly used for the production of this blue, which therefore is still frequently described as *Diphenylamine blue*; it is also sometimes called *Methyl blue*, because methyldiphenylamine was occasionally used for its production. Other names for the same product are:

Bleu direct, bleu lumière, bleu de Lyon, bleu de Mulhouse, bleu de nuit, bleu de Paris, light blue, night blue, Paris blue, Bavarian blue.

This product forms a microcrystalline powder of a bronzy appearance, completely insoluble in water, sparingly soluble, with a brilliant blue colour, in spirit. Its transformation into the soluble diphenylamine blues of commerce will be described hereafter.

When the same process of phenylation (the particulars of which will be given below) is applied to the ordinary rosaniline of commerce—which is, as will be remembered, a mixture—various products are obtained. Of these the following may be said to have been isolated:—

Monophenyl-rosanilines. These are the product of a very moderate phenylation. They are still soluble, in the shape of their acetates, in water, and dye fine purple shades. They have now, owing to the greater cheapness of methyl violets, almost completely disappeared from the market, in which they formerly played an important part under the name of *Regina purples* or *Regina violets*. It was customary to prepare them, not by the action of pure aniline on magenta acetate, but rather by that of the recovered oils or *échappés* from the magenta process, which contained a large proportion of *o*-toluidine. The action of the latter is slower than that of aniline; it is, therefore, easier to stop the reaction before a considerable proportion of the diphenyl or ditolyl rosaniline is formed. The *regina purples* consisted, therefore, to a great extent of the *o*-tolylrosaniline, the acetate of which is represented by the following formula:

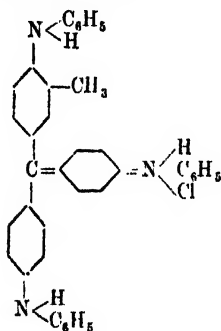


Regina purple.

Diphenylrosanilines. These were invariably obtained, together with the *regina purples*, from which they are distinguished by their complete

insolubility in water. They are, however, still of a purple shade; they are invariably present to some extent in crude tri-phenylrosaniline blue, if the latter be prepared with acetic instead of benzoic acid. This is the reason why such blue is always of a redder shade than the blue prepared with benzoic acid, in which the proportion of diphenyl derivatives is reduced to a minimum. A product which consists chiefly of diphenyl-rosanilines, is known under the name of *spirit purple*, *spirit violet*, or *opal violet*; it has also been sold as *regina spirit purple*. From it the *soluble violets* and *purples*, and *alkaline purples* of commerce are derived by sulphonation.

Triphenylrosanilines (see Supplement). The triphenyl derivatives of ordinary rosaniline may be subdivided into two classes: crystalline and uncrystallisable blues. The former may be extracted from every crude blue melt prepared with benzoic acid. They represent in a state of approximate purity the triphenyl derivative of the higher homologue of pararosaniline, and may therefore be represented by the following formula:



It is to this product, which forms the base of the high-class alkaline and water blues of commerce, that one should reserve the name of *Opal blue*, which has, however, been indiscriminately applied to a number of various products. This opal blue forms, in the shape of its pure hydrochloride, a mass of distinct, though very small, glistening crystals of a greenish brass-colour. It is completely insoluble in water and in spirit. If it be treated with alcoholic caustic soda, the free base is obtained in the shape of a tarry substance from which the acetate may be prepared by dissolving it in glacial acetic acid, and re-precipitating with water. This acetate is soluble in spirit, and, though sparingly, also in water. It was formerly sold and used under the name of *Opal blue 6 B for cotton*, *Gentian blue*, *Hessian blue*; also the names of *Bleu lumière*, *Bleu de nuit* (originally used for the para derivative), were occasionally applied to it. In Germany it was sold under the name of *Feinblau*, *Spirit-blau*. The latter expression is applied, however, to all blues soluble in spirit, not only to this acetate. Its use has been much restricted of late, owing to the unwillingness of the dyer to use spirit in the dye-bath.

The second class of triphenyl derivatives of ordinary rosaniline, comprises the uncrystallisable portions of crude blue melts. They contain a mixture of triphenyl- and diphenyl-

rosanilines in various proportions, quite inseparable by the means which are at our disposal. They are (in the shape of hydrochlorides) insoluble in water, soluble in spirit. Caustic soda transforms them into a mixture of the corresponding bases, which are tarry masses. Their shade varies from a purplish-blue to a distinct clear blue of great strength and purity which, however, always shows a purplish hue if looked at by artificial light. This blue forms the starting-point for the production of innumerable brands and qualities of alkaline and water blues, varying in their shade and in the purity and strength of their colour. They are designated, according to the redness of shade, by the letters 3 R, 2 R, R, B, 2 B, and 3 B, whilst 4 B, 5 B, and 6 B may be said to be reserved for the derivatives of the true opal blue of varying purity. A large number of fancy names, such as *China blue*, *Marine blue*, *Serge blue*, &c., have been invented for this kind of blues.

Besides these blues a special kind of low-class blue should be mentioned which, under the name of *Blackley blue*, has enjoyed, and still enjoys, much favour, especially for dyeing paper-pulp, and also for the production of cheap woollen materials. This is the sulphonation product of a peculiar kind of phenyl rosaniline, prepared by acting with aniline upon crude magenta. It is consequently very impure, but also very cheap. It contains a mixture of the phenylation products of all the substances contained in crude magenta.

Tri-*p*-tolylrosaniline has been prepared by acting with *p*-toluidine in the presence of benzoic acid upon ordinary rosaniline base. It is a blue of remarkable beauty and brilliancy of shade, which offers, however, great resistance to the process of sulphonation. It has, therefore, only been manufactured and sold in the shape of its hydrochloride, which is soluble in spirit. It is sold for dyeing cotton under the name of *Grünlichblau* (Höchst) or *6 B extra opal blue* (English manufacturers). It has largely gone out of use of late years.

Manufacture of blues.—An immense number of prescriptions for blue melts has been published, and a larger number still circulates amongst manufacturers. It would be perfectly useless to reproduce any of them. The principles upon which they are based may be thus briefly stated:—

For the production of good blues a perfectly pure magenta base is the first requirement. For its preparation crystallised fuchsin only should be employed. If crude magenta or any of the magenta residues (*cerise*, *grenadine*, &c.) be used, the base obtained can only be employed for the production of *Blackley blues*. Pure pararosaniline, the base prepared from parafuchsin (*Neufuchsin*), should be used for the production of the so-called diphenylamine or methyl-blues (direct blues); whilst crystallised base from ordinary fuchsin forms the starting-point for all the ordinary blues from 4 R to 6 B, as well as for regina purples.

The second condition for the production of good blues is the use of very pure aniline, perfectly free from toluidine. It was in the manufacture of blues that the necessity of operating with pure aniline was first felt. The term *aniline*

for blue was, therefore, and is still occasionally, applied to perfectly pure aniline, boiling within one degree, and having a specific gravity of 1.0268-1.0270. Such aniline can only be prepared from pure crystallisable benzene.

If these two conditions—pure magenta base and pure aniline—be fulfilled, the shade of the blue obtained is still dependent upon:

1. The proportions of base and of aniline in the melt. It may be said that greenish blues will only be obtained if a very large excess of aniline be used, whilst reddish blues are produced in melts rich in magenta base.

2. The time and temperature of the melt. The formation of blue begins below 100°. It proceeds quickly at a higher temperature; 120°-140° may be assumed to be the most favourable temperature. From 140°-180° certain impurities (diphenylamine?) are formed, which impair the tendency of crystallisation of the blue. The temperature of high-class blue melts should therefore not be raised above 140°. The time required by a blue melt depends upon the proportion of base to aniline, and, to some extent, the quantities operated upon. The process proceeds quickly in highly-concentrated melts. Melts for high-class blues, which contain a large proportion of aniline, require prolonged heating—20 hours, and even more, before being finished. As a rule, the progress of the melt is tested by placing a drop of the melt on filter paper moistened with spirit. The gradual change of colour may thus be observed with great accuracy. When the melt is finished, there should be no reddish rim visible in the spot produced on the paper.

3. The nature and proportion of the acid used in the melt. It has already been said that organic acids only should be used, the action of hydrochloric acid being too slow. Acetic and benzoic acids are now used exclusively. The action of acetic acid is quicker than that of benzoic acid, but it seems impossible to transform all the rosaniline into its triphenyl derivative by the use of acetic acid. Benzoic acid acts more slowly, but it continues its action until all the rosaniline is transformed into the triphenyl derivative. At the same time, the whole of the melt is, even with benzoic acid, not entirely transformed into crystallisable opal. Moreover, acetic acid produces (by its simultaneous reaction on aniline) some acetanilide, which remains in the blue and is apt to prevent its subsequent crystallisation, whilst no benzanilide is formed by heating aniline with benzoic acid. For these reasons acetic acid is employed in the production of low-class reddish-blues (in concentrated melts), whilst benzoic acid is used only for the production of high-class opals. The greater part of the benzoic acid may be recovered from the melt, whilst the recovery of the acetic acid does not pay.

There is no advantage in using other acids instead of acetic and benzoic acid. As a rule, it may be said that the fatty acids (formic, butyric, valeric acids) act similarly to acetic acid, whilst the aromatic acids (toluic, phthalic, cinnamic acids) may take the place of the benzoic acid.

Upon these conditions all the prescriptions for blue melts are based. Taking the quantity of magenta base to be operated upon as unity,

the quantity of aniline added varies from four to twenty-five times its weight, the quantity of the organic acid from $\frac{1}{10}$ to $\frac{1}{2}$. The conditions of time and temperature have already been stated.

The apparatus necessary for blue-making is very simple so far as the melt is concerned, enamelled cast-iron pots with a lid and stirrer being always used. In the early times of the manufacture of aniline colours it was believed that blue melts could only be made in glass, and on a very small scale. In the 'Fuchsin' factory at Lyons the blue was therefore manufactured in large numbers of glass flasks heated in a sand-bath. At present it is believed that blue melts are best under control in large quantities; large melting-pots are therefore used as a rule. While the melt is in progress ammonia is given off, which carries a certain amount of aniline away. It is advisable to condense this aniline, and to absorb the ammonia by water or sulphuric acid.

When the melt is finished it must be worked up. This may be done by a variety of methods. Of these the simplest—which is, as a rule, resorted to in the manufacture of low-class and Blackley blues—consists in neutralising the melt with a quantity of caustic soda just sufficient to saturate the acid added to the melt. The excess of the aniline is then driven off with steam and recovered. The blue base remains in the still, and is run out whilst still hot, in a tarry state, together with the water. On cooling, it solidifies into a very brittle mass, which may be powdered, dried, and subjected to the process of sulphonation to be described hereafter.

For the production of high-class blues this simple process cannot be adopted. A separation of the crystallisable opal from the uncrystallisable blue, which invariably accompanies it, must take place, and for this separation the melt requires a special treatment. For this there are two distinct processes, of which one is very complete, although costly, because it requires large quantities of spirit. We may call it the *English process*, because it was worked and carried out chiefly in English factories. The other process, which is now used in most of the German works, is very rapid, and requires but little spirit. On the other hand, it does not give so pure a product; we may call it the *German process*.

The *English process* is the final outcome of the original French process for working up the blue melts, which consisted in boiling them out with dilute hydrochloric acid. The aniline was dissolved out together with the organic acid present, whilst the blue remained in the shape of its hydrochloride as a fine blue precipitate, which was filtered off and washed. It was then ready for sulphonation. When it was discovered that this blue was a mixture of different colouring matters it became customary to separate these by boiling the crude blue with spirit. This dissolved out the lower-class blues, leaving a better product as a residue. By repeating this process frequently, a residue was obtained at last which was quite insoluble in spirit. This represented the purest opal blue obtainable. It was by this tedious process that the once famous 'Bleu Mavi,' or 'Bleu MAVI' was obtained in

France and Switzerland. The improved English process much simplified things, and at the same time gave better yields and a purer colour by producing the opal blue in a crystallised condition, in which it is totally insoluble in spirit. This process consisted in adding to the melt (prepared with benzoic acid and a large excess of aniline), while still hot, a certain quantity of aniline hydrochloride; on cooling, the opal blue, being gradually converted into the hydrochloride, settled out in small glistening crystals, whilst the low-class blue remained dissolved in the aniline. The opal was then filtered off, and washed with spirit until quite pure. If necessary, it could be re-converted into base by treatment with alcoholic caustic soda. The base, re-dissolved in aniline, could again be converted into hydrochloride by again adding aniline hydrochloride. The opal then came out in very fine crystals, which represented the blue in a state of greatest purity. The aniline liquors obtained from these crystallisations had to be distilled in order to recover the spirit. They were then made alkaline in order to decompose the aniline hydrochloride present, the aniline was driven off by steam, and the remaining low-class blue obtained in the shape of base as described. Owing to the large quantities of spirit used for washing the crystallised opal, and the consequent loss of spirit by evaporation, this process (which may be recommended for laboratory experiments) was costly, and unable to compete with the rapid and cheap German process.

The German process is based upon the fact that the crystallisable blue opal is insoluble in a very hot solution of aniline hydrochloride, whilst the common non-crystallisable blues are soluble in this liquid. The solution of the aniline salt must, however, be so concentrated (in order to act properly) that it would solidify into a mass of crystals if cooled in the least degree. It is rather fused aniline hydrochloride that is required, and not an actual solution of the salt in water. In order to operate properly with such liquids, closed vessels must be used. The following is the principle upon which the plant in the majority of German works is constructed.

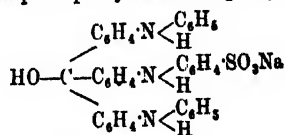
Near the melting-pot a battery of closed iron vessels, lined with lead, is erected. The first of these is filled with a quantity of hydrochloric acid, just sufficient to neutralise the aniline contained in the blue melt. The melt, when finished, is introduced into this vessel by means of air pressure. The vessel is fitted with a stirrer, which stirs up the mixture into a homogeneous mass. This is then pressed into a second vessel, which contains some filtering arrangement, upon which the blue crystals are deposited. The liquid which issues from this vessel is diluted with water, when the common blue hitherto dissolved in it is quickly deposited. The blue crystals remaining on the filter are washed with water, and may be purified by boiling them with spirit.

Blue soluble in water.—Very little of the blue that is manufactured is used in the opal state, viz. soluble in spirit. By far the largest proportion of it must be transformed into products soluble in water in order to become a marketable article. For this purpose sulphonation is resorted to.

The sulphonation of triphenylrosaniline takes place very easily, the phenyl radicles attached to the amino groups being readily substituted by the sulpho group SO_2H . As there are three of these phenyl radicles present, three sulpho groups may be introduced into the molecule of the blue. The pure, crystallisable, high-class opal blue is more easily sulphonated than the common blues. The sulphonation takes place in progressive stages, one sulpho group being introduced after the other. It is difficult to introduce more than two sulpho groups by the use of ordinary sulphuric acid. Fuming sulphuric acid must be resorted to in order to produce the trisulpho derivative. As this, however, is hardly ever required, being much too soluble for the purposes of the dyer, common sulphuric acid is invariably used, but the 'extra-strong' quality of 95-97 p.c. H_2SO_4 is, as a rule, preferred.

If this acid be allowed to act upon an aniline blue, the reaction begins at about 30° and results at first in the formation of the mono-sulpho derivative. The following are its properties:

In the free state triphenylrosaniline monosulphonic acid forms blue flakes; which are quite insoluble in water, in a solution of sodium bicarbonate, or even in weak ammonia. Sodium carbonate dissolves it on boiling; caustic soda in the cold. The solutions are perfectly colourless. They contain, in fact, the sodium salt of monosulphotriphenyltriaminotriphenylcarbinol:



The dry sodium salt is jet black.

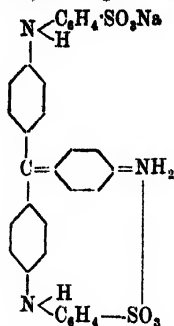
This compound has the curious property of combining with wool in an alkaline bath. The wool remains colourless, but after being washed with water it becomes brilliantly blue if immersed in weak sulphuric acid.

This curious property, discovered by Nicholson, has been made use of by wool dyers, who prefer the 'alkaline' or 'Nicholson' blues to all others for the production of bright and brilliant blues.

The alkaline blues originally manufactured by Nicholson and other makers were as nearly as possible the pure sodium salts of the monosulpho derivative. Owing to the difficulty of dissolving them even in boiling water, another kind of alkaline blues was produced later on; these new alkaline blues contain a proportion of the disulpho derivative. They form blue powders, easily soluble in water, giving a solution which is distinctly blue. The use of these new alkaline blues is exactly similar to that of the old quality.

If the sulphonation of the opal blue be carried farther by raising the temperature and allowing the reaction to continue for a longer period, the monosulpho acid gradually disappears and is replaced by the disulpho derivative. This is insoluble in weak sulphuric acid, but rather soluble in pure water, with an intensely blue colour. Its sodium salt forms bright coppery masses soluble in water with blue colour.

This salt contains probably the compound represented by the following formula:



The disulpho derivatives of the various classes of triphenyl-rosanilines are known under the names of *Cotton blue*, *Water blue*, *China blue*, *Navy blue*, *Guernsey blue*, and many others, which are again sub-divided by the use of the letters R and B. Thus a 6B cotton blue is the disulpho acid of a very high-class, crystallisable Opal blue, whilst a 4R Guernsey or Navy blue would be a reddish-tinted blue, manufactured from an opal prepared with acetic acid and a small excess of aniline in the melt.

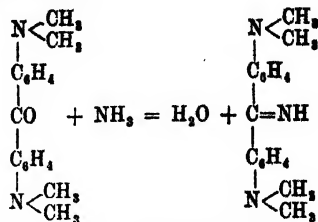
The process of sulphonation, though very simple in theory, requires great care and attention on the part of the manufacturer. The sulphonation is carried on in cast-iron pots into which the necessary quantity of sulphuric acid is introduced. The opal blue, which should be finely powdered and perfectly dry, is then stirred in, and the temperature raised gradually. Samples should be drawn from time to time, and the precipitate produced by the addition of water must be examined as to its solubility in water, weak ammonia, sodium carbonate, and caustic soda. When the desired degree of solubility is obtained, the liquid is poured into water, and the blues filtered off and carefully washed. When quite free from acid, they are dissolved in the necessary quantity of caustic soda; the solution is then filtered, and evaporated to dryness in jacketed pans. Cotton blues should be freed from the excess of sulphuric acid by the addition of slaked lime. The solution of the calcium salt is filtered and converted into the sodium salt by double decomposition with sodium carbonate. After another filtration, the solution of the blue is evaporated to dryness. Certain artifices are required to produce porous masses, such as the brand known as *China blue*, which is manufactured for export, and is required to possess a given bulk for a given weight.

Appendix to basic triphenylmethane colouring matters.

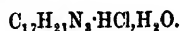
Auramine. This dye-stuff, although a derivative of diphenylmethane, is so closely connected with the manufacture of crystallisable violet that it cannot be omitted from this article.

It has been shown that crystal violet, as well as *Victoria blue* and other dye-stuffs, are manufactured from dimethyl and diethyl diamino-benzophenone. Now, if these ketones be heated with ammonium chloride in the presence of zinc chloride, an interesting reaction takes

place at the temperature of 150°-160°. The oxygen of the ketone is replaced by the imino group NH, thus:



The imides thus obtained are yellow colouring matters, and have received the name of *auramines*. The auramine of commerce is imino-tetramethyl-di-*p*-amino-diphenylmethane hydrochloride, containing one molecule of water of crystallisation:



It forms a yellow powder easily soluble in water. It is exclusively used for dyeing and printing on cotton.

Substituted auramines may be obtained by using the hydrochlorides of primary bases instead of sal-ammoniac. Thus a phenylated auramine of orange colour may be produced by acting with aniline hydrochloride upon tetramethyldiaminobenzophenone.

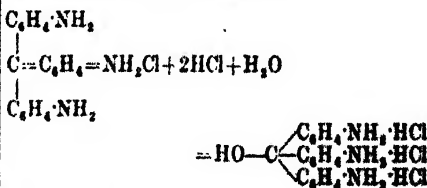
The auramines were discovered by Caro and Kern in 1884. They form the subject of the Eng. Pats. 5512, 1884, and 5741, 1884, and the D. R. PP. 29060 and 31936. (*See art. AURAMINE*, vol. i. 431.)

II. THE AURIN GROUP.

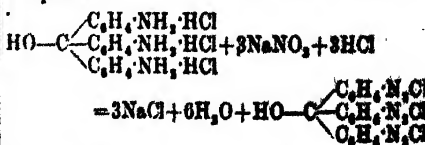
The members of this group contain oxygen in the place of the pentavalent nitrogen of the preceding one. If magenta and its congeners may be considered as quinone-imides, the aurins are the corresponding quinones.

The generic relation between the fuchsin and the aurin groups will be best seen by showing how the typical representative of the former, parafuchsin, may be transformed into the first representative of the aurin group, aurin itself.

We know that parafuchsin, if treated with an excess of acid, is transformed into the triacid salt of triaminotriphenylcarbinol:

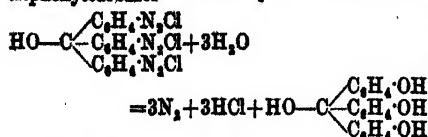


Now this salt, if treated with nitrous acid, is transformed into the corresponding diazonium compound.

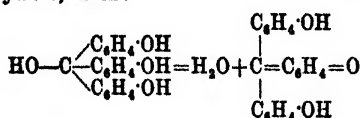


This, on being boiled with water, loses

nitrogen and is transformed into trihydroxy-triphenylcarbinol



The latter loses, *in statu nascendi*, one molecule of water, being transformed into its inner anhydride, aurin:



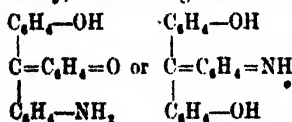
Thus aurin is parafuchsin in which all nitrogen has been replaced by oxygen.

This mode of formation has long been known, not for aurin itself, but for its higher homologue, rosolic acid, which was prepared from the ordinary fuchsin or magenta by the process described. The many co-ordinate points of aurin and rosolic acid were recognised at an early period. On the other hand, chemists were aware of the distinct difference between aurin and rosolic acid, which is just as considerable as that existing between parafuchsin and its higher homologue.

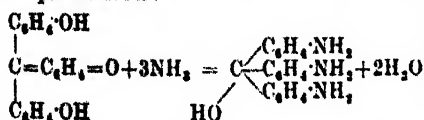
When an insight into the nature of the fuchsin group had been obtained, the knowledge of the constitution of the aurin group followed as a natural consequence.

But even before this was the case, another connection was discovered between aurin and fuchsin.

It had long been known that aurin (the mode of formation of which will be given later on) may be modified by heating it with alcoholic ammonia. F. Persoz produced a red dye-stuff, which he called *Pæonine*, by this process. This had, in all probability, the following constitution:



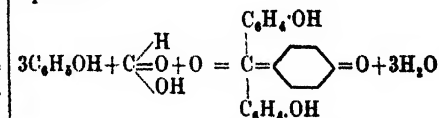
In 1878, Dale and Schorlemmer, whose researches on aurin are of great importance, showed that aurin, by very prolonged heating with alcoholic ammonia, may be transformed into pararosianiline



Thus the connection of the two typical dye-stuffs was definitely established. At present we know that the aurin group contains the acid counterparts of the basic members of the fuchsin group. A considerable number of them are known and described in chemical literature. As, however, almost all of them are of no practical value it would be useless to enumerate them in this article. We will therefore describe only those substances of the aurin group which are of some practical interest. There are very few of them.

1. **Aurin** $\text{C}_{11}\text{H}_{11}\text{O}_3$. The discovery of this substance, or one very nearly related to it, dates as far back as 1834, when F. Runge, the pioneer of the chemistry of coal-tar, observed that crude carbolic acid (containing cresol) was transformed into an acid red dye-stuff by oxidation. Later on (1859), Kolbe and Schmitt and F. Persoz simultaneously observed that pure phenol, when heated with oxalic acid, or with oxalic acid and sulphuric acid, was transformed into a similar red substance. The manufacture of the new dye-stuff was first taken up in Lyons by the firm of Guinon and Marnas. Later on, it was carried out on a large scale by C. Calvert and by C. Lowe; also by Roberts, Dale & Co., in Manchester. The crude aurin thus obtained is a non-crystallisable, brittle, pitchy mass, of a brilliant green metallic aspect, insoluble in water, but soluble in caustic soda solution, with a magnificent red coloration. It dyes silk and wool from an acid bath, producing an orange shade on these fibres. It was much used on silk in former days, but its use has been abandoned since the introduction of the azo-colouring matters, which produce brighter and faster shades.

The researches of Dale and Schorlemmer, Zulkowski, and others have shown that common aurin consists of a mixture of a number of substances which, in a pure state, are well crystallised. Of these, aurin itself $\text{C}_{11}\text{H}_{11}\text{O}_3$, oxyaurin $\text{C}_{11}\text{H}_{11}\text{O}_4$, methylaurin $\text{C}_{12}\text{H}_{13}\text{O}_3$, and pseudo-rosolic acid $\text{C}_{20}\text{H}_{15}\text{O}_4$, may here be mentioned. All these substances are produced by the action of nascent formic acid (generated from the oxalic acid) upon phenol. This mode of formation of aurin itself may be represented by the following equation:

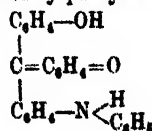


A large number of other reactions have been observed in which aurin is formed to a greater or lesser extent. Thus, for instance, it is obtained by acting with formaldehyde, with iodoform, with chloroform and caustic potash on phenol. These reactions have never attracted the attention of manufacturers, aurin having lost its practical interest.

The sodium salt of crude aurin is known in commerce under the name of *Yellow Corallin*.

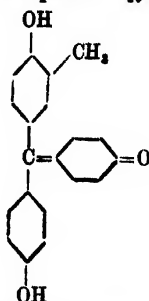
2. **Pæonin**, *corallin red*, *aurin red* is the sodium salt of the reaction product of alcoholic ammonia upon aurin, which has already been mentioned and the constitution of which is given above.

3. **Azulin** is a similar product, of a dirty violet shade, obtained by heating aurin with aniline. It is probably phenylated pæonin:



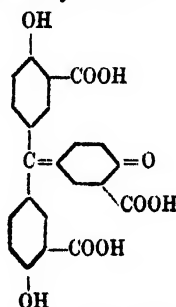
4. **Rosolic acid** is the name which was originally given by Runge to the oxidation product of crude carbolic acid. For a long time it was considered to be identical with aurin. At

present this name is reserved for the product obtained from the ordinary fuchsin of commerce by the diazotising process. It forms magnificent blue needles, which, being homologous to true aurin, have the composition $C_{26}H_{18}O_8$:



It dyes silk and wool orange shades, similar to those obtained with aurin. It is of no practical interest.

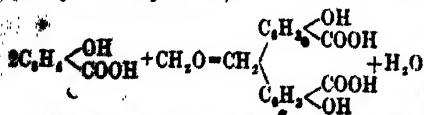
5. Chrome violet $C_{22}H_{12}O_8Na_3$ is the only member of the aurin group which is of considerable practical value. It is the sodium salt of aurin tricarboxylic acid:



It was discovered in 1889 by Sandmeyer, and patented (D. R. P. 49970, J. R. Geigy). It is prepared by acting with formaldehyde, or with a mixture of methyl alcohol and sodium nitrite, upon a solution of salicylic acid in sulphuric acid. The carboxyl groups are in the *ortho*-position to the hydroxyl groups. The result of this arrangement is that the dye-stuff combines readily with metallic mordants of the iron group, and especially with chrome mordant, producing violet shades of considerable fastness on cotton. It is chiefly used for printing on cotton.

The process patented for the production of chrome violet is interesting, because it forms a general and excellent synthetical method for the production of the aurins. It is strictly analogous to the synthetical method adopted for the production of 'Neu-fuchsin' by the 'Farbwerke' of Höchst. Two stages may be distinguished in the process:

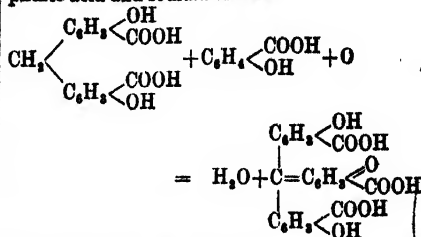
(a) In the first stage, formaldehyde (or methylal) acts upon two molecules of the phenol—in the case of chrome violet, salicylic acid—forming the diphenylmethane derivative (methylene salicylic acid):



This reaction may be facilitated by the addi-

tion of condensing agents, such as hydrochloric acid and others.

(b) In the second stage, the diphenylmethane derivative is simultaneously condensed and oxidised with another molecule of the phenol into the corresponding aurin by the mixture of sulphuric acid and sodium nitrite:

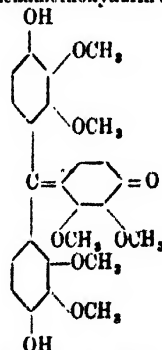


Any phenol, or substitution product of a phenol, may be substituted for the salicylic acid in this process.

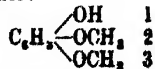
Later on, N. Caro (Ber. 25, 940) prepared a large number of carboxylated aurins by this process, substituting resorcylic, gallic, and cresotinic acid for the salicylic acid in the patented process. The compounds obtained proved to be very similar to chrome violet.

6. Of the large number of aurins prepared, only one more need be mentioned here: pittacal, a curious substance discovered in 1835 by Reichenbach in certain portions of beechwood tar. Liebermann more closely investigated this substance, and gave to it the name of *eupittonic acid* (Ber. 1876, 9, 334; 1878, 11, 1104). Hofmann determined its constitution (*ibid.* 1878, 11, 1455; 1879, 12, 1371, 2261).

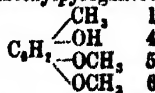
Pittacal is hexamethoxyaurin:



formed by the simultaneous oxidation of dimethylpyrogallol:



and dimethyl methylpyrogallol:



which are both contained in wood tar. The methyl group of the second compound yields the central carbon atom in the same way as occurred with cresol in the formation of the rosolic acid observed by Runge.

Pittacal is an orange substance, crystallising in beautiful crystals when pure. Its solution in caustic alkalis is of a beautiful blue colour.

By heating pittacal with ammonia, Grätzel

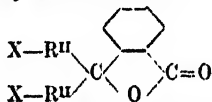
obtained a violet colouring matter, which proved of no practical value (*v. EUPHONIC ACID*, vol. ii. 689).

III. THE PHTHALEIN GROUP.

The phthaleins were discovered by Baeyer in his memorable researches on the condensation of phthalic acid with aromatic hydrocarbons and phenols. Their constitution was, however, at first misunderstood. In 1880, when the curious properties of phthalic anhydride became more definitely known, the error was corrected and the phthaleins were recognised as congeners of the triphenylmethane group.

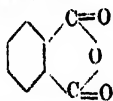
It is a well-known fact that every *o*-dicarboxylic acid is capable of forming, by losing the elements of water, an inner anhydride. These anhydrides act very easily on phenols, in some cases without the addition of condensing agents. Water is again eliminated, and a dye-stuff formed in every instance. Of the many colouring matters thus obtained, only those prepared from phthalic anhydride have, with one exception, become of general and practical interest, and these will here be described.

The central carbon in these dye-stuffs is afforded by one of the carbonyl groups of the anhydride of an *o*-dicarboxylic acid. If we restrict our consideration to phthalic anhydride, the formula may be thus modified:

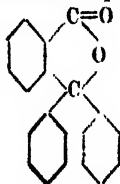


phthalic acid being benzene *o*-dicarboxylic acid.

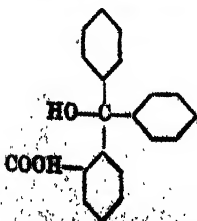
Phthalic anhydride, although perfectly symmetrical in its constitution



acts, in condensations, like an asymmetrical compound, only one of the carbonyl groups being attacked and losing its oxygen. Thus, by being condensed with two molecules of benzene it yields diphenyl-phthalide or phthalophenone:



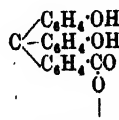
which is the parent substance of all the phthaleins, just as triphenylmethane is the parent substance of the fuchsin and aurin groups. Diphenyl-phthalide, however, is but the inner anhydride of triphenylcarbinol *o*-carboxylic acid:



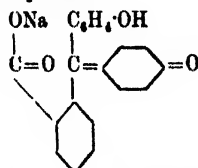
hence the near relation between the phthalein, fuchsin, and aurin groups.

Formerly it was considered as probable that the anhydride structure of phthalophenone was preserved in the dye-stuffs derived from it. At present, almost all chemists are of the opinion that such is not the case, that the carboxyl group becomes free after the condensation has taken place and that it simply serves as a salt-forming group of minor importance. The quinonoid structure is shifted to the pyrone ring which is always present in all the really useful members of this group. Phenolphthalein and diamminophthalophenone, which do not contain the pyrone ring, are of no value as dye-stuffs. The constitution of the more important members of this group will be seen from the structural formulæ given for each of them.

1. Phenolphthalein $\text{C}_{20}\text{H}_{14}\text{O}_4$ was discovered by Baeyer in 1871 (*Ber.* 1871, 4, 658). Its constitution is



it may be considered as a substituted phthalophenone, but as in the free state it has no quinonoid structure, it is also colourless. It is easily prepared by heating phthalic anhydride with phenol in presence of sulphuric acid or stannic chloride. It forms pale-yellow crystals, which dissolve with a fine red colour in caustic alkalis. In the salt so formed the quinonoid structure is established and the substance thereby becomes a dye-stuff:



The practical importance of phenolphthalein is very small. Its only use is that of an indicator for alkalimetric purposes.

For observations on the colourless salts of phenolphthalein and on its value as a colorimetric standard, see Kober and Marshall, *J. Amer. Chem. Soc.* 1911, 33, 59. For the behaviour of phenolphthalein derivatives as indicators, see Rupp, *Arch. Pharm.* 1911, 249, 56.

2. Tetranitrophenolphthalein $\text{C}_{20}\text{H}_6\text{N}_4\text{O}_{12}$ has been proposed as an orange colouring matter for wool. Its sodium salt $\text{C}_{20}\text{H}_6\text{N}_4\text{O}_{12}\text{Na}_2$ is sold as an orange powder under the name of *Aurotine*. It was discovered by C. Dreyfus, H. Bull, and T. Hall, and patented in England under 3441 (1889), in Germany under 52211. In a pure state free tetranitrophenolphthalein forms orange crystals, melting at 344° .

It has long been known that phenolphthalein is not a good dye. The same applies to all the ordinary typical phthaleins. Phthalophenone (diphenylphthalide) is but a poor chromogen, but its properties are at once improved (as has already been shown above) if the two phenyl-radicals in its molecule be linked together by another group, preferably oxygen. We thus come to chromogens containing the pyrone ring

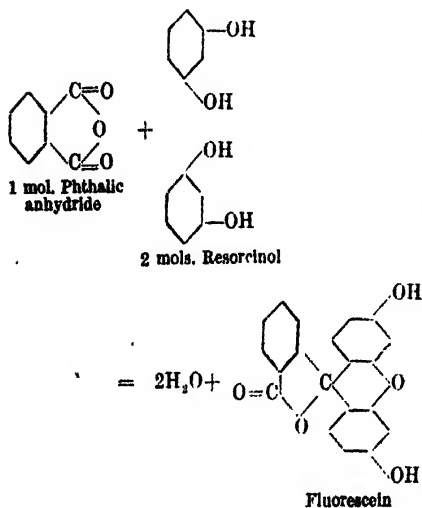
combined with the structure of triphenylmethane derivatives, which, by the introduction of auxochromic groups, give rise to some of the most beautiful dye-stuffs yet discovered. As in all cases, the auxochromic groups introduced may be either the hydroxyl or the amino group; and in the latter hydrogen may be replaced by organic radicles. We thus get phthalein colouring matters of either phenolic (acid) or aminic (basic) character. For a long time the former alone were known; we will, therefore, consider them first.

A. Acid phthalein dye-stuffs.

The prototype of these is—

1. *Fluorescein* $C_{20}H_{12}O_5$. This beautiful substance is formed most easily if phthalic anhydride and resorcinol be mixed in molecular proportions and heated to 190° . In the factories this operation is carried out in enamelled cast-iron pots, heated in an oil bath. The ingredients melt, and large quantities of steam are given off. When the reaction is finished the mass solidifies into a cake of dark-brown colour, which consists of almost pure fluorescein.

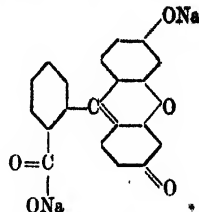
In this reaction two molecules of resorcinol combine with one of phthalic anhydride. At the same time they interact upon one another, losing one molecule of water, and forming the pyrone ring:



Fluorescein in a free state has thus a constitution quite analogous to that of phenolphthalein, although the presence of the pyrone ring is indicated by the intense brick-red colour of the substance. It is quite insoluble in water, sparingly so in the majority of other solvents. If, however, we dissolve it in alkaline liquids, it assumes, like phenolphthalein, its quinonoid nature and this change is marked by the intensity of its colour. In caustic alkalis and in ammonia it dissolves with a brown colour. The solutions have, especially when dilute, a most brilliant and beautiful green fluorescence. Hence the name of the substance.

Concerning the nature of the changes which take place when fluorescein is treated with

alkali, see Baeyer, *Annalen*, 1910, 372, 80, part iii.



Sodium salt of Fluorescein, showing quinonoid structure combined with pyrone ring

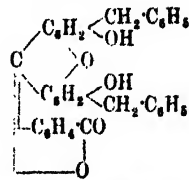
The crude fluorescein obtained in the manufacture, as above described, seems to contain two modifications of the substance (which may be isomerides). By treating the crude cake with boiling spirit, a certain amount of a soluble, non-crystallisable fluorescein is extracted, whilst the greater proportion of it remains undissolved, and is obtained as a crystalline residue on filtering. This process of purification is invariably used in the manufacture of the dye-stuff. Both the soluble and the insoluble part are worked up in the manner to be described hereafter, the insoluble fluorescein giving the better and purer qualities of the dye-stuffs, whilst the low-class qualities are made from the soluble fluorescein obtained by evaporating the alcoholic extract.

A small quantity of the fluorescein manufactured is transformed into its sodium salt



which is sold, under the name *Uranin*, in the shape of a yellow powder, very soluble in water. It is used for dyeing pale yellows on silk.

If benzyl chloride and some sulphuric acid be added to the fluorescein melt a substance is obtained which is supposed to be benzyl-fluorescein:



Its sodium salt is sold as a yellow dye-stuff under the name *Chrysolin*. This substance, discovered by Reverdin in 1877, is not of much practical importance.

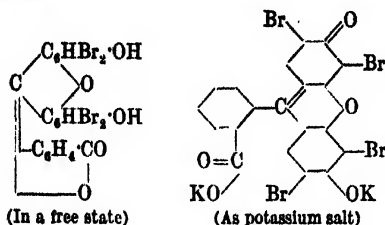
By far the greater part of the fluorescein produced is transformed into very beautiful red colouring matters by the introduction of halogen atoms into its molecule. The dye-stuffs so prepared are known by the generic name of *Eosins*.

If fluorescein be treated by substituting reagents, it is generally observed that four atoms of hydrogen are replaced by other groups. Further investigations have shown that this substitution takes place in the phenyl radicles, which entered the fluorescein in the shape of resorcinol, whilst the phenyl radicle derived from the phthalic anhydride is never attacked by these reagents.

The most important of the dye-stuffs so prepared is

2. *Eosin* $C_{22}H_6O_5Br_2K_2$, the potassium salt

of tetrabromofluorescein. The sodium salt is also occasionally met with, but it does not crystallise so well. The constitutional formula of eosin is:



Eosin is prepared by acting with four molecules of bromine upon one molecule of fluorescein. The crystallisable, modification of the latter is used for the manufacture of a good product. On the small scale a solution of the fluorescein in glacial acetic acid is prepared, and the bromine introduced gradually.

For manufacturing purposes glacial acetic acid is too expensive. The following process, which admits of operating in aqueous solutions, may be used instead.

The bromine is dissolved in exactly the necessary quantity of caustic soda, and the solution is evaporated to dryness. The resulting salt consists of a mixture of sodium bromide and sodium bromate. It is dissolved in water and mixed with a solution of the theoretical quantity of fluorescein in caustic soda. The mixture is then acidified with hydrochloric acid. The bromine generated acts at once upon the fluorescein, and the precipitate obtained is eosin, which need only be dissolved in a solution of potassium carbonate and evaporated to crystallisation.

The quantity of bromine used may be reduced to half (two molecules or four atoms) by using a mixture of potassium bromide and potassium or sodium chlorate, instead of the salt obtained by evaporating the solution of bromine in caustic soda.

This process, although cheap and simple, is not generally used, because the bromine is found to act too energetically. A certain amount of the eosin is destroyed, and the remainder is not so brilliant in colour as it might be.

The bromination proceeds much better in an alcoholic solution; alcohol is, therefore, frequently used for the purpose in the manufacture of eosin. The fluorescein is finely ground, and suspended in strong spirit. The necessary quantity of bromine is added. The bromination takes place slowly and gradually, and an excellent product is obtained. The spirit is recovered by distillation.

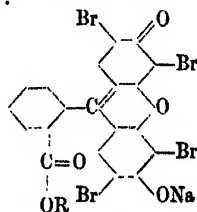
In order to reduce the bromine in this as in the aqueous process to two instead of four molecules, the addition of a chlorate is necessary. But a chlorate must be used which is soluble in spirit. Cupric chlorate is preferred to any other. It is prepared by mixing concentrated aqueous solutions of sodium chlorate and cupric chloride or sulphate. The solution obtained is added to the operation in progress.

Eosin forms either a dark-brown powder, or dark-brown crystals with a green metallic lustre. The potassium salt may also be obtained in flesh-coloured crystals by re-crystallisation from spirit. These crystals contain alcohol of crys-

tallisation. According to strength and purity of shade, the commercial eosins are distinguished by certain letters and additions, such as 'eosin B,' 'A,' 'GGF,' 'DH,' 'extra,' 'extra-fine,' 'soluble,' and others. All these brands dissolve easily in water, with a scarlet coloration. Dilute solutions show a marked greenish fluorescence.

Eosin is used for dyeing silk and other fibres, also for staining paper, and for preparing red inks of a very fine scarlet colour. Large quantities are used for the last-named purpose. Eosin is not a fast colour, but its brilliancy of shade secures a ready sale for the large quantities produced.

3. Eosin soluble in spirit (*Primrose, methyl eosin*). These names are applied to certain products, which are produced by boiling eosin, dissolved in spirit, with caustic soda and methyl iodide, or ethyl bromide. The carboxyl group is thus alkylated, whilst the hydroxyl group remains combined with alkali. The sodium salts thus obtained form glistening crystals, insoluble in water but soluble in spirit. They have the constitution:



in which R stands for either methyl or ethyl. Small quantities of these substances are prepared and employed as an addition to the vermilion used in cotton printing, in order to increase the brilliancy of its shade. Spirit eosin was formerly also used for silk dyeing, but for this purpose it has been replaced by the bluish eosins soluble in water, to be described later on.

If the hydroxyl group of eosin is also to be alkylated, this can only be effected by acting with alkyl iodide or bromide upon the silver salt of eosin. The dialkyl-ethers thus obtained are colourless.

4. Eosin scarlet (*Eosin B, BN, BW, scarlet, J, JJ, V, &c.*). Sodium salt of dinitrotribromofluorescein $C_{20}H_6N_2O_8Br_3Na_2$.

If fluorescein be treated with nitric acid, dinitrofluorescein is obtained, which has found no application as a colouring matter. But by subsequent bromination it yields a brilliant scarlet. The same product (or an isomeric very similar to it) may be prepared by first brominating the fluorescein and then treating it with nitric acid.

This dye-stuff was hailed with enthusiasm when it made its appearance in 1875, but its use was soon much restricted by the introduction of the scarlet azo-dyes which are quite as brilliant, and at the same time faster, cheaper, and more easy in their application.

5. Erythrosin (*Bluish Eosin, Dianthin, Primrose soluble, Pyrosin B, and other names*).

This is the sodium salt of tetraiodofluorescein $C_{20}H_6O_8I_4Na_2$. The potassium salt is also met with occasionally. It is prepared by iodinating fluorescein with iodine and oxidising agents, such as mercuric oxide, iodic acid, cupric chlorate,

&c. It may also be prepared by introducing iodine monochloride into an alcoholic suspension of fluorescein.

Erythrosin dissolves in water, with a fine red colour, and very slight fluorescence. It dyes silk in shades which are much more bluish than those obtained with eosin.

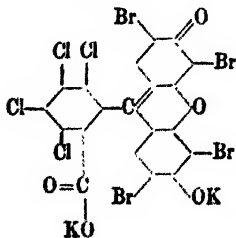
Erythrosin was introduced into the market in 1876 by Bindschedler and Busch. It was well received by the silk dyers. Owing to the high price of iodine, a mixture of eosin and Bengal red is now used for producing the same shades.

There is one application, however, for which pure erythrosin is still required—for producing orthochromatic dry plates for photographic purposes. As a sensitiser of silver bromide, erythrosin holds a prominent place amongst all the colouring matters hitherto tried.

Di-iodofluorescein was sold and used for a very short time as an orange dye-stuff, under the name 'Pyrosine J.'

6. Phloxin (*Potassium salt of dichloro- or tetrachloro- tetrabromofluorescein*).

This colouring matter, discovered in 1876 by Nöltting, together with the following ones, formed a new departure in the manufacture of the eosin dyes. The characteristic feature of these substances is the fact that they contain halogen atoms substituted for hydrogen, not only in the resorcinol groups, but also in the phenyl group derived from the phthalic anhydride. Now, it has already been said that a substitution of this kind cannot be effected in ready-made fluorescein. To prepare phloxin, therefore, or any of its congeners, a special fluorescein must be used, prepared not with ordinary phthalic anhydride, but with the anhydrides of dichloro- or tetrachloro- phthalic acid. Dichlorophthalic acid is best prepared by oxidising dichloronaphthalene, whilst tetrachlorophthalic acid may be obtained by chlorinating phthalic anhydride in the presence of finely divided iron. Both acids give colouring matters of very similar shades, the tetrachloro derivatives being but very little bluer than the dichloro derivatives. The process of manufacture of the dye-stuffs is identical with that described for eosin. The constitutional formula of phloxin is

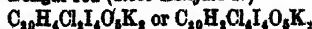


if derived from tetrachlorophthalic acid. The phloxin derived from dichlorophthalic acid contains, of course, two atoms of chlorine less.

Commercial phloxin is a red powder, soluble in water, with a red colour and no fluorescence. It dyes beautiful bluish-red shades on silk, which resemble those obtained with erythrosin.

7. *Cyanosin* is the monomethyl ether of phloxin. It is soluble in spirit, and dyes shades still bluer than phloxin.

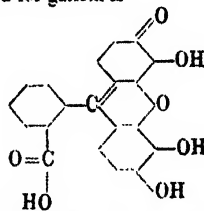
8. Bengal red (*Rose Bengale N*)



is the iodo derivative of this series. It is the bluest eosin dye-stuff obtained. It is very expensive, and was formerly used in large quantities to produce the most brilliant bluish-reds on silk. It has now, to a great extent, been replaced by the rhodamines. Its methyl ether, soluble in spirit, received the name of *Cyanosin B*. Its application never became important.

The phthalein derivatives of resorcinol are all very brilliant dyes. There are, however, some other acid phthaleins which, although important as colouring matters, are of much more sober hues. They are derivatives of pyrogallol.

9. *Gallein* $\text{C}_{20}\text{H}_{12}\text{O}_7$. If phthalic anhydride be condensed with pyrogallol, the reaction takes place quite as easily as with resorcinol. The product obtained is, as might be expected, a dihydroxyfluorescein. The constitutional formula now adopted for gallein is



For the manufacture of gallein it is not necessary to prepare pure pyrogallol. Gallic acid may be used instead, which, losing carbon dioxide, is at once transformed into gallein by the action of the phthalic anhydride.

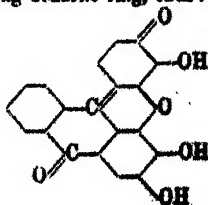
Gallein is generally sold in the shape of a violet paste. It is sparingly soluble in water, easily soluble in caustic alkalis, with a bright-blue coloration. It dyes mordanted wool and cotton. Chrome mordants are used preferably, and dark-violet shades are obtained.

On account of the similarity of the application of gallein to that of alizarin, gallein is also sold under the name of *Alizarin violet* or *Anthracene purple*.

10. *Cœrulein* (*Alizarin green, Anthracene green*) $\text{C}_{20}\text{H}_8\text{O}_6$. This is one of the most important dye-stuffs for wool and cotton, dyeing a beautiful and very fast olive green on chrome mordants. The cotton printer uses it constantly, both pure and mixed, with other dye-stuffs of the alizarin family.

It was discovered in 1871 by A. Baeyer, who obtained it by heating gallein with concentrated sulphuric acid to 200°. By the same process it is now prepared in immense quantities on the large scale.

In this process the substance loses one molecule of water and the carboxyl group forms a new hexagon ring by condensing with the neighbouring benzene ring, thus:



Cerulein forms a black paste, insoluble in water. It is soluble in caustic alkalis, with a greenish-blue coloration.

11. Cerulein S (soluble cerulein)

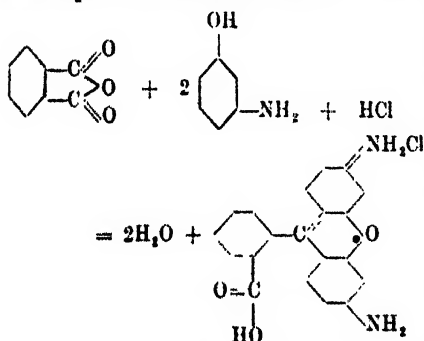


This is the product of the reaction of sodium bisulphite upon cerulein; its manufacture is carried on by the Badische Anilin and Soda works at Ludwigshafen. It forms a black powder, soluble in water, with a brown coloration. It is easily decomposed by the addition of acids or by heat. It is used for the same purposes as cerulein, and is very convenient, on account of its easy solubility. In dyeing with it, it is, of course, decomposed, the ordinary cerulein being deposited on the fibre.

B. Basic phthalein dye-stuffs.

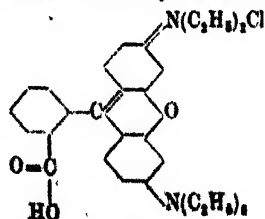
For a long time these were not known. The manner in which they might be obtained had, of course, suggested itself to the consideration of chemists, but the substances required for their synthesis seemed to be quite out of the reach of the manufacturer. In 1887, however, M. Cere-sole, of the Badische Anilin- und Soda-Fabrik, successfully effected the synthesis of the first basic phthalein, which proved to be of such value that a thorough search for a good means of preparing the necessary ingredients was made, which led to complete success.

To obtain the basic substance analogous to fluorescein, it is merely necessary to replace one of the hydroxyl groups of resorcinol by an amino-group; or, in other words, to employ *m*-aminophenol instead of resorcinol:



Experience has shown that the compound thus obtained has no practical value. If, however, diethyl *m*-aminophenol is used instead of the *m*-aminophenol, a most beautiful colouring matter is obtained, known under the name of

1. Rhodamin B $C_{24}H_{21}N_2O_3Cl$. The commercial product is the monohydrochloride:

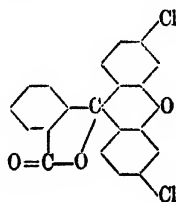


It forms beautiful needles of a metallic green appearance, easily soluble in both water and spirit. Weak solutions show a most mag-

nificent orange fluorescence, which disappears on heating, and reappears in the cold. This is the most beautiful red colouring matter ever prepared, dyeing silk, wool, and cotton a most brilliant pink of a bluish shade.

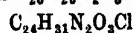
The process described for the production of rhodamin is patented by the Badische Anilin- und Soda-Fabrik, Eng. Pat. 15374, 1887; D. R. P. 44002. The diethyl-*m*-aminophenol is prepared from diethylaniline by heating it with fuming sulphuric acid to 60°, diethylaniline *m*-sulphonic acid is formed, which yields the phenol by fusion with caustic soda.

There is, however, another process for the manufacture of rhodamin, discovered by the Farbwerke of Höchst (D. R. P. 48367, 1888). It consists in treating free fluorescein with phosphorus pentachloride, when the fluorescein chloride

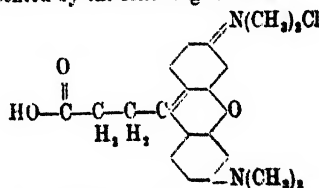


is formed. This is transformed into rhodamin if heated with diethylamine under pressure.

2. Rhodamin S $C_{26}H_{22}N_2O_3Cl$, and



These two colouring matters, which are identical in their practical properties and applications, are not, strictly speaking, triphenylmethane derivatives; nor are they derived from phthalic acid. They must, however, be mentioned here, because they are near congeners of rhodamin B. They are obtained by treating dimethyl- or diethyl-*m*-aminophenol, not with phthalic, but with succinic, anhydride. Succinic acid is the typical *o*-dicarboxylic acid of the fatty series. Like phthalic acid, it forms an anhydride, which condenses with resorcinol into fluorescein-like dye-stuffs; these, however, offer no practical interest. The succineins of dimethyl- and diethyl-*m*-aminophenol, however, show a sufficient difference from rhodamin to be manufactured and sold as a special brand. The constitution of the dimethyl compound may be represented by the following formula:



It is, therefore, not a triphenylmethane derivative. It is sold in the shape of its zinc double chloride.

Rhodamin S shows great affinity to un-mordanted cotton. It is one of the few members of this group which may be considered to be what is now called a substantive colouring matter.

The properties of rhodamin S are very similar to those of rhodamin B. It forms crystals with a green metallic lustre, easily soluble in water, with a red coloration, and a marked

yellow fluorescence. The shades obtained with it are yellower than those produced with rhodamin B.

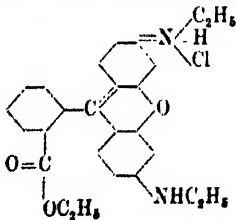
Rhodamin B and S remained for some time the only important members of this magnificent group of dye-stuffs. After a while, however, some new representatives of it made their appearance, of which the more important may be here shortly described.

Rhodamin G $C_{28}H_{27}N_2O_2Cl$ is obtained by heating rhodamin B with aniline hydrochloride. One of the ethyl groups is split off in the shape of ethyl chloride and the recovered dye-stuff is a tri-ethyl-rhodamin which dyes wool and silk in red shades of a much more yellowish tinge than the original rhodamin B.

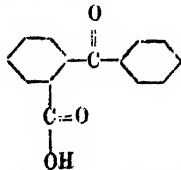
The process of alkylation, which produced such remarkable results in the eosin group, proved equally applicable to the rhodamins. It was carried out at first by using alkyl chlorides, but later on it was discovered that a much cheaper and simpler way to the same end consists in saturating alcoholic solutions of rhodamins with hydrogen chloride. As this is a method which is exclusively applicable to the alkylation of organic acids, the possibility of using it for the rhodamins formed a proof of the presence of a free carboxyl group in the dye-stuffs and went a long way in establishing the modern views about their constitution.

Rhodamin 3B, *Anisoline*, was the first of the alkylated rhodamins. It dyes a more bluish shade of red than rhodamin B, and is, if possible, even more brilliant and pure in its tinge, which strongly resembles that of certain flowers such as the 'Crimson Rambler' rose.

Rhodamin 6G was obtained by the same process from *sym*-diethylrhodamin (produced by the condensation of phthalic acid with two molecules of mono-ethyl-*m*-aminophenol), and has consequently the following constitution:

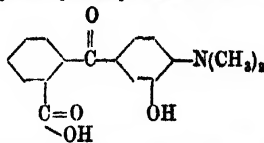


When once the constitution of the rhodamins was recognised, it was clearly seen that they may also be considered as derivatives of *o*-benzoyl-benzoic acid:

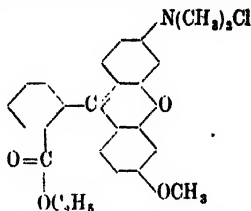


Suitable substitution products of this acid may therefore be used for the synthesis of rhodamins. This is important because it enables us to produce asymmetrical rhodamins, whilst the original process was applicable only to the production of symmetrical members of this important class of dye-stuffs. As an example of this method, *Rhodamin 12 GM* may be quoted,

which is prepared by acting with dimethyl-amino-hydroxybenzoylbenzoic acid:

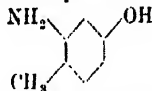


upon monomethylresorcinol and subsequent esterification of the product obtained. This dye-stuff is consequently quite asymmetrical and has the constitution:



It dyes silk, wool, and cotton a beautiful yellowish red.

If in the process given for the production of rhodamin 12 GM the monomethylresorcinol be replaced by *m*-amino-*p*-cresol:



a new and exceedingly beautiful dye-stuff is obtained, which is sold under the name *Irisamin 4* or *Rhodin 3G*. It dyes silk, wool, and mordanted cotton a flaming, beautiful red.

Several other members of this group have been prepared by various methods, amongst which the reaction of formaldehyde upon ready formed rhodamins may be mentioned. All the rhodamins have also been found applicable not only to the regular dyeing of textile fabrics, but also to the staining processes so largely used for paper, wood and confectionery. Very large quantities of these dyes are used for such purposes.

Few groups of synthetical dye-stuffs have proved so prolific as that of which a short description has here been given. The triphenyl-methane group contains some of the oldest artificial colouring matters known, but for more than half a century it has continued to yield new additions to the vast number of such compounds which chemical science has placed at the disposal of our textile industries. O. N. W.

SUPPLEMENT.

Recent progress in this group of colours, which already contains dyes of almost every shade, and suitable for nearly all kinds of dyeing processes, has been mainly towards the production of colours having greater fastness than is possessed by many of the earlier members of the group. It is interesting to note that whilst work has been undertaken in very numerous directions, the most important practical results have thus far been obtained upon a few fairly well defined lines.

In addition to the extension of the group in new directions, some interesting conclusions in connection with the constitution of phenylated

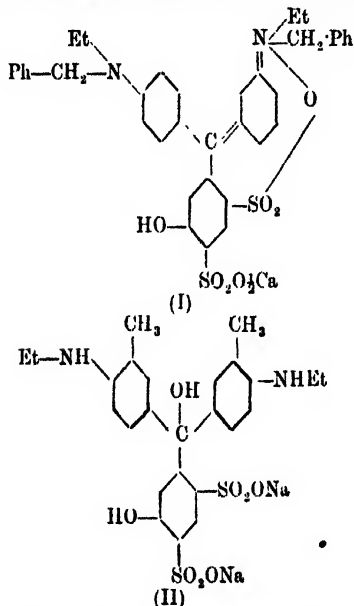
fuchsin need to be noted, whilst the connection between colour and chemical constitution and other problems of a theoretical nature concerning the triphenylmethane compounds have not ceased to claim attention.

The application of Brilliant Green as an antiseptic and in connection with the detection of typhoid carriers, is of considerable interest, and our knowledge in this field has been greatly added to by the work of Fairbrother and Renshaw (J. Soc. Chem. Ind. 1922, 41, 134 T), whilst Casella (Eng. Pat. 14742, 1912) claims that compounds of the rosaniline group which have halogens in the 'ortho' position to the amino group are of value in medicine on account of their action on tripanosomes.

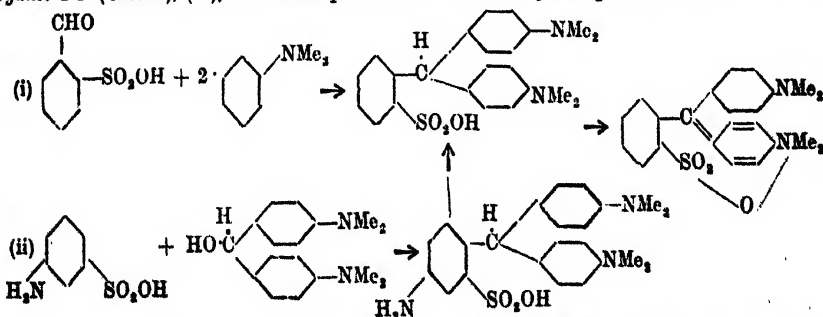
I. THE FUCHSIN GROUP.

(A) Diamino-triphenyl-methane derivatives.

In this group the extension of the 'Patent Blue' class calls for most notice. Substitution



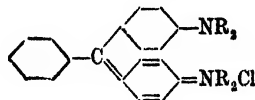
derivatives such as Patent Blue A, (I), and Cyanol FF (Casella), (II), have been produced



By the use of such groups as NO₂, COOMe, CN, or the halogens Cl and Br, in place of the sulphonic acid group in the ortho position, it has been possible to produce other products having similar properties. In this connection a further

by the use of ethyl-benzyl-aniline and mono-ethyl-o-toluidine respectively in place of dimethyl- or diethyl-aniline in the processes for the manufacture of 'Patent Blue.' When patent blue itself is oxidised (D. R. PP, 80961, 81478; Friedl. 3, 152, 153) a new dye, Cyanin B (M. L. B.), is produced, which is faster to light and washing than patent blue, and dyes similar shades. Concerning the structure of cyanin B, little is definitely known, but it is considered probable that during the oxidation an ethyl group is removed.

Very interesting and useful results have been obtained from investigations of the effect produced upon the tinctorial properties of compounds of the malachite green type

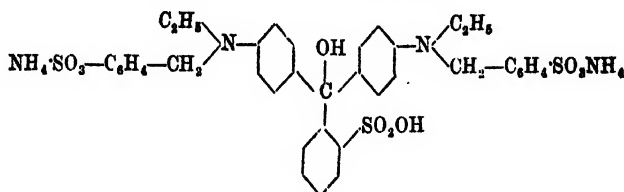
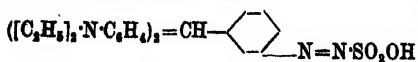


by substitution in the third phenyl group. Not a little of the work of this nature has resulted from the desire to explain the very bluish shade of patent blue and its fastness to alkalis in comparison with other closely related colours.

In the first instance it was considered that the hydroxy group present in the 'meta' position was responsible for these differences. Sandmeyer (J. Soc. Dyers and Cols. 1895, 154) and Suais (Bull. Soc. chim. 1897, 517) independently succeeded in showing that this was not the case, but that the effects mentioned were due to the sulphonic acid group in the 'ortho' position to the methane carbon atom. This conclusion was arrived at in two ways: (i) by condensation of benzaldehyde o-sulphonic acid (see Vol. I. p. 569) with dimethylaniline followed by oxidation of the leuco compound thus produced, and (ii) by condensation of tetramethyl-diamino-diphenyl-carbinol with metanilic acid, elimination of the amino group from the resulting leuco compound, then oxidation of the product. In either case the final product is the ortho-sulphonic acid of malachite green, and this resembles patent blue in that it gives dyeings fast to alkali and more blue to tone than malachite green. The two series of reactions may be represented thus:

observation of Suais (Bull. Soc. Ind. Mulhouse, 1912, 82, 703) is of interest. He concludes that the property of fastness to alkalis is not confined to the dyes containing an acid group in the 'ortho' position to the central carbon atom,

but is shared by the 'meta' diazo-sulphonates of this series. As instance of this class of compounds he mentions a green dye obtained by oxidation of the leuco base:



This latter is produced from the corresponding amine by treating its diazo compound with sulphite.

The following are some representative commercial products in which ortho substitution of the type mentioned above occurs:

Erioglaucine A

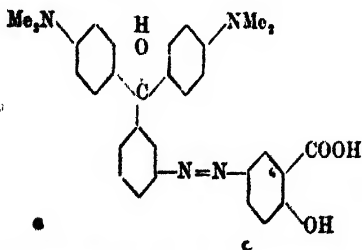
is obtained by condensation of benzaldehyde *o*-sulphonic acid with ethyl-benzyl-aniline sulphonic acid, oxidation of the leuco compound produced and conversion of the product into the acid ammonium salt (D. R. P. 89397; Frdl. 4, 184). It gives bright shades fast to alkali. *Eriochlorine* is said to be the above mixed with yellow and violet.

Benzyl Green B is a product in which the sulphonic acid group in the ortho position to the methane carbon atom of erioglaucine A is replaced by a chlorine atom.

Seloglaurine, obtained by condensation of *o*-chloro-benzaldehyde with dimethylaniline and oxidation of the leuco compound formed (D. R. P. 94126), is *o*-chloro-malachite green. When the same aldehyde is taken but condensed with ethyl-benzyl-aniline, or mono-ethyl-*o*-toluidine, the dyes produced are *Night Green 2B* and *Selocyanine* respectively. The introduction of further substituents in the benzaldehyde used is exemplified in *Glacier Blue*, which is made from 2:5-dichloro-benzaldehyde and mono-methyl-*o*-toluidine (D. R. P. 71370), and *Night Blue B*, made from 2-chloro-5-nitro-benzaldehyde and ethyl-benzyl-aniline sulphonic acid. An interesting extension of this series is found in the dye produced by the condensation of benzaldehyde 2:4-disulphonic acid with one molecule of diethyl-*m*-amino-phenol and one molecule of mono-ethyl-*m*-amino-*p*-cresol, closing the pyrone ring then oxidising the leuco compound thus formed. The dye gives red shades on silk, but does not colour cotton (U.S. Pat. 1006738).

The development of malachite green derivatives has not been entirely along these lines, and a number of 'para' compounds have been described (cf. Fr. Pat. 422843; Eng. Pat. 1913, 7757; and J. pr. Chem. 1915, 91, 341).

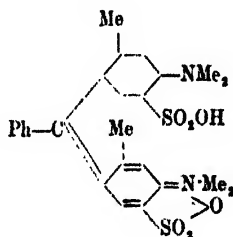
Azo Green



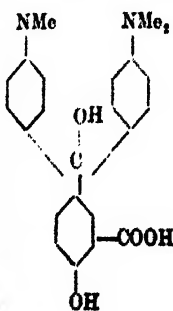
a 'meta' derivative, is an interesting colour

which is a member both of the triphenyl-methane and of the azo group of dyes. It is formed by diazotisation of *m*-amino-malachite green and coupling with salicylic acid, and is a mordant colour giving yellowish-green shades on chrome mordanted wool. It is also used for calico printing (cf. also Eng. Pat. 234950).

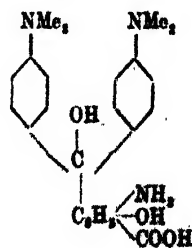
Green dyes of considerable fastness are also produced by condensation of benzaldehyde (or homologues not containing an amino group in the para position) with alkyl, or aryl, derivatives of *m*-toluidine sulphonic acid and oxidation of the leuco compound formed. Alternately, the condensation product of benzaldehyde and *m*-toluidine may be sulphonated then oxidised (Bayer, Fr. Pat. 461810). The dyes are of the type:



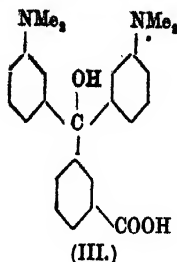
A number of mordant colours derived from malachite green, chiefly by the introduction of hydroxyl and carboxylic acid groups into the third phenyl residue, are included in the series of chrome colours of the Bayer company, e.g. *Chrome violet* (I.) (D. R. P. 58483; Frdl. 3, 120). *Chrome bordeaux* (II.), and *Chrome green* (III.) (D. R. P. 60606; Friedl. 3, 25).



(I.)



(II.)

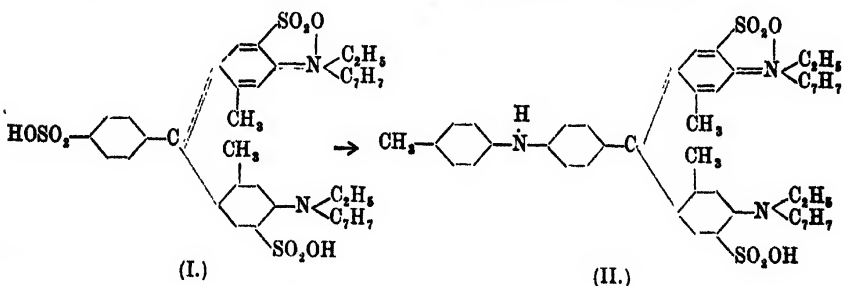


An interesting comparison of the properties of Malachite Green, with those of an analogous furane dye, has been made by Renshaw and Naylor (J. Amer. Chem. Soc. 1922, 44, 832), whilst Bogert and Nisson (Proc. Nat. Acad. Sci., 1924, 10, 421) have similarly compared a bis-triphenylmethane dye.

(B) Triamino-triphenyl-methane derivatives.

In this group considerable interest is attached to the work dealing with the phenylation products of rosaniline and *p*-rosaniline. Baeyer and Villiger (Ber. 1904, 37, 2870), Lambrecht (Ber. 1907, 40, 145), and Knecht (J. Soc. Dyers and Col., 1907, 119), have succeeded in showing that the phenylation of rosaniline proceeds rather differently from what has been generally assumed in the past. As the result of this work

it is concluded that whilst *p*-rosaniline may be converted into triphenyl-*p*-rosaniline by phenylation in the usual manner, in the case of rosaniline the reaction cannot be made to proceed beyond the formation of diphenyl-rosaniline. It is considered that this difference is due to steric hindrance, the methyl group in the ortho position to one of the amino groups in ordinary rosaniline preventing the entrance of the phenyl nucleus into the amino group of that aromatic residue, whereas in *p*-rosaniline this effect is not observed, as no methyl group is present in the ortho position to any of the amino groups. Baeyer and Villiger concluded from the examination of a sample of commercial aniline blue that it consisted of almost pure diphenyl-rosaniline. The production of *ppp*-triamino-triphenyl-methane colours from derivatives of *pp*-diamino-triphenyl-methane is of interest and forms a link between the products of this and of the preceding group of dyes. The Bayer company describes the preparation of triamino-triphenyl-methane colours, which give bluish shades, by treating *pp*-diamino-triphenyl-methane compounds containing a halogen or alkoxy group in the para position to the methane carbon, with amines or their salts (Fr. Pat. 474260), or by similar treatment of the corresponding para sulphonic acid derivatives (D. R. P. 287003). The latter process is exemplified by the formulæ:

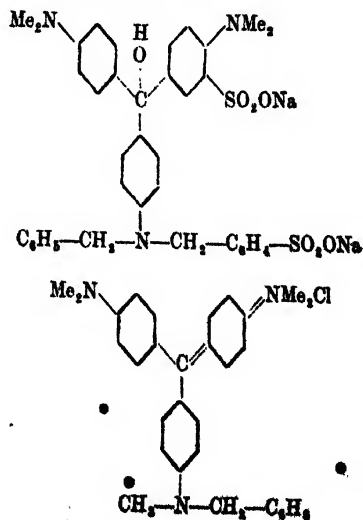


and it is stated that this should prove to be a cheap technical method for the production of dyes of this type. In passing from (I.) to (II.), the shade of the dye changes from green to blue. For this type of process, see also D. R. PP. 292998, 293322 (M. L. B.).

Suais (Bull. Soc. Ind. Mulhouse, 1912, 82, 691) describes the treatment of crystal violet (magenta, Paris violet, malachite green, and brilliant green react similarly) with *m*-toluylene-diamine at 160°-180°C., whereby a yellow fluorescent basic dye is produced and dimethylaniline liberated. It is probable that the products produced in this way are identical with the compounds obtained from the condensation of Michler's ketone with *m*-diamines (Eng. Pat. 1352, 1895).

In connection with the development of this group of dyes, the relationship that exists between *Eriocyanin A* (which may be prepared by condensation of tetra-methyl-diaminobenzhydrol monosulphonic acid with dibenzylaniline mono- or di-sulphonic acid and oxidation of the leuco compound produced (D. R. P. 88085; Fridl. 4, 219), and the much older colour *Benzyl Violet 7B* (1866), is perhaps worthy of

mention. This is clearly seen by comparison of their respective formulæ:



The important colour *Azo Green* (see above), is directly derived from *mpp*-tri-amino-triphenylmethane, and green azo-triphenylmethane dyes closely related to it are mentioned in D. R. PP. 175825, 175826 (M. L. B.).

According to Copisarow (Chem. Soc. Trans. 1920, 117, 1542) *Carbazol Blue* is a tricarbazyl-methane compound represented by $(C_{11}H_7NH)_3C = C_6H_4NHCOOH$. It is produced by fusing together carbazol and oxalic acid, and the linkage to the central carbon atom is presumed to be in the *para* position to the nitrogen atom in each carbazol nucleus.

Auramine.

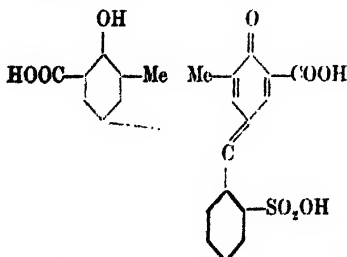
In D. R. P. 287994, the Badische company indicate that very good yields of N substituted 4:4'-diamino-diaryl-thio-benzophenones are readily obtained from the corresponding hydrocarbons by treatment with polysulphides. The products are useful for the production of auramine derivatives (see article on AURAMINE, vol. i. p. 431).

II. AURIN GROUP.

In this group a considerable number of colours have been described which are related to the members of the diamino-triphenylmethane group in the same way as aurin is related to para-rosaniline.

Most of the colours of this sub-group contain carboxyl groups in the ortho position to the hydroxyls, and are of value as chrome colours. As in the case of the compounds of the Patent Blue group, increased fastness to alkalis is obtained by the introduction in the third benzene nucleus of a substituent (halogen, sulphonic acid, &c.) in the ortho position to the methane carbon atom. The following are typical commercial products of this class:

Eriochrome cyanin R is obtained by condensing benzaldehyde-*o*-sulphonic acid with *o*-cresotinic acid and oxidising the leuco compound produced (D. R. P. 189938; Frdl. 9, 200). This colour gives red dyeings on wool which change to violet-blue when after-chromed.



If *o*-cresotinic acid is condensed with an *o*-chloro-benzaldehyde, and the product oxidised, the resulting dye is *Eriochrome azurol B* (D. R. PP. 198909, 199943; Frdl. 9, 201, 204). For the preparation of *Chrome azurol S*, an *o*-chloro-benzaldehyde sulphonic acid is used in the condensation (D. R. P. 199943; Frdl. 9, 204). Members of the Chromoxan series of dyes (Bayer) are said to be produced in a similar manner from naphthalene aldehydes.

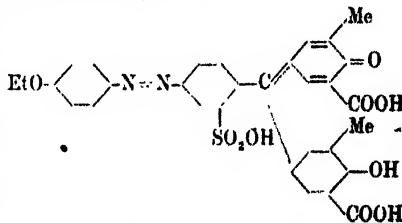
The use of penta- and tetra-chloro-benzalde-

hydes for the production of colours of this group has been described in D. R. P. 234519 (Bayer) and Eng. Pat. 13970, 1915 (Casella) respectively. The use of chlorination products of xylene—which are first converted to chloro-aldehyde-benzoic acid derivatives—for the production of dyes of this group has also been described by Casella (Eng. Pat. 16317, 1914).

When di-ortho-substitution products of benzaldehyde are used it is stated that colours of great depth and fastness result (D. R. PP. 199943, 213502).

In patent literature various chrome colours, belonging to this group, are also described, in which the non-hydroxylated benzene nucleus contains an amino, or substituted amino group (Eng. Pat. 12130, 1910; Fr. Pat. 417490; D. R. P. 252287 (M. L. B.); Fr. Pats. 424723, 425676 (Bayer); and Eng. Pat. 10335, 1911 (Geigy)), and these products give fast shades when chromed.

Azo colours which are members of this group have also been investigated, and the Bayer company (Fr. Pat. 413383; U.S. Pats. 1021364, 1021365, 1021366) describe the production of dyes which give yellow to red shades on wool from an acid bath, the colours passing to blue or black when after-chromed. These products are obtained by condensing amino-benzaldehyde (or its nuclear substitution products, e.g. *o*-chloro-*m*-amino-benzaldehyde) with 2 mols. of an aromatic hydroxy-carboxylic acid, diazotising and coupling the leuco compound produced, then oxidising the product. Green and Sen (Chem. Soc. Proc. 1912, 28, 137) have also examined azo dyes of somewhat similar type, but obtained by condensing azo-aldehydes with hydroxy-toluic or salicylic acids. The following formula represents a typical member of the series obtained by them:



The dyes are polygenetic, dyeing wool directly in red shades, and producing various shades with different metallic mordants. The final oxidation may, in the production of the chrome lakes (which are black), be carried out on the fibre by dyeing with the azo-methane derivative then treating with an acid solution of bichromate. A similar dyeing with a leuco compound, followed by simultaneous oxidation and formation of chrome lake on the fibre, is referred to in respect of other dyes of this sub-group in Eng. Pat. 25007, 1910; Fr. Pat. 421564 (A. G. F. A.).

In the true aurin group—that containing dyes derived from *ppp*-tri-hydroxy-triphenyl-carbinol—considerable attention has been paid to the production of chrome colours. A number of such products, belonging to the triphenylmethane or diphenyl-naphthyl-methane groups, have been described (cf. D. R. PP. 216924, 217571, 216686; Eng. Pat. 11083, 1911, &c.), most of them being prepared by condensation of hydroxy-

aldehydes (or their derivatives) with hydroxy-carboxylic acids (or derivatives), though use has also been made of the methylene-dialcyclic acid process. This work has resulted in the range of colour obtainable with this type of dye being considerably extended. In a large number of cases the after-chroming of material dyed with these products gives rise to a very marked change in shade.

Products have also been investigated in which the hydroxyl group in the third benzene nucleus is in the meta position to the methane carbon atom (Fr. Pat. 404800). In such cases the meta hydroxyl group may be introduced either by use of hydroxy- or amino-aldehydes; in the latter case the amino group is converted to hydroxyl by use of the diazo compounds either before or after the oxidation of the leuco triphenyl-methane derivative (D. R. P. 234805).

III. THE PHTHALEIN GROUP.

Here questions of structure and constitution have been responsible for a considerable amount of work. On the other hand, evidence is not lacking of attempts to extend the list of commercially useful products belonging to this group. The structure of the salts of the phthaleins has been discussed at length by Green (J. Soc. Chem. Ind. 1909, 638), whilst the production of isomeric forms of fluorescein and their salts has been described by H. v. Leibig and their probable constitution considered (J. pr. Chem. 1912, 86, 472). The effect of the introduction of additional auxochromes into compounds of the phthalein and benzein series of dyes has been studied by Watson (Chem. Soc. Trans. 1915, 107, 1579).

Various attempts have been made to obtain new dyes of this series, and the following are typical examples of these. By introduction of nitro groups, either by use of nitro derivatives of phthalic acid, or nitro-resorcinol and its derivatives (D. R. P. 245231), products have been obtained which give good dyeings on chrome mordanted wool. D. R. P. 290508 describes the condensation of pyrogallol (or other derivatives of resorcin having a para position to one of the OH groups free) with α -hydroxy-naphthoyl-*o*-benzoic acid, whereby chrome mordant dyes of the phthalein series are produced. Wool dyes have been prepared by treatment of eosin, or phloxin, with aniline, whereby the halogen is wholly or partially replaced by the amine residue, followed by sulphonation of the product (Chem. Zentr. 1913, 2, 2126). Colours of this group have been described by Lucius and Brüning (D. R. PP. 290540, 291883), in which selenium has been introduced into the molecule by treatment of phthalins—obtained by reduction of phthaleins—either with selenium halides or selenium oxy-chloride.

In the rhodamine group it is interesting to note the description by Block (Bull. Soc. Ind. Mulhouse, 1913, 83, 81) of the use of tetrachlorophthalic anhydride in the production of derivatives of rhodamine, as in the acid group it may be used for the preparation of phloxin. When condensed with dimethyl-*m*-amino-phenol it is stated that it yields a dye giving shades which are very fast to light and alkali.

Intermediates.

In conclusion, it should be noted that the extension of the triphenyl-methane group of dyes has given rise to a considerable amount of investigation of the derivatives of benzaldehyde and to the manufacture of quite a number of these, which were previously but rarely met with. For further details the article on BENZ-ALDEHYDE, vol. i. 565, should be consulted.

A. E. E.

TRIGEMININE. Pyramidone butyl chloral hydrate.

TRILITE. Syn. for trinitrotoluene, used as an explosive.

TRINOL. Syn. for trinitrotoluene.

TRIPHYLITE. A manganese lithium phosphate LiMnPO_4 , occurring naturally as large, rough (orthorhombic) crystals and coarsely cleavable masses. By the isomorphous replacement of manganous oxide by ferrous oxide it passes into the closely allied mineral lithiophyllite (LiFePO_4). The colour is grey or bluish, but, the mineral being readily weathered, the masses are usually dark brown on the surface. Triphylite occurs in pegmatite-veins, often in association with spodumene and other lithium-bearing minerals, and sometimes with tin ore. It is found at Bodenmais in Bavaria, Hurléaux and Chanteloube in Haute-Vienne, Branchville in Connecticut, Pala in California, the Black Hills in South Dakota, and King's Mountain in North Carolina. Containing 8.1-9.4 p.c. of lithia, it has occasionally been collected when mining for other minerals, and used as a source of lithium salts.

L. J. S.

TRIPLASTITE. An explosive consisting of a mixture of di- and trinitrotoluene (70 pts.), gun-cotton (1.2 pts.), and lead nitrate (28.8 pts.).

TRIPLITE. Fluo-phosphate of manganese and iron $(\text{Mn,Fe})(\text{Mn,Fe})\text{FPO}_4$, crystallised in the monoclinic system. Calcium and magnesium are also often present in small amount. The rough crystals and compact masses are dark-brown to black with a resinous lustre; the powder is yellowish-grey. Sp.gr. 3.6-3.8; H. 5-5½. The mineral is soluble in hydrochloric acid, and with sulphuric acid evolves hydrofluoric acid. It occurs in pegmatite-veins and in quartz-veins in the vicinity of granite masses; and is found at Limoges in France, Rabenstein in Bavaria, &c. In the Singar mica mines, in the Gaya district of Bengal, it occurs in considerable quantity as large masses with pitchblende. A variety containing very little iron and of a pale salmon-pink colour is found with wolframite and bismuth minerals in White Pine Co., Nevada.

L. J. S.

TRIPOLITE or TRIPOLI v. DIATOMITE.

TRITICUM. Couch grass or Agropyrum of the B.P. The dried rhizome of *Agropyron repens* (Beauv.).

TRITOL, TRITOL. Syn. for trinitrotoluene.

TRITOPINE v. OPIUM.

TRIXIDIN. Trade name for an emulsion of antimony trioxide.

TROCHOL. A neutral unsaponifiable crystalline substance obtained by the saponification of red Japanese bird-lime made from the bark of *Trochodendron aralioides*. After purification by precipitation from chloroform solution by light petroleum and recrystallisation from chloroform-

alcohol, trochol forms colourless needles or prisms $C_{28}H_{44}O_8 \cdot \frac{1}{2}(C_2H_5O + H_2O)$, m.p. 252° , $[\alpha]_D^{15} + 20^\circ$ (in chloroform alcohol). Yields a *diacetate*, colourless prisms, m.p. 217° ; *dibenzate*, colourless needles, m.p. 172° (sintering at 145°). Trochol occurs as the palmitic ester in the bird-lime; by heating the components together at 200° in a vacuum the ester is obtained as a colourless viscous substance (Hidekichi Yanagisawa, J. Pharm. Soc. Japan, 1921, No. 471, 405; 1922, 179). *Trochic acid* $C_{27}H_{50}O_8$, white powder, m.p. 225° , exists in the bird-lime in the free state (cf. Yushichi Nishizawa, J. Chem. Soc. Japan, 1922, 43, 154). Trochol yields a *diphenylcarbamate* $C_{28}H_{44}O_8(CO \cdot NPh)_2$, colourless prisms, m.p. 167° ; *formate*, nacreous scales, m.p. 306° , and *phthalate*, a white crystalline powder, m.p. 224° – 228° . On oxidation with hydrogen peroxide in glacial acetic acid the alcohol gave a dihydroxymonoketone, *trocholone* $C_{28}H_{42}O_8$, an amorphous powder, m.p. about 100° ; *trochol peroxide* $(C_{28}H_{42}O_8)_2$, colourless scales, m.p. 215° ; (*semicarbazone*, fine white needles, m.p. 290° ; *acetyl derivative*, fine white needles, m.p. 205° ; *oxime*, small white needles, m.p. 217°), and *trocholic acid* $C_{28}H_{42}O_8$, white granules, m.p. 282° (diacetate, white crystalline powder, m.p. 145°). The authors conclude that trochol is a secondary-tertiary, but not a primary alcohol. When a mixture of trochol and chromic anhydride is treated with water an odour of butyric acid is produced, and acetic acid can be isolated by the distillation of the mixture with steam (Hidekichi Yanagisawa and Norikazu Takashima, J. Pharm. Soc. Japan, 1923, No. 494, 251–258; Chem. Soc. Abstr. 1923, 124, i. 1008).

TROGERITE v. URANIUM.

TROILITE. A name applied by Haidinger to ferrous sulphide FeS, occurring in meteorites. V. PYRRHOTITE.

TRONA, URAO, or NATURAL SODA. The sodium carbonates occurring as minerals are: *thermonatrite* $Na_2CO_3 \cdot H_2O$ (orthorhombic); *natron* (*q.v.*) $Na_2CO_3 \cdot 10H_2O$ (monoclinic); *trona* $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (monoclinic); and possibly the anhydrous salt. Of these, trona is by far the most important and constitutes the larger part of the deposits of natural soda. It forms beds of white, cavernous material with acicular or bladed crystals lining the cavities; and is usually intermixed with more or less earthy matter and sodium chloride and sulphate. It is deposited from the water of soda-lakes and forms an efflorescence on the surface in desert regions. The Natron Lakes of Lower Egypt are well known, and similar lakes and surface efflorescences of soda are met with in many parts of the Sahara and Sudan. Extensive deposits are found in the neighbourhood of Lake Chad, and a large deposit has been opened up at Lake Magadi in Kenya Colony, East Africa. The latter has an area of 324 sq. miles, and the reserves of over a hundred million tons of soda are being constantly increased by springs in the lake. The material contains 98.5 p.c. of soda crystals, with sodium chloride 0.2, and sodium sulphate 0.1 p.c. Soda-lakes also occur in the western states of North America, viz. in Arizona, California, and Nevada.

The name 'trona' is said to be of Arabic

origin; and 'urao' is a native name for the soda deposited at the bottom of a lake at Lagunilla in Venezuela.

References.—F. W. Clarke, *Data of Geochemistry*, 3rd ed., Bull. U.S. Geol. Survey, No. 616, 1916; A Lacroix, *Minéralogie de la France et de ses Colonies*, 1909, vol. iii. R. Wegscheider in C. Doelter's *Handbuch der Mineralchemie*, 1911, vol. i. 141–193.

L. J. S.

TROOSTITE. A constituent of steel intermediate in characteristics between sorbite and martensite (*q.v.*). It is obtained by quenching highly heated steel in oil or by quenching from the transformation temperature in cold water, and is plentiful in tempered steels.

It acquires a deep brown or black tint when etched with picric acid, and can thus be distinguished under the microscope. Benedicks regards it as a colloidal solution of carbon in iron (J. Iron and Steel Inst. 1905, ii. 352; 1908, ii. 217). The name troostite is also given to a variety of *Willemite* (*q.v.*).

TROPACOCAINE v. COCAINE AND SYNTHETIC DRUGS, TROPEINES.

TROPÆOLINE v. AZO-COLOURING MATTERS.

TROPEINES. The Solanaceous Alkaloids.

This group comprises the following members, and possibly others not yet fully examined:—

Atropine and hyoscyamine $C_{17}H_{23}O_2N$;

Noratropine and norhyoscyamine

$C_{16}H_{21}O_2N$

Apostropine and belladonnine $C_{17}H_{21}O_2N$;

Tropacocaine $C_{11}H_{15}O_2N$ (*see p. 221*);

Hyoscine (scopolamine) $C_{17}H_{21}O_2N$;

Meteloidine $C_{15}H_{21}O_2N$.

These are all tertiary bases except *nor-atropine* and *nor-hyoscyamine*, and on hydrolysis furnish an acid and an amino alcohol. Of the eight naturally occurring alkaloids only three are of importance in medicine, viz. atropine, hyoscyamine, and hyoscine. Homatropine, a synthetically prepared tropeine, is also of importance in medicine. The best known sources of the three alkaloids are belladonna (*Atropa Belladonna* (Linn.)), henbane (*Hyoscyamus niger* (Linn.)), stramonium (*Datura Stramonium* (Linn.)), all of which are used in medicine. Other plants which contain them in important quantities, and either are or may be used commercially as sources of the alkaloids, are *Hyoscyamus muticus* (Linn.), *H. albus* (Linn.), and *H. reticulatus* (Linn.), *Datura Metel* (Linn.), *D. arborea* (Linn.), *D. quercifolia* (H. B. and K.), *Duboisia myoporoides* (R. Br.), *Duboisia Leichhardtii*, *Scopolia carniolica* (Jacq.), and *S. japonica* (Maxim.), *Mandragora officinarum* (Linn.), and *Solandra longifolia*. As a rule, at least two of the alkaloids are found together in each plant, but *H. muticus* is remarkable in containing only hyoscyamine. It is probable that atropine rarely, if ever, occurs preformed in plants, and the traces generally found in the extracted alkaloids are due to racemisation of hyoscyamine either during the drying of the plant or by the action of chemical agents used for extraction. In general, the alkaloids are present in the stem, leaves, root, and seed, and the amount of total alkaloid present in each of these parts shows great variation.

Preparation.—The method used for the extraction of these alkaloids varies to some extent with the material employed, but the

following general process gives good results as a rule. The finely-ground, air-dry drug is exhausted by percolation with cold 90-95 p.c. alcohol and the greater part of the solvent removed by distillation. The semi-solid extract is then treated with dilute (0.5 p.c.) hydrochloric or sulphuric acid, until no more alkaloid is removed. This acid liquid is filtered, shaken with small quantities of chloroform, if necessary, to remove traces of chlorophyll, oil, or other soluble non-basic matters, then made slightly alkaline with dilute ammonia, and the alkaloid extracted by means of chloroform. The latter is distilled off, leaving, as a rule, a clean gum-like residue. From this, by solution in chloroform and careful addition of light petroleum, hyoscyamine may be caused to separate in crystalline form. If hyosine be present it remains dissolved in the chloroform, and may be caused to separate by further addition of light petroleum. The salts of these alkaloids being more stable than the free alkaloids they are best purified by recrystallising their salts from water. Hyoscyamine may be finally purified by re-crystallisation from alcohol by addition of water. The best source of hyoscyamine is the Egyptian plant, *Hyoscyamus muticus*.

ESTIMATION OF TOTAL ALKALOIDS. Dunstan and Ransom have devised the following methods:

For the root.—Exhaust by hot percolation 20 grms. of the finely-powdered root with a mixture of equal parts of chloroform and absolute alcohol. Agitate the solution with two successive quantities of 25 c.c. of distilled water, adding a small quantity of dilute sulphuric acid. The salts pass into the aqueous layer, and the colouring matter remains dissolved in the chloroform. Wash the aqueous extract with a little pure chloroform to remove adhering impurity, then add ammonia in slight excess, and dissolve out the liberated alkaloids by agitation with chloroform in the usual way. The residue of alkaloid left on the evaporation of the chloroform is dried at 100° and weighed and finally titrated (Pharm. J. 1883-4, [iii.] 14, 623).

For the leaves.—20 grms of the finely-powdered dry leaves are exhausted with absolute alcohol. The liquid is largely diluted with water, acidified with hydrochloric acid, and repeatedly extracted by agitation with chloroform until the whole of the chlorophyll, fat, &c., has been removed. The liquid is then made alkaline with ammonia, and extracted with chloroform, which, on evaporation, leaves a residue of alkaloid. This must be dried at 100° before being weighed. This process answers equally well for stems or fruit capsules, and for seeds, if the latter are first extracted with light petroleum to remove oil (Pharm. J. 1885-6, [iii.] 16, 237).

Extract of the leaves.—From 1 to 2 grms. of the extract are dissolved, as far as possible, in warm dilute hydrochloric acid, any residue being extracted with the dilute acid until all the alkaloid has been dissolved. The acid liquid is then extracted with chloroform until nothing further is removed, and, after this treatment, is made alkaline with ammonia, and the free alkaloid removed by agitating again with chloroform, which on evaporation leaves a residue of alkaloid that is dried at 100°C. and

weighed and finally titrated (*ibid.* 1885-6, [iii.] 16, 238).

Alcoholic extract of the root.—2 grms. of this extract are dissolved as far as possible in dilute hydrochloric acid. This solution is then treated as described under the leaf extract (*ibid.* 1885-6, [iii.] 16, 777).

No method is yet available for the quantitative separation and estimation in mixtures of the individual mydriatic alkaloids, but the approximate amounts of each present may sometimes be determined by careful fractionation with gold chloride.

Atropine $C_{17}H_{23}O_3N$ is the racemic form of hyoscyamine, from which it is readily formed by the action of alkalis. It was first obtained by Mein (Annalen, 1833, 6, 67) from the root of *Datura Stramonium* (Linn.), and called by him *daturine*. Geiger and Hesse obtained it independently (*ibid.* 1833, 5, 43; 6, 44; 7, 269) from belladonna root, and their material was analysed by Liebig, who assigned to it the empirical formula now in use. Atropine is stated to occur with hyoscyamine and a little hyosine in belladonna and stramonium and with more hyosine in *Scopolia japonica* (Maxim), but there is reason to believe that the alkaloid does not exist pre-formed in plants, although it may be produced in the course of preparation by the action of alkalis on hyoscyamine. In any case, the commercial alkaloid is now obtained invariably by conversion of hyoscyamine by the action of very dilute alcoholic alkali hydroxide (Will and Bredig, Ber. 1888, 21, 2797; cf. Gadamer, Arch. Pharm. 1901, 239, 294).

Properties.—Prismatic crystals, m.p. 118°. Readily soluble in alcohol or chloroform, less soluble in ether or hot water, sparingly soluble in cold water. The aqueous solution is alkaline to litmus, hæmatoxylin, and phenolphthalein. The fact that atropine is alkaline to phenolphthalein serves to distinguish it and its isomer from most other alkaloids. Atropine is optically inactive. One of the most remarkable properties of atropine is that of causing sustained dilatation of the pupil of the eye, a property which is often made use of in detecting it and other alkaloids of this group, several of which exert this mydriatic action. A drop or two of an aqueous solution, containing 1 part of atropine in 130,000 parts of water, when introduced into the eye of a cat is sufficient to produce this effect. When taken internally atropine is highly poisonous. It diminishes glandular secretions, causes paralysis of the vagus terminations, and acts as a sedative to involuntary muscles. Some of the alkaloid is apparently excreted unchanged in the urine.

The ordinary salts of atropine are crystalline and soluble in water. The sulphate



is commonly used in medicine; it forms colourless needles, m.p. 187°-188°, 194° (dry). The aurichloride $B \cdot HAuCl_4$ appears as an oily precipitate when produced in the ordinary manner. This soon solidifies to a crystalline mass, which may be re-crystallised from water acidified with hydrochloric acid. The crystals melt at 137°-139°. This salt and the picrate, m.p. 175°-176°, are useful for the identification of the alkaloid,

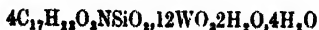
since the corresponding salts of the other alkaloids of this group melt at different temperatures.

Reactions and constitution.—Among the characteristic qualitative reactions of atropine may be mentioned one which has been modified by Labat (Bull. Soc. Pharm. Bord. April, 1914, 148), and consists in treating a particle of the alkaloid with 2 c.c. of a 10 p.c. solution of sulphuric acid and adding one drop of a saturated aqueous solution of potassium chromate, on warming, the characteristic hawthorn odour develops and changes to that of benzaldehyde. The latter odour is also produced when the alkaloid is boiled with a dilute solution of sodium hypobromite. This well-known test introduced by D. Vitali (Zeitsch. anal. Chem. 1881, 20, 563; Pharm. J. 1881, [iii.] 12, 459) has been modified by Arnold (Arch. Pharm. 1882, 20, 564), also by Flückiger (Pharm. J. 1886, [iii.] 16, 601), whilst E. Beckmann (Arch. Pharm. 1886, [iii.] 24, 481) points out that veratrine gives a somewhat similar reaction unless certain modifications are employed; and Droop Richmond (Analyst, 1918, xliii. 506) demonstrates other points which should be noted. Other characteristic colour reactions are described by Richard (Chem. Zeit. 1904, 28, 1048).

The reactions of atropine and other alkaloids with mercuric chloride were described by A. W. Gerrard (Pharm. J. 1884, [iii.] 14, 718), who in a later paper (Pharm. J. 1891, [iii.] 21, 898) modifies and more precisely defines the method of making the test, and gives details of the distinctive reactions observed with atropine, hyoscyamine, homatropine, and hyoscyne, under these conditions. The value of Gerrard's test has also been confirmed by Flückiger (Pharm. J. 1886, [iii.] 16, 601), who found cocaine gave a pure white precipitate which very soon turned red.

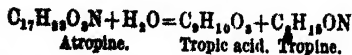
Amongst the more modern researches which may be mentioned are those of Eder in the Schweiz. Wchschr. f. Chem. u. Pharm. 1913, 51, 228; and Schweiz. Apoth. Zeit. 1917, 54; the latter of which contains a series of papers on the detection of atropine, whilst Wasicky (Zeitsch. anal. Chem. 1915, 54, 393) describes a colorimetric method of identifying atropine and allied alkaloids by means of *p*-dimethylamino-benzaldehyde.

In 1917, Rasmussen (Ber. Deut. pharm. Ges. 1917, 27, 193) described a method based on the precipitation of the sparingly soluble silicotungstate



as foreshadowed by O. Javillier (Bull. Sci. Pharm. 1910, 315); this salt is soluble in less than 1 part in 40,000 water.

Atropine readily undergoes hydrolysis with either acids or alkalis; in the latter case it yields tropic acid and tropine in accordance with the equation



When the hydrolysis is effected by an acid, especially concentrated hydrochloric acid, the tropic acid loses the elements of water, and

atropic acid $C_8H_7O_3$ results, whilst at a high temperature this latter compound is more or less changed into its polymers α and β -is-atropic acid $C_{16}H_{19}O_3$.

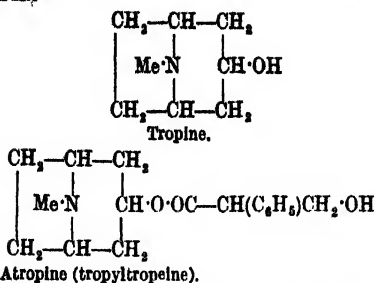
The hydrolysis of atropine is preferably effected by heating the alkaloid with saturated barium hydroxide solution to 60° or 80° for a few hours. Dilute sulphuric acid is added until a drop ceases to give a pink coloration with phenolphthalein. The liquid is filtered, and the filtrate acidified with hydrochloric acid and twice shaken with ether, the ether is separated, and on evaporation yields the acid constituents of the hydrolysis; to obtain the basic product, the aqueous layer is shaken with an excess of alkali hydroxide and extracted with chloroform.

Atropine yields an anhydride (*apotropine*) (see below) when heated with dilute nitric acid (Pesci, Gazz. chim. ital. 1881, 11, 438; 1882, 12, 60), which Hesse subsequently isolated from belladonna root and named atropamine (Annalen, 1892, 271, 124; cf. Merck, Zeitsch. anal. Chem. 1892, 31, 229; and Hesse, Annalen, 1893, 277, 290). Apotropine is not mydriatic.

TROPINE $C_8H_{15}ON$ forms large, colourless tablets, m.p. 63°; b.p. 229°; sp.gr. 1.0392 at 76°/4°, soluble in water, alcohol, or ether. It is a strong base, which forms crystalline salts. It is poisonous, but does not dilate the pupil of the eye. Tropine and tropic acid unite to form tropine tropate $C_8H_{15}NO \cdot C_8H_9O_3$, and this salt, when heated with dilute hydrochloric acid, loses water and furnishes atropine, identical with the natural alkaloid (Ladenburg, Annalen, 1883, 217, 74). Similarly, by heating other organic salts of tropine with dilute hydrochloric acid, dehydration occurs, with production of the acyl derivative of tropine. The bases thus formed have been called by Ladenburg *tropéines*. In this way *l*-atropine (*l*-tropyltropine), *d*-atropine (*d*-tropyltropine), *pseud*oatropine (*atro*-lactyltropine), and atropamine (*ap*oatropine, *atro*pyltropine) have been prepared (cf. Wolfenstein and Mamlock, Ber. 1908, 41, 723; and Wolfenstein and Rolle, *ibid.* 1908, 41, 733). Several of the tropéines exert a mydriatic action. *Phenylglycolyltropine* or *mandelyl*-tropine $C_{16}H_{21}O_3N$ is used in medicine under the name *homatropine*. Its mydriatic effect is less persistent than that of atropine. As a result of Ladenburg's work it has been generally assumed that only those tropéines produce a mydriatic effect which contain an alcoholic (not phenolic) hydroxyl in the aromatic acid residue, thus acetyl-, benzoyl-, and salicyl-tropéines are not mydriatic, whilst mandelyltropine is mydriatic. Jowett and Pyman find that this is not strictly true, mydriasis being produced by terebyltropine (Chem. Soc. Trans. 1906, 89, 360), and only slightly by *o*-carboxy-phenylglyceryltropine (*ibid.* 1906, 91, 93; 1906, 95, 1020; and Proc. Int. Cong. Appl. Chem. 1909) which should be very active. Certain tropéines containing a lactone group become less active when the lactonic grouping is opened by the action of alkali.

Tropine has been the subject of numerous investigations especially by Ladenburg, Merling and Willstätter culminating in its synthesis by the last-named from suberone as a starting-point (Ber. 1901, 34, 2163; Annalen, 1903, 326, 23). On the basis of these results tropine and atropine

are now generally represented by the following formulæ—

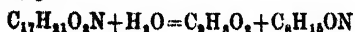


Tropine undergoes a series of interesting decompositions under the action of various reagents. The most interesting of these are as follows: When heated with dehydrating agents it furnishes *tropidine* $\text{C}_8\text{H}_{11}\text{N}$ (Ladenburg, *Annalen*, 1883, 217, 177), a strongly alkaline oil, b.p. 162° – 163° , sp.gr. 0.9467 at $19^\circ/4^\circ$, which has an odour recalling that of coniine. On oxidation with chromic acid tropine yields in turn *tropinone* $\text{C}_8\text{H}_{11}\text{ON}$ (Willstätter, *Ber.* 1896, 29, 396), m.p. 41° – 42° , b.p. 224° – 225° , *tropinic acid* $\text{C}_8\text{H}_{13}\text{O}_4\text{N}$ (Merling, *Annalen*, 1883, 216, 348; Willstätter, *l.c.*), and finally *ecgoninic acid* $\text{C}_8\text{H}_{11}\text{O}_5\text{N}$ (see under *Cocaine*), which was shown by Willstätter and Bode to be *N*-methylpyrrolidine-2-acetic acid (*Ber.* 1901, 34, 519), thus proving the presence of a pyrrolidine ring in tropine. For a detailed account of the important researches in the tropine series, Schmidt's *Über die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide*, i. 1900; ii. 1904 (Enke, Stuttgart), should be consulted.

Atropamine (*Apo-atropine*) $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$ is the *anhydro* derivative of atropine (Pesci, *Gazz. chim. ital.* 1881, 11, 538; 1882, 12, 60). It is reputed to occur naturally associated with atropine and hyoscyamine in the solanaceous plants (Hesse, *Annalen*, 1892, 271, 124; Merck, *Zeitsch. anal. Chem.* 1892, 31, 229; and Hesse, *Annalen*, 1893, 277, 290); but is best prepared from either of the two latter alkaloids by adding the substances gradually to strong nitric or sulphuric acid, or by heating them with acetic or phosphoric anhydrides.

Atropamine crystallises from ether in prisms, m.p. 60° – 62° , which are very slightly soluble in water and petroleum ether, readily in alcohol, chloroform, benzene, and carbon bisulphide. It forms salts which crystallise well from water. The sparing solubility of the hydrochloride and hydrobromide affords a ready means of separating atropamine from the other alkaloids of this group. The aurichloride crystallises from water in fine yellow needles, m.p. 110° – 112° .

On hydrolysis atropamine yields atropic acid and tropine



Atropamine is optically inactive, does notadden phenolphthalein (being thus unlike atropine and hyoscyamine), but colours red litmus blue. It has a bitter taste, does not possess mydriatic properties, but produces a burning sensation when dropped into the eye. The hydrochloride $\text{B}\cdot\text{HCl}$, m.p. 237° – 238° , forms leaflets, and the aurichloride $\text{B}\cdot\text{H}\cdot\text{AnCl}$, needles, m.p. 110° – 112° .

Belladonnine $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$. This alkaloid is stated to occur in the leaves and root of *Atropa Belladonna* (Linn.) (Hübschmann, *J.* 1858, 376; Kraut, *Ber.* 1890, 13, 165; Dürkop, *ibid.* 1889, 22, 3183; Hesse, *Annalen*, 1891, 282, 100); and is generally found in the mother-liquors of hyoscyamine and atropine. According to Merling (*Ber.* 1884, 17, 381) it has the formula $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$, and is isomeric with anhydro-atropine (apostropine), and this was confirmed by Hesse (*l.c.* 1892, 271, 123; 1893, 277, 295), who stated that it can be prepared by the action of (1) sulphuric acid on atropine or hyoscyamine, or (2) hydrochloric acid on atropamine (apostropine). Belladonnine is a resinous, uncrystallisable base, which is hydrolysed with much greater difficulty than the other solanaceous alkaloids, yielding tropine $\text{C}_8\text{H}_{13}\text{ON}$ and atropic acid (Merling). It appears to be devoid of mydriatic power.

The salts are amorphous $\text{B}_2\text{H}_2\text{PtCl}_4$ and BHAnCl_4 , are yellow pulverulent precipitates quite insoluble in cold water.

Homatropine (Mandelyltropine)



is the chief artificial tropeine used in medicine. It is a lower homologue of atropine, in which the CH_2OH group is replaced by OH , and is prepared by passing hydrogen chloride gas through a mixture of 7 parts of tropine, 10 parts of mandelic acid, and 2 parts of water; it crystallises from dry ether in prisms, m.p. 99° – 100° , it is also soluble in castor and olive oils, and such solutions are employed in ophthalmic surgery for instilling into the eye. Homatropine resembles atropine and hyoscyamine in its general physiological effects, but it is much less toxic and in small doses is a true hypnotic. It has a powerful mydriatic effect which is produced and passes off more rapidly than is the case with the natural tropeines. Homatropine hydrobromide crystallises in flat rhombic prisms or plates, m.p. 212° – 214° ; the hydrochloride has m.p. 219° – 227° ; the sulphate, m.p. 222° – 226° ; the aurichloride forms yellow prisms slightly soluble in water, it is precipitated first as an oil, but subsequently becomes crystalline; homatropine methobromide has m.p. 192° – 196° .

Hyoscyamine $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$. An isomeric of atropine. It is the most common of the solanaceous alkaloids, being the principal alkaloid in *Atropa Belladonna* (Linn.) (Schmidt, *Arch. Pharm.* 1905, 243, 303), and *Hyoscyamus niger* (Linn.), and *H. albus* (Linn.), the sole mydriatic alkaloid in *H. muticus* (Linn.) (Dunstan and Brown, *Chem. Soc. Trans.* 1899, 75, 74; 1901, 79, 72), and the chief alkaloid in *Datura Stramonium* (Linn.), *Duboisia myoporoides* (R. Br.), *Scopolia carnolica* (Jacq.) (Dunstan and Chaston, *Pharm. J.* 1889–1890, [iii.] 20, 461), and *S. japonica* (Maxim.) (Schmidt, *Arch. Pharm.* 1888, [iii.] 26, 185, 214), and in other similar plants; it exists in minute quantities in lettuce, *Lactuca virosa* (Linn.) and *L. Scariola* (Linn.) (Dymond, *Chem. Soc. Trans.* 1892, 61, 90).

Preparation.—Hyoscyamine may be extracted from the various plants containing it by means of the process described in the introduction to this section. The best source of the alkaloid is the stem and leaves of *Hyoscyamus*

muticus, since this material is free from other mydriatic alkaloids of this group. It may also be obtained from henbane or stramonium. In preparing the alkaloid great care must be taken not to leave it in contact with alkalis, since these readily convert it into atropine. Hyoscyamine is but little used in medicine, and is generally used merely as a source of atropine, into which it readily passes by simple racemisation. When atropine and hyoscyne are also present in the plant these alkaloids are obtained with the hyoscyamine. The isolation of pure hyoscyamine from the mixture of the alkaloids is a difficult operation. The greater part of the atropine may be removed by repeated crystallisation from dilute alcohol, the hyoscyamine for the most part remaining dissolved. The isolation of pure hyoscyamine can be effected by repeated crystallisation from hot petroleum, or it may be usefully accomplished by converting the alkaloid into the aurichloride and repeatedly crystallising this salt from dilute hydrochloric acid until it melts at the proper temperature. The alkaloid may be regenerated from the aurichloride by decomposing it with hydrogen sulphide in the usual manner.

Hyoscyamine crystallises from alcohol or hot petroleum in slender needles with a peculiar tendency to come out in a jelly-like mass, it melts at 107° . In its solubilities it closely resembles atropine. The specific rotatory power of the pure base taken in 50 p.c. alcohol is $[\alpha]_D -22^{\circ}$, but as met with in commerce it generally contains a small proportion of atropine, and rarely has a higher rotation than $[\alpha]_D -21^{\circ}$ (Carr and Reynolds, Trans. 1910, 97, 1328). It resembles atropine in taste and physiological action, though its activity is much greater.

When heated the alkaloid sublimes, with partial decomposition, and it is said to be slightly volatile with steam. When hyoscyamine is heated to a temperature slightly higher than its melting-point, it is converted into atropine (Schmidt, Ber. 1888, 21, 1829). This conversion also takes place with great facility when hyoscyamine is warmed or even allowed to stand in the cold, with caustic alkalis or alkali carbonates, but it only takes place extremely slowly in presence of ammonia (Will, Ber. 1888, 21, 1717, 2777). Hyoscyamine exerts a strong mydriatic action, and is a powerful poison.

Many of the ordinary salts of hyoscyamine are crystalline and soluble in water. The sulphate $B \cdot H_2SO_4$ crystallises well from alcohol and melts at 205° – 209° . A 4 p.c. aqueous solution gives $[\alpha]_D -27.8^{\circ}$. The aurichloride $B \cdot HAuCl_4$ crystallises from alcohol in anhydrous golden yellow hexagonal plates, m.p. 165° ; but, unlike atropine aurichloride, it does not melt when heated under water. This salt is less soluble in acidified water than atropine aurichloride, from which it may be separated by repeated crystallisation.

Hyoscyamine auribromide $B \cdot HAuBr_4 \cdot H_2O$ crystallises in deep red-coloured and highly lustrous needles, the anhydrous salt sinters at 155° and melts sharply at 160° . The hydrobromide forms fine needles, m.p. 151° ; the picrate crystallises in plates, m.p. 165° ; the oxalate forms very long prisms, m.p. 176° ; and

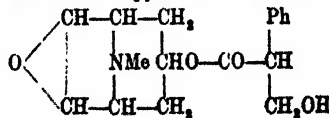
the methobromide crystallises in colourless crystals, m.p. 210° – 212° .

Reactions.—The qualitative reactions of hyoscyamine are, for the most part, identical with those of atropine. When heated with acids or alkalis, like atropine, it undergoes hydrolysis into *tropine* and *tropic acid*. On reversing this reaction by heating together the tropine and tropic acid, atropine and not hyoscyamine is formed. According to Gadamer (Arch. Pharm. 1901, 239, 294) hyoscyamine is, in the first place, converted by alkalis into atropine, and it is really this alkaloid which is hydrolysed. The same author states that by the action of water at atmospheric temperature hyoscyamine is resolved into *r*-tropine and *l*-tropic acid, and consequently hyoscyamine must be *l*-trotyl-*r*-tropine; Amenomiya (*ibid.* 1902, 240, 498) has synthesised *l*-hyoscyamine and *d*-hyoscyamine. Ladenburg and Hundt's *d*- and *l*-atropines (Ber. 1889, 22, 2590) are regarded as mixtures of *d*- and *l*-hyoscyamine with atropine.

As in the case of atropine, atropamine and belladonnine result from the action of strong acids, and acid anhydrides upon hyoscyamine.

Detection.—Hyoscyamine may be detected by its mydriatic action and by most of the reactions described under atropine. Its partial separation from atropine may be effected by recrystallisation from dilute alcohol, but it can only be completely separated and identified by preparing its aurichloride, which is characterised by its melting-point.

Hyoscyne (l-Scopolamine) $C_{17}H_{21}O_4 \cdot N \cdot H \cdot O$. This alkaloid was first isolated by Ladenburg (Annalen, 1880, 206, 299). Some years later, E. Schmidt (Arch. Pharm. 1890, 228, 139, 435) obtained a crystalline alkaloid from *Scopolia carniolica*, which he afterwards found to be the chief constituent of the alkaloid obtained by Ladenburg (*see* Hesse, Annalen, 1892, 271, 120; 1893, 276 84; and Schmidt, Arch. Pharm. 1892, 230, 207; 1894, 232, 409). Hyoscyne occurs in small amounts together with hyoscyamine and other alkaloids in many solanaceous plants, and is more abundantly present in the various species of *datura* (Arch. Pharm. 1905, 243, 303). Its exact constitution has recently been decided by Hess and Wahl (Ber. 1922, 55, 1979), following much work on the subject by Willstätter and his collaborators (*Zeitsch. physiol. Chem.* 1912, 79, 146), Hesse (Ber. 1918, 51, 1007); and King (J. Chem. Soc. 1919, 115, 476). From the work of these authors, hyoscyne is the *l*-trotyl ester of oscine,



Further, Tutin (Trans. Chem. Soc. 1910, 97, 1793) has shown that scopoline may be obtained in its optically active form, and must contain either one or two asymmetric carbon atoms; while King (*loc. cit.*) shows *l*-hyoscyne to be a molecular combination of *l*-trotyl-*d*-oscine, and *l*-trotyl-*l*-oscine. *l*-Hyoscyne base is an uncrystallisable oil readily soluble in water. The specific rotation of an aqueous solution has been recorded as $[\alpha]_D -28^{\circ}$, but the alkaloid employed may have

been partly racemised during its isolation, there being no method of purifying the amorphous base.

Hyoscyne hydrobromide $B \cdot HBr3H_2O$ has m.p. $193^\circ-194^\circ$, $[\alpha]_D$ (in water) -25.9° ; it forms large rhombic tablets; the commercial salt generally contains 11-12 p.c. of water and is variable in its optical rotation, owing to the presence of *d*-*l*-hyoscyne. The picrate forms slender matted needles, m.p. $187^\circ-188^\circ$, the aurichloride, yellow prisms, m.p. $198^\circ-200^\circ$, and the auribromide, brown prisms, m.p. 210° . The aurichloride forms needles with serrated edges, m.p. $204^\circ-205^\circ$; the auribromide forms red leaflets, m.p. $187^\circ-188^\circ$.

By the action of alkalis or by direct heat hyoscyne is racemised to *i*-scopolamine. Hyoscyne resembles atropine and hyoscyamine in its physiological action, producing more powerful but less lasting paralyzing effect upon the peripheral nerve endings and depression of the motor area. It does not, however, stimulate the brain initially, and is consequently employed by preference for cerebral affections. It is of great use in acute mania.

When warmed with dilute alkalis or barium hydroxide *l*-hyoscyne is hydrolysed, yielding tropic acid and a new base, which has been variously called oscine, scopoline, or oxytropine. If hydrolysis be effected with dilute hydrochloric acid *l*-tropic acid and *d*-*l*-oscine result.

d-*l*-Hyoscyne (*i*-Scopolamine, *Atrascine*) $C_{17}H_{21}O_4N$ is the optically inactive isomeride of hyoscyne. It forms 2 crystalline hydrates; with $2H_2O$, m.p. $37^\circ-38^\circ$, with $1H_2O$, m.p. $56^\circ-57^\circ$, the anhydrous base melts at $82^\circ-83^\circ$. It furnishes crystalline salts, the hydrobromide crystallises in rhombic tables, containing $3H_2O$, and has m.p. 181° , other salts are the hydriodide, m.p. 192° , the picrate, m.p. $173^\circ-174^\circ$, the aurichloride which forms needles with one edge serrated, m.p. $214^\circ-215^\circ$, and the methobromide, m.p. $216^\circ-217^\circ$.

Oscine (*Scopoline*) $C_{17}H_{21}O_4N$ results from the hydrolysis of hyoscyne (Hesse, Annalen, 1892, 271, 114; 1933, 276, 84; Luboldt, Arch. Pharm. 1898, 236, 11). It crystallises in prisms from light petroleum or chloroform, m.p. $109^\circ-110^\circ$, b.p. $241^\circ-243^\circ$. It is readily soluble in water and alcohol, and less readily in ether. Oscine is optically inactive, but unlike tropine it can be resolved into its *d*- and *l*-constituents (Tutin, Trans. Chem. Soc. 1910, 97, 1793).

Like tropine, oscine contains a hydroxyl group and is readily esterified, forming a series of esters, the scopolines. None of the scopolines have been used in medicine.

i-Oscine yields a crystalline monoacetyl derivative, m.p. 53° , a benzoyl derivative, m.p. $68^\circ-70^\circ$, together with other crystalline salts. The hydrochloride forms (hydrated) tablets and (anhydrous) prisms, m.p. $273^\circ-274^\circ$, the picrate crystallises in flattened rhombs, m.p. $237^\circ-238^\circ$, the *d*-*l*-isomerides have the same melting-points.

Mandragorine $C_{15}H_{21}O_4N$ was obtained by Ahrens (Ber. 1889, 22, 2159) from *Mandragora officinarum* (Linn.), and from the same source by Hesse (J. pr. Chem. 1901, [iii.] 64, 274), along with hyoscyamine, hyoscyne, and norhyoscyamine. According to Thoms and Wentzel (Ber.

1901, 34, 1023), Ahrens' mandragorine was merely a mixture of hyoscyamine with hyoscyne and possibly a third alkaloid (*v.* MANDRAGORA ROOT, vol. iv. p. 210).

Meteloidine $C_{15}H_{21}O_4N$ was obtained by Pyman and Reynolds (Chem. Soc. Trans. 1908, 93, 2077) from *Datura meteloides* (DC.) along with atropine, and hyoscyne (scopolamine) to the extent of 0.07 p.c. It crystallises in tabular needles, m.p. $141^\circ-142^\circ$, and furnishes a crystalline, optically inactive hydrobromide $B \cdot HBr, 2H_2O$, m.p. 250° (anhydrous), and an aurichloride, m.p. $149^\circ-150^\circ$. On hydrolysis by baryta water meteloidine furnishes tiglic acid $CHMe : CMe \cdot COOH$ and a new base teloidine $C_{15}H_{21}O_4N$, which crystallises with $1H_2O$ and has m.p. $168^\circ-169^\circ$ (anhydrous); the aurichloride $B \cdot HAuCl_4 \cdot 3H_2O$ has m.p. 225° , and crystallises in hexagonal plates.

Norhyoscyamine $C_{15}H_{21}O_4N$ occurs in *Scopolia japonica* (Maxim), *Datura Metel* (Linn.), *Datura meteloides*, *Duboisia Myoporoides*, *Duboisia Leichhardtii*, *Salandra longifolia*, and *Mandragora officinarum*. It is a white crystalline base, m.p. 140.5° , strongly basic in character (being alkaline to phenolphthalein). It forms beautifully crystalline salts, of which the following have been characterised: the hydrochloride, m.p. 207° , the sulphate, m.p. 249° , oxalate, m.p. $245^\circ-246^\circ$, aurichloride, m.p. $178^\circ-179^\circ$, platinichloride, m.p. 141° , picrate, m.p. 220° . A solution of the base in 50 p.c. ethyl alcohol gives $[\alpha]_D -23.0^\circ$.

On treatment with methyl iodide it yields hyoscyamine (its nitrogen methyl derivative), and by the action of dilute alkalis gives rise to noratropine (Carr and Reynolds, Trans. Chem. Soc. 1912, 101, 946; Petrie, Proc. Linn. Soc. N.S.W. 1917, 815).

Noratropine $C_{15}H_{21}O_4N$ is a white crystalline base, m.p. $113^\circ-114^\circ$, which readily combines with water forming a monohydrate, m.p. 73° ; it is optically inactive, being the racemic modification of norhyoscyamine, it forms well-crystallised salts of which the following have been characterised: the hydrochloride, m.p. 193° , the sulphate, m.p. 257° , and the aurichloride ($B \cdot HAuCl_4$), which forms rosettes of leaflets which melt under hot water and crystallise on cooling, m.p. 157° .

Both norhyoscyamine and noratropine possess mydriatic properties, but are less active than hyoscyamine or atropine.

Pseudohyoscyamine was the name given to a compound isolated by Merck (Arch. Pharm. 231, 117) from the plant *Duboisia myoporoides*. The formula $C_{17}H_{21}O_4N$ was wrongly assigned to it; subsequent investigations, however, of the alkaloids of this plant (Carr and Reynolds, Trans. Chem. Soc. 1912, 101, 946) have shown that the so-called pseudohyoscyamine of Merck was impure nor-hyoscyamine contaminated with a little hyoscyamine.

Solandrone. Solandrone was the name given by Petrie to the alkaloid isolated from solandra leaves in 1908. When later it was characterised it was found to be identical with norhyoscyamine (*l.c.*).

Tropacocaine (*Benzoylpseudotropine*)

$C_{15}H_{21}O_4N$

was first isolated by Giesel (Ber. 1891, 24, 2336), from Java coca leaves and subsequently by

Hesse (J. pr. Chem. 1902, [ii.] 66, 401) from Peruvian coca. Hara and Sakamoto have described the preparation of trapoocaine from the petroleum extract of coca leaves produced in Java (J. Pharm. Soc. Japan, 1924, 503, 33; Chem. Soc. Abstr., 1924, 126, i. 870). It crystallises in needles, m.p. 49°, and its solubility in dilute ammonia affords a means by which it can be separated from the accompanying alkaloids. Its alcoholic solution is strongly alkaline and optically inactive. The hydrochloride has m.p. 283° (decomp.), and the aurichloride, m.p. 208°.

On warming with either mineral acids, or alkalis, the base undergoes hydrolysis and furnishes benzoic acid and pseudotropine (Liebermann, Ber. 1891, 24, 2338).

Pseudotropine $C_8H_{11}ON$ is isomeric with tropine, it forms colourless tablets or prisms, is optically inactive, and has m.p. 108°, and b.p. 240°; it readily esterifies with organic acids, furnishing a series of derivatives which from their analogy with the tropeines have been called pseudotropine, but, unlike the former, exert no mydriatic action. F. H. C.

TROPILENE v. KETONES.

TROTYL. Syn. for trinitrotoluene, used as an explosive.

TRUFFLES, subterranean fungi, highly prized as food. Many species are known. König divides the edible truffles into two chief classes—

(1) **White truffles**, the best of which is the African truffle, *Tuber niveum* (Desf.) or *Terfezia Leonis* (Tul.), but also including the Italian truffle, *Tuber magnatum* (Pico.) or *Tuber album* (Balb.), with a garlic-like odour, and the German white truffle, *Tuber album* (Bull.) or *Charomyces meandriformis* (Vitt.), of much less value.

(2) **Black truffles**, which include the highly prized French truffle *Tuber melanospermum* (Vitt.), which is usually in size between a walnut and an apple, of dark brown or black colour, and covered with polygonal warts. It possesses a strong aromatic odour, resembling that of the strawberry; the winter truffle, *T. brumale* (Vitt.) occurs in France and Italy, resembles the French truffle, but has not such an aromatic smell and taste. The summer truffle, *T. aestivum* (Vitt.) is the one most usually found in England, generally in beech, oak, or birch woods, and in marly soils. It is gathered from July to September.

König gives, as the mean composition of truffles—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
77.1	7.6	0.5	6.6	6.4	1.9

Chatin (Compt. rend. 1890, 110, 376, and 435) found the dry matter in French truffles to vary from 20.8 to 25.0 p.c. of the original fresh material, and to contain from 4 to 9 p.c. of its weight of nitrogen, and from 5.6–11.2 p.c. of ash. The ash, in different samples, contained: silica 10–35 p.c., potash 17–28, soda 0.6–2.1, lime 0.0–3.4, magnesia 0.2–3.1, ferric oxide and traces of alumina 3.2–8.4, mangnous oxide, traces to 0.05, phosphorus pentoxide 18.4–30.2, sulphur trioxide 2.1–4.6, chlorine with traces of iodine 0.2–0.4 p.c. Much larger proportions of potash and phosphorus pentoxide were found in the ash of truffles by Kohlrausch and Loewecke,

quoted by König. The amount of alumina is also apparently very variable, since Pizzi (quoted by König) found, in the ash of black truffles, 5.77 p.c. of alumina, in that of white truffles, 7.17 p.c.

As to the nature of the nitrogenous constituents of truffles, little appears to be known; probably a considerable proportion of it is in the non-proteid form.

In the non-nitrogenous extract, mannitol, trehalose and malic and citric acids have been found.

For an examination of the *tubulane* or Caucasian truffles, and of various species of *Terfezia*, known as 'terfias' and 'kames' in the north of Africa and in Western Asia v. Chatin (Compt. rend. 1893, 114, 46; and Revue intern. des falsific. 1893, 14).

Truffles are sold, either in the fresh condition, imbedded in lard, dried, or cooked and preserved in olive oil, or in hermetically sealed cases.

König gives, as the mean of 9 analyses of the air-dried product—

Water	Protein	Fat	N free extract	Crude fibre	Ash
4.4	33.9	2.0	24.9	27.1	7.7

H. I.

TRUXILLINES v. COCAINE AND THE COCA ALKALOIDS.

TRYEN, *p*-iodo-*o*-sulphoxy-cyclo-hexatriene pyridine.

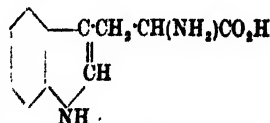
TRYGASE v. SYNTHETIC DRUGS.

TRYPAFLAVIN (*Diaminomethylacridinium chloride*), a yellow dyestuff employed therapeutically in the form of a 0.1 p.c. solution as a bactericide. The solution is sensitive to sunlight and turns brown on exposure even to diffused daylight. Kept in the dark, or in dark-coloured bottles, especially in strong solutions, it may be preserved unchanged.

TRYPAN BLUE AND TRYPAN RED. Azo-dyes derived from benzidine having a strong trypanocidal action.

TRYPSIN v. FERMENTATION.

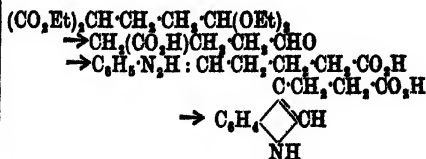
TRYPTOPHAN, β -indole- α -aminopropionic acid



It has been known since the researches of Gmelin, Barnard, and others of the earlier physiologists that on tryptic digestion a substance is formed from proteins that gives a reddish-violet coloration with chlorine or bromine. Other methods of decomposing proteids, such as putrefaction or alkali or acid hydrolysis, give rise to the same substance, for which the name *tryptophan* was suggested by Neumeister (Zeitsch. Biol. 1890, 26, 234), and *proteinchromogen* by Stadelmann (*ibid.* 491). The compound itself was not known until 1901 when Hopkins and Cole (J. Physiol. 1901, 27, 418) isolated it from the products formed by the tryptic digestion of casein; they showed that it possessed the formula $C_{11}H_{13}O_2N_2$, yielded scatole and indole when heated, and adopting Neumeister's suggestion named it *tryptophan*.

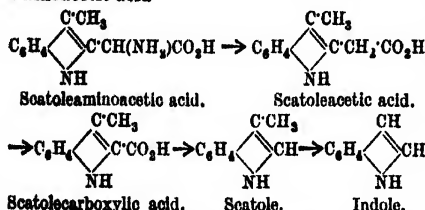
Tryptophan occurs among the products of

Ellinger (Ber. 1905, 38, 2884) further showed that Nencki's scatoleoacetic acid was identical with indole propionic acid obtained by a similar synthetic process from ethyl propionacetal-malonate

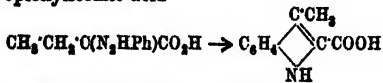


Indole-3-aldehyde $\text{C}_8\text{H}_7\text{NO}$ is obtained

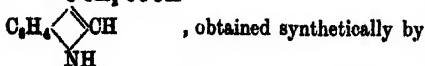
by oxidising tryptophan with ferric chloride (Hopkins and Cole, J. Physiol. 1903, 29, 451; Ellinger, Ber. 1906, 39, 2515), and can also be prepared by the action of chloroform and potassium hydroxide on indole; it condenses with hippuric acid to form an *azlactone*, or its 1-acetyl derivative (Ellinger and Matsuoka, Zeitsch. physiol. Chem. 1920, 109, 259), which on hydrolysis yields *α*-benzoylaminoindolyl-acrylic acid. This compound on reduction and subsequent hydrolysis yields *α*-amino-*β*-indole-propionic acid, identical with *dl*-tryptophan



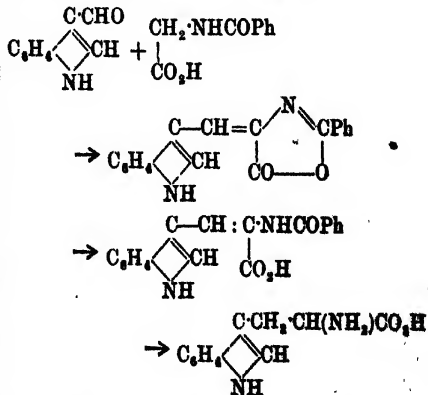
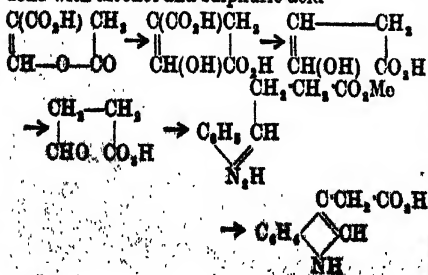
Ellinger (Ber. 1904, 37, 1801), however, showed that Nencki's so-called scatole carboxylic acid was not identical with the synthetic product obtained by Wislicenus and Arnold (*ibid.* 1887, 20, 3304) from the phenylhydrazine derivative of propionylformic acid



but was in reality the isomeric *indole acetic acid*
 C_8H_7COOH



condensing β -aldehydopropionic acid (obtained from aconic acid) with phenylhydrazine and subsequent treatment of the ester of the hydrazone with alcohol and sulphuric acid



Ellinger and Flamand (Ber. 1907, 40, 3029; Zeitsch. physiol. Chem. 1908, 55, 8).

Properties.—The tryptophan obtained from proteids is levorotatory in aqueous solution. Hopkins and Cole (J. Physiol. 1901, 27, 418) found $[\alpha]_D^{20} -33^\circ$, H. Fischer (Zeitsch. physiol. Chem. 1908, 55, 74) found $[\alpha]_D^{20} -34.5^\circ$ for one specimen, whilst others gave values varying from -29.75° to -40.3° ; Abderhalden and Baumann (*ibid.* 412) found $[\alpha]_D^{20} -30.33^\circ$. In alkaline or acid solution, L-tryptophan is dextro-rotatory, having $[\alpha]_D^{20} +5.7$ to $+6.3^\circ$ in a 2-3% solution in N/2NaOH solution, or $+4.45^\circ$ in

+6.12° in 10-12 p.c. N/1NaOH solution (Abderhalden and Kempe, *ibid.* 1907, 52, 207; Abderhalden and Baumann, *l.c.*); lower values were found by Fischer (*l.c.*), $[\alpha]_D^{20} +5.56^\circ$ to $+5.69^\circ$ in a 2-3 p.c. solution of a N/1NaOH solution. This is probably due to partial racemisation as Abderhalden and Baumann (*l.c.*) found $[\alpha]_D^{20} +5.27^\circ$ for a specimen that had been repeatedly recrystallised; a 6 p.c. solution in N/1 hydrochloric acid gave $[\alpha]_D^{20} +1.31^\circ$ (Abderhalden and Kempe, *l.c.*). *l*-Tryptophan crystallises in six-sided and rhombic plates, is sparingly soluble in cold, readily so in hot water and has a slightly bitter taste; it darkens when heated at 240° and melts at 252° (Hopkins and Cole, *l.c.*), at 273° (Neuberg and Popowsky *l.c.*), at 289° (corr.) (Abderhalden and Kempe, *l.c.*). The brown pigment found in its solutions on standing is probably a condensation product (Abderhalden, *Zeitsch. physiol. Chem.* 1912, 78, 159).

dl-Tryptophan is prepared synthetically and also readily formed from *l*-tryptophan which racemises on crystallisation from pyridine, or by the action of ammonia or by heating at 170° with hydrochloric acid (Abderhalden and Baumann, *l.c.*; Allers, *Biochem. Zeitsch.* 1907, 6, 272; Neuberg, *ibid.* 276); the racemic compound differs from the natural compound only in being optically inactive and in having a sweet taste. For the dissociation constants, see Aristides Kanitz (*Biochem. Zeitsch.* 1910, 29, 126).

Reactions.—The Adamkiewicz or Liebermann reaction given by certain proteins—namely, the formation of a blue-violet ring at the junction of the two liquids when concentrated sulphuric acid is added to a mixture of the protein with acetic acid or ether—is due to the presence of tryptophan in the protein and of glyoxylic acid in the acetic acid or ether (Adamkiewicz, *Ber.* 1875, 8, 161; v. Liebermann, *Zentr. Med. Wissensch.* 1887, 321, 450; Hopkins and Cole, *Proc. Roy. Soc.* 1901, 68, 21; *J. Physiol.* 1901, 27, 418; Cole, *J. Physiol.* 1903, 30, 311; Osborne and Harris, *J. Amer. Chem. Soc.* 1903, 25, 853; Bardachzi, *Zeitsch. physiol. Chem.* 1906, 48, 145; Dakin, *J. Biol. Chem.* 1907, 2, 289). According to Homer (*Proc. Camb. Phil. Soc.* 1912, 16, 405), who has studied the behaviour of tryptophan towards certain aldehydes, it is formaldehyde rather than glyoxylic acid that is the substance essential to the formation of the characteristic violet colour in the Adamkiewicz reaction (see also Fearon, *Biochem. J.* 1920, 14, 548).

For other colour reactions of proteins due to the presence of tryptophan, see Cole (*l.c.*); Dakin (*l.c.*); Fleig (*Proc. Soc. Biol. med.* 1908, 64, 192); Rosenheim (*Biochem. J.* 1, 233); Granström (*Beitr. Chem. Physiol. Path.* 1908, 11, 133); Heimrod and Levene (*Biochem. Zeitsch.* 1910, 25, 18); Mörner (*Zeitsch. physiol. Chem.* 1919, 107, 203).

The red-violet colour produced by chlorine or bromine water on tryptophans is only given by free tryptophan, not by its polypeptides. The coloration attains a maximum when the amount of halogen is equivalent to four atoms per gram-molecule of tryptophan, and when concentrated solutions are used red amorphous

precipitates of the monohalogen derivatives are obtained $C_{11}H_{11}O_2N_2Cl$ and $C_{11}H_{11}O_2N_2Br$. These compounds are soluble in amyl alcohol, ether, or ethyl acetate, and the use of these solvents has been suggested to render the reaction more intense. The addition of excess of halogen converts the red compounds into yellow perhaloids $C_{11}H_{11}O_2N_2Cl_2$ and $C_{11}H_{11}O_2N_2Br_2$ (Neuberg and Popowsky, *Biochem. Zeitsch.* 1907, 2, 357; Neuberg, *ibid.* 1910, 24, 423; Abderhalden and Kempe, *l.c.*).

Detection and estimation.—According to Herzfeld (*Biochem. Zeitsch.* 1913, 55, 253) a distinct blue colour may be detected if there is 1 part of tryptophan in 1,000,000 by means of *p*-dimethylaminobenzaldehyde; 20 grms. of *p*-dimethylaminobenzaldehyde are dissolved in 500 c.c. concentrated hydrochloric acid and 500 c.c. water. To 50 c.c. of the solution to be tested 10 c.c. of the reagent are added and the mixture diluted to 100 c.c. with concentrated hydrochloric acid. The colour can be estimated against an ammoniacal copper sulphate solution; see also Fasal (*Biochem. Zeitsch.* 1912, 44, 392); Thomas (*Ann. Inst. Pasteur.* 1920, 34, 701); for a colorimetric method for the estimation of tryptophan, Levene and Rouiller (*J. Biol. Chem.* 1907, 2, 481); Fürth and Nobel (*Biochem. Zeitsch.* 1920, 109, 103, 124); Fürth and Lieben (*ibid.* 1921, 116, 224; 1921, 122, 58); Ide (*Z. expt. Med.* 1921, 24, 166); Lüscher (*Biochem. J.* 1922, 16, 556).

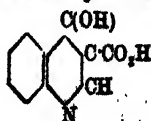
For the estimation of tryptophan in proteids, Homer (*J. Physiol.* 48, iv-v) recommends hydrolysing the proteid with baryta and estimating the tryptophan by means of bromine which has been standardised against a known solution of pure tryptophan. See also Folin and Looney (*J. Biol. Chem.* 1922, 51, 421).

For the microchemical detection of tryptophan in plants, see Kretz (*Biochem. Z.* 1922, 130, 86).

Tryptophan is decomposed on heating into carbon dioxide, indole and scatole; when fused with potassium hydroxide, scatole, to the extent of 65 p.c. of the calculated amount, is the chief product (Hopkins and Cole, *l.c.*).

Tryptophan is coloured yellow to orange by *Bacillus proteus vulgaris* only at P_H 8.9-9.4. The practical bearing of this is concerned with the manufacture of Stilton cheese (Mattick and Williams, *Biochem. J.* 1921, 15, 213). *l*-Tryptophan is converted by *B. proteus* into *l*-indole lactic acid (Sasaki and Otsuka, *Biochem. Z.* 1921, 121, 167).

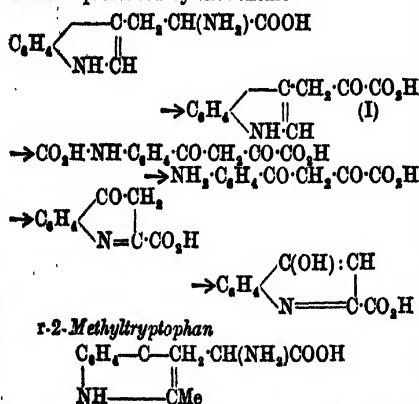
In the animal economy, tryptophan undergoes bacterial decomposition with the formation chiefly of indole; in the case of dogs it is partially converted into kynurenic acid (4-hydroxyquinoline 3-carboxylic acid)



(*u*. QUINOLINE) and excreted as such. The administration of tryptophan causes an increased excretion of kynurenic acid (Kretschy, *Ber.* 1879, 12, 1873; Wein. Akad. Ber. 1881, 52, 18, 171; Monastch. 1883, 4, 156; A. 16; Schmin. *Zeitsch. physiol. Chem.* 1897, 22, 497; Capaldi,

1897, 23, 82; Mandel and Jackson, Amer. J. Physiol. 1898, 2, 1; Camps, Ber. 1901, 34, 2703; Mandel and Schneider, Proc. Amer. Physiol. Soc. 1900, ix-x; Amer. J. Physiol. 1901, 5, 427; Gies, *ibid.* 1901, 5, 191; Glaessner and Langstein, Beitr. chem. Physiol. Path. 1901, 1, 28; Ellinger, Ber. 1904, 37, 1801; Abderhalden, London and Pinoussch, Zeitsch. physiol. Chem. 1906, 82, 139; Homer, J. Biol. Chem. 1915, 22, 391; Matsuoka, J. Biol. Chem. 1918, 85, 333; Späth, Monatsh. 1921, 42, 89).

Ellinger and Matsuoka (Zeitsch. physiol. Chem. 1920, 109, 259) find that when indolepyruvic acid (I) is administered subcutaneously to a dog, it is possible to isolate from the urine kynurenic acid in amount rather less than one-half of that obtained when tryptophan is injected; and the conclusion is drawn that the conversion of tryptophan into kynurenic acid is best represented by the scheme



crystallises with 1MeOH in colourless prisms, m.p. 263°-273°, according to the rate of heating; the picrate, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises in orange plates, m.p. 173° (Barger and Ewins, Bio-Chem. J. 1917, 11, 58).

Salts of l-tryptophan.—l-Tryptophan has an acid reaction towards litmus, and forms salts both with acids and bases; the *copper salt* ($\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2$)₂Cu, sparingly soluble grey-blue precipitate (Abderhalden and Kempe, Zeitsch. physiol. Chem. 1907, 52, 207); the *silver salt* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Ag}$; the *sodium salt* has $[\alpha]_D +2.50^\circ$ in 2 p.c. solution (H. Fischer, l.c.). The *hydrochloride* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{HCl}$ has m.p. 251° and $[\alpha]_D -13.44^\circ$ in 2 p.c. aqueous solution (H. Fischer); the *picrate* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ forms bright red lustrous needles or plates, m.p. 195°-196° (decomp.); the *picrolonate*



forms orange red needles, m.p. 203°-204° (Mayeda, Zeitsch. physiol. Chem. 1907, 51, 261).

Esters and acyl derivatives.—The *methyl ester* $\text{C}_{11}\text{H}_{11}\text{N}_2 \cdot \text{COOMe}$ forms crystalline plates, m.p. 89.5° (corr.); the *hydrochloride*



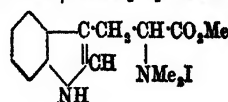
crystallises in microscopic needles, melts with decomposition at 214° (corr.); the *hydrochloride of l-tryptophan* $\text{C}_{11}\text{H}_{11}\text{N}_2 \cdot \text{COCl} \cdot \text{HCl}$ melts and decomposes at 238° (corr.) (Abderhalden and Kempe, l.c.). The *phenylcarbamide derivative* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{CONHPh}$ crystallises in

needles, m.p. 166°; the *naphthylcarbamide* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{CONH} \cdot \text{C}_{10}\text{H}_7$, m.p. 159°-160°; the *benzenesulphonic derivative* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{SO}_3\text{Ph}$ melts and decomposes at 185° and forms a sparingly soluble sodium salt; the *β-naphthalenesulphonic derivative* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{SO}_3 \cdot \text{C}_{10}\text{H}_7$ melts at 180°, the *sodium salt* at 304° (corr.) (Abderhalden and Kempe, l.c.); Ellinger and Flamand, Ber. 1907, 40, 3029).

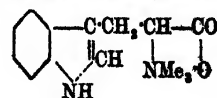
d-Tryptophan-anhydride, m.p. 230°-245° (decomp.), has $[\alpha]_D +20.59^\circ$ in water (Fränkel and Feldsberg, Biochem. Zeitsch. 1921, 120, 218).

Other derivatives of tryptophan are *monochlorotryptophan* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$, an amorphous red precipitate, m.p. 280°, converted by excess of chlorine into the *perchloride* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}_4$, a yellow precipitate decomposing at about 100°; *monobromotryptophan* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Br}$, an amorphous red precipitate with a black reflex, m.p. 270°-280°; the *perbromide* $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Br}_4$ is yellow and decomposes at 75° (Neuberg and Popowsky, Biochem. Zeitsch. 1906, 2, 357).

The *betaine* of tryptophan is identical with the alkaloid *hypaphorine*, discovered by Greshoff (Mededeelingen uit's Lands Plantentuin, 1890, 7, 29) in the seeds of *Erythrina hypaphorae* (Boerl.), and is of considerable biochemical interest as it is the only naturally occurring simple derivative of tryptophan. The alkaloid can be synthesised from tryptophan by the action of methyl iodide, sodium hydroxide and methyl alcohol, which yields the *iodide of methyl α-trimethylamino-β-indolepropionate*



m.p. 197°, and this on hydrolysis gives *hypaphorine* or *α-trimethylamino-β-indolepropionobetaine*



of which the *nitrate* has m.p. 215°-220° and $[\alpha]_D +94.7^\circ$. Greshoff found $[\alpha]_D 91^\circ$ -93° for the natural base (van Romburgh and Barger, Chem. Soc. Trans. 1911, 2068).

M. A. W.

TSCHIEFFKINITE.* A titanate-silicate of cerium earths (Ce_2O_3 , &c., 23-47 p.c.) of doubtful composition, and probably only an alteration product lacking in homogeneity. Two analyses (R. Hermann, 1886) show ThO_2 20.9 and 14.4 p.c. The mineral is black, opaque, and pitchy, with a brown weathered crust on the exterior. Sp.gr. 4.2-4.5. It is found in pegmatite in the Ilmen Mtns., Urals; Kanjamalai Hill, near Salem in Madras; Nelson and Bedford counties in Virginia, here as masses up to 20 lb.; and in Madagascar.

L. J. S.

TSCHEN or CHEN. Chinese coins of a brass or bronze-yellow colour, containing 55-64 p.c. copper, 28-35 p.c. zinc, and from 1-2 p.c. tin, 2-4 p.c. iron, and 1-6 p.c. lead; and occasional

* This is the usually-accepted spelling, but the transiteration from the Russian (тешкинитъ) is partly German and partly French. The original spelling is Тешкинитъ (G. Zee, 1869); and the Russian equivalent would be Чешкинитъ.

ally small quantities of antimony, arsenic, and nickel (Pöpplein, Chem. Zentr. 1859, 484).

TSCHERMIGITE. The mineralogical name for ammonium-alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. In nature it is found as crystalline crusts on lignite containing streaks of pyrites at Tschermig, Bräx, and Dux in Bohemia. The white, fibrous, platy masses somewhat resemble fibrous gypsum; but distinct cubo-octahedral crystals are also found. In some quantity it has been found in bituminous shale near Wamsutter in Wyoming (E. T. Erickson, J. Wash. Acad. Sci. 1922, 12, 49). It is also recorded as a volcanic product from the solfatara of Pozzuoli near Naples.

L. J. S.

TSCHEWKINITE v. TSCHEFFKINITE.

TSE-HONG. A mixture of white lead, alumina, ferric oxide, and silica, used by the Chinese for painting on porcelain.

TSING-LIEN. A red pigment used in porcelain painting. Consists of a mixture of stannic and lead silicates with copper oxide or cobalt and gold.

TUBA. The Malay name for *Derris elliptica* (Benth.), used in Java to kill fish. Contains tubatrin $\text{C}_{12}\text{H}_{11}\text{O}_5$, white crystals from alcohol, m.p. $163^\circ\text{--}165^\circ$, soluble in most organic solvents, insoluble in water, acids, and alkalis. Reduces ammoniacal silver and alkaline copper solutions. Produces in fish, frogs, and mammals general motor paralysis. Lethal dose for rabbit (intravenous) 0.009 grm. per kilo (Ishikawa, Jap. Med. Lit. 1917, 1, 7; Chem. Abstr. 1917, 11, 2371; cf. Greshoff, Ber. 23, 3537; van Sille-voldt, Arch. Pharm. 1899, 237, 595; Power, Arch. Pharm. 1903, 6, 1).

TUFA v. TLAVERINA.

TUFF or VOLCANIC TUFF (from Ital. *Tufo*).

A pyroclastic rock consisting of more or less compacted dust and fragmentary material ('ashes,' *lapilli*, *scoriae*), produced by volcanic explosions. The composition varies between wide limits, depending on the kind of lava or rock from which the material has been derived; petrologists distinguish rhyolite-tuff, trachyte-tuff, andesite-tuff, basalt-tuff, palagonite-tuff, and ultrabasic-tuff. Further, there may be an intermixture of fragments of sedimentary rocks and other foreign material; and if deposited in water they are stratified, and may shade off into shale, limestone, sandstone, &c. They also vary much in texture and physical characters, from loose and earthy to hard and compact. Those interbedded with the older sedimentary strata may have their characters so obliterated that they are difficult to recognise as tuffs. For instance, the green roofing slates of the English Lake District were deposited as tuffs in Ordovician times; and other silicified tuffs are now used for road-stones.

The *pozzolana** of the Phlegrean Fields, the island of Ichia, and elsewhere near Naples, is an incoherent trachyte-tuff which has been extensively used, mixed with lime, for making hydraulic mortar, cement (pozzolanic cement), concrete, and artificial stone. The colour varies from yellow to grey (*tufo giallo* and *tufo bigio*). A similar sandy tuff which has been used for the same purpose (Roman cement) since the time of the Romans also occurs in the extinct

* The word *pozzolana*, *pozzolana*, *pozzolana*; from *pozzo* near Naples

volcanic district around Rome. Here also there is a more compact, though soft and easily worked, granular tuff, in which the catcombs are excavated; and a harder stony tuff (*tufo liscide*) employed as a building stone. Another compact tuff, which has been much used as a building stone in ancient and modern Rome, is the *peperino*† (*lapis Albanus*) of the Alban Hills. This is a leucite-basalt-tuff, showing black grains suggestive of peppercorns embedded in a grey ground. Sandy volcanic tuffs similar in character to pozzolana occur at many other localities, from some of which it is exported for the manufacture of cement, e.g. Santerin, Auvergne, Hungary, Canary Islands (here known as 'tosca'), Crimea, Eifel. In the Eifel it is known locally as *trass* (or duckstein), and is extensively quarried in the Brohl and Nette valleys, between Andernach on the Rhine and the Laacher See. This also is a trachyte-tuff, composed largely of glassy fragments of pumice, with fragments of *grauwacke* and clay-slate. It is dull and earthy with a yellowish, grey, or brown colour; 40–70 p.c. is soluble in hydrochloric acid. The looser material is used for the manufacture of hydraulic cement, whilst some of the more compact is employed as a building stone, and as a fire-stone in ovens. The latter is very porous (weight per cubic foot, 85½ lbs.; porosity, 29–45 p.c.), is easily worked, and it hardens on exposure; on account of its lightness it is especially adapted for vaults and arches.

Analysis I is of yellow pozzolana (poailip tuff) from Cape Posillipo, Naples (also CO_2 3.16; Mn_2O_3 0.54; 90 p.c. of the material is soluble in hydrochloric acid; sp.gr. 2.46); II pozzolana from near Naples (ignited material; also NaCl 2.56); III red pozzolana from near Rome; IV, *trass* from Brohl valley, Rhine; V, *trass* from Andernach; VI, blue *trass* (duckstein) from Plaidt, Nette valley, Rhine (also MnO 0.58).

	I.	II.	III.	IV.	V.	VI.
SiO_2	53.27	59.14	46.15	58.32	57.5	53.07
Al_2O_3	15.53	21.28	23.19	20.88	10.1	18.28
Fe_2O_3	4.37	4.76	6.42	4.15	3.9	3.43
CaO	3.10	1.90	8.52	2.19	7.7	1.24
MgO	0.68	—	2.25	1.10	1.1	1.31
K_2O	8.22	4.37	3.01	3.91	6.4	4.17
Na_2O	trace	6.23	trace	4.11	—	3.73
H_2O	9.84	—	10.40	5.87	12.6	12.78

98.71 100.24 99.94 100.53 99.3 98.59

I. L. S.

TULA METAL. An alloy of silver, copper, and lead made at Tula in Russia.

TUNG OIL is obtained from the seeds of *Aleurites cordata* (Muell. Arg.) *Elaeococca cordata* [BL]; *Elaeococca vernica* [Juss.]; *E. sinensis* (*Dryandra vernica* [Curt.]), and *A. fordii*, trees indigenous to China and Japan. Trees belonging to the same species also grow abundantly in Indo-China, Tonkin, Annam, and Cambodia.

The fruits form a nut, in which three seeds, having a hard shell and an oleaginous kernel, are enclosed; in China the oil is frequently termed 'nut oil,' and in Europe and America is known as China wood oil.

Three kinds of seeds are distinguished—

† Not to be confused with 'peperino' (a *Trachyte*).

yellow, drab, and white. The seed of the Japanese tung tree is smaller than that of the Chinese variety (*Aleurites fordii*), and yields an oil which gelatinizes less readily on heating. A Japanese oil had the following characters: iodine value, (Wijs) 150.2, (Häbl.) 154.4; saponif. value, 193.2; acid value, 0.9; sp. gr. at 15°/15°, 0.9342; n_D^{25} = 1.4982. Two samples had n_D^{40} , 1.5078 and 1.5116 respectively, and showed a decrease in refractive index of 0.000395 for each 1°C. rise in temperature (H. E. Goldsmith, Ind. Eng. Chem. 1923, 15, 786; J. Soc. Chem. Ind. 1923, 938 A).

The viscosity is intermediate between that of Chinese tung oil and raw linseed oil (Gardner and Bailey, Chm. 138, U.S. Paint Manufacturers Assoc. Nov. 1921). There are four species of tung oil trees in Japan, viz. (a) Japanese tung oil tree, *Aleurites cordata*, (b) Chinese tung oil tree, *A. fordii*, (c) Kangtong tung oil tree, *A. montana*, and (d) Bakoly (or tropical) tung oil tree, *A. moluccana* (better known as candlenut oil). Of these (a) is grown all over the interior of the country and the others in Formosa.

Other analyses are as follows:—

Oil contents.	(a)	(b)	(c)	(d)
In seeds, p.c.	37.77	44.11	37.43	23.61
In endosperm, p.c.	59.15	66.29	59.78	70.66
Time for drying at 95°C. (min.)	65	55	60	270
Sp. gr. (15°C.)	0.9340	0.9488	0.9372	0.9267
Acid value	0.47	1.52	0.59	0.80
Saponif. value	194.79	196.76	194.31	195.13
Iodine value (Wijs)	151.37	157.17	154.85	146.31
Refract. index (25°C.)	1.5065	1.5210	1.5147	1.4785
Reichert-Meissl value	0.39	1.10	0.35	0.71
Unsap. matter, p.c.	0.41	0.59	0.99	0.97

(I. Miura, Kōgyō-Kwagaku Zasshi, J. Chem. Ind. Japan, 1923, 26, 316-321; J. Soc. Chem. Ind. 1923, 42, 786 A.)

Analyses of the oil from *A. montana* and

Japanese *A. fordii*, and a comparison with the proposed American standard, based on the examination of oils from the Chinese *A. fordii*, are as follows:—

	<i>A. montana</i> .	<i>A. fordii</i> (Japanese).	American specification, for China wood oil.
Specific gravity at 15°/15°C.	0.9467	0.9430	0.939-0.943
Refractive index n_D^{15}	1.494	1.4917	n_D^{25} 1.515-1.520
Acid value	3.4	Nil	7.0 max.
Saponification value	203	204	190-195
Unsap. matter, p.c.	0.6	—	0.75
Iodine value	141.4	157.7	163
Heat test	18"	19.5"	12"
Iodine jelly test	45"	35"	—
"Titre test"	54-54.5	—	—

The heat test is considered the most satisfactory criterion (Rau, Robertson, and Simonsen, Indian Forest Rec. 1924, 10, 1; Analyst. 1924, 49, 399).

In China the seeds are roasted, crushed between stones, and expressed in wooden presses. The kernels contain about 53 p.c. of oil, but yield only 40-41 p.c. The cold-drawn oil is pale yellow (*white tung oil*), and is the variety chiefly imported into Europe as China wood oil. The oil obtained by hot pressing is dark brown (*black tung oil*), and is consumed at home; it has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. This odour, attributed to damaged kernels, precludes its use for many purposes. Tung oil is also expressed in Madagascar, where the oil is known under the name 'Bakoly oil,' probably a corruption of 'bannoulier' (*Aleurites moluccana*; candlenut oil). The Chinese and Japanese oils differ in specific gravity, iodine value, and gelatinizing power (see *Characteristics under Oil, Fat, and Wax*). The chief shipments of oil are made from Hankow and Wuchow in

China; comparatively smaller quantities are exported from Japan (Hokkaido).

Tung (China wood) oil contains little, if any, saturated fatty acid and relatively little oleic acid, elaeostearic acid, $C_{19}H_{35}O_2$, being the characteristic acid. Both the glyceride and the fatty acid (α -acid) derived from it change to isomeric forms (β) of higher melting-point by exposure to light or under the influence of catalysis (Bauer and Herberts, Chem. Umschau, 1922, 29, 230; cf. Morrell, J. Soc. Chem. Ind. 1918, 181 T). It does not yield any ether-insoluble bromide. In the 'elaidin test' an oily layer is obtained resting on the lower, nearly solid product; when stirred up, the whole mass flows.

Tung oil contains from 75 to 85 p.c. of glyceryl α -elaostearate, which changes under the influence of light into the solid geometrical isomeride, glyceryl β -elaostearate. Both the α - and the β -triglycerides increase in weight at about the same rate when exposed to the air in thin films. After standing for 10 months in a closed brown glass bottle, β -elaostearin became insoluble in acetone and no longer melted, but charred at about 235°. Both α - and β -elaostearic acids

m.p. 45° and 72° respectively, were prepared from tung oil which had stood for some time, by extracting it with ethyl alcohol and fractionally crystallising the extract from this solvent at about 0°. Another acid (m.p. 106.5°), presumably a cleavage product, was obtained from the residue insoluble in cold alcohol. After 8-10 days a thin layer of the α -acid was transformed into a clear yellow syrup, whilst the β -acid was only transformed into a clear yellow, viscous syrup after 4 weeks' exposure. Only two of the three possible geometrical isomerides of elaeostearic acid have been obtained. It is considered that the α -acid is probably the *cis-cis* form and the β -acid the *cis-trans* form. Bromination of both α - and β -acids yields the same tetrabromide (m.p. 114°). The transformation of the α - into the β -geometrical isomeride, on treatment with bromine, is considered to be a peculiarity confined to compounds containing two double linkings separated by two methylene groups, a constitution which explains the high reactivity of elaeostearic acid. Evidence is adduced in favour of the view that the conversion of the α - into the β -acid plays very little part in the mechanism of the drying of tung oil, which appears to be a colloidal phenomenon involving transformation from the sol to the gel form rather than a case of molecular polymerisation (A. Eibner, O. Merz, and H. Munzert, Chem. Umschau. 1924, 31, 69; Chem. Soc. Abstr. 1924, 126, i. 609). Boeseken and Ravensway (Rec. trav. Chim. 1925, 44, 241) conclude from refractometric determinations that elaeostearic acid has three double bonds and belongs to the linolenic series. This is confirmed by Kaufmann (Ber. 1926, 59, 1390), who finds that thiocyanogen is absorbed at only two of the double bonds, but that the third double bond can be saturated with bromine when the oil is exposed to the rays of a mercury vapour lamp. Kaufmann thus found two specimens of tung oil to have the following composition: I. elaeostearin, 78.5; olein, 22.8 p.c.; II. elaeostearin, 87.1; olein, 13 p.c.

Thomas and Yu (J. Amer. Chem. Soc. 1923, 45, 120) have devised a qualitative test for elaeomargaric acid, which consists in treating the insoluble magnesium salts from tung oil with 90 p.c. alcohol, and then liberating the fatty acid in the absence of air. A yield of about 20 p.c. (m.p. about 44°) is obtained.

The oil may be identified by its strong characteristic smell, and also by the manner in which it dries. Although it forms a skin more rapidly than does linseed oil, the skin it yields, e.g. on a glass plate, when dry, is opaque, wax-like, and has no elasticity. Therefore, tung oil cannot replace linseed oil, but is nevertheless largely used as a substitute for it. A number of patents have been taken out for the manufacture of boiled oils, varnishes, rubber substitutes, and linoleums, in which larger or smaller quantities of tung oil are used in place of linseed oil. V. VARNISH.

Drying of Tung Oil.—Tung oil appears to dry in about two days in moist air, but the resulting film is always wrinkled or cracked and uneven. In dry air a smooth coherent film is obtained, but the time required is about 14-21 days. In either case, however, the full gain in weight (12.9-13.3 p.c.) requires about

21-30 days, and it is concluded that tung oil is really a slow-drying oil, and that the rapid apparent rate of drying in moist air is not 'drying' in the usual sense (i.e. oxidation and polymerisation), but is a colloidal coagulation in which moisture acts as the coagulant (W. Schmidt, Farben-Zeit. 1924, 20, 1281; J. Soc. Chem. Ind. 1924, 43 B, 604).

A characteristic property of tung oil is that it forms a jelly on being heated to 250° for a short time, or even when kept at 180° for an hour or two. Tung oil gelatinised by heating to 200°-250°C. and extracted with ether yields an extract which can be divided into two fractions by treatment with acetone, viz. 12 p.c. of a thick insoluble oil, a bimolecular triglyceride of elaeostearic acid, and 88 p.c. of oil soluble in acetone. The former fraction (thick oil) is soluble in benzene, ether, and chloroform, and is converted by heating or exposure to air into a solid insoluble mass having about the same iodine value as the acids from the thick oil and as the acids isolated from the solid product insoluble in ether obtained by heating tung oil. Coagulated tung oil contains, in addition to unchanged oil, oily and solid polymerisation products both in the sol and gel form. Substances such as naphthenic acid, linseed oil, and colophony, which prevent the coagulation of tung oil, merely reduce the tendency of the sol to pass into the gel form. The formation of the gel is favoured by exposure to the air, rise of temperature, and by the addition of a little gelatinised oil. It is also caused by the action of light, with the initial formation of *α -elaostearin* (*cis* form) and *β -elaostearin* (*trans* form), which are respectively soluble and insoluble in acetone. The β -glyceride easily polymerises to a substance insoluble in the usual organic solvents. Tung oil dries, with the formation of crystalline masses of β -elaostearin, but heated (i.e. polymerised) tung oil, on the contrary, dries evenly, as β -elaostearin is in this case not present (J. Marcusson, Z. Deuts. Oel. u. Fettind. 1923, 43, 162-163; Chem. Zentr. 1923, 94 [iv.] 207; J. Soc. Chem. Ind. 1923, 42, 938 A). On exposure to the light the oil also becomes solid. The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents for oils, and shows no tendency to melt again on being heated to 250°. The gelatinisation is not due to oxygen absorption, since it takes place when air is excluded. Chapman (Analyst, 1912, 37, 543) has made a critical examination of various polymerisation tests, and has shown that greater importance should be attached to the hardness of the jelly obtained under standard conditions than to the time required to effect the polymerisation. The time, however, is the basis of the so-called Browne method, which is commonly employed by varnish chemists, and is officially adopted by the American Society for Testing Materials (Analyst, 1912, 37, 410). It consists in heating 5 c.c. of the oil at 282° and noting the time required for complete solidification. This should not take more than 12 minutes for a pure oil. Jameson (Analyst, 1920, 45, 328) has shown that the time is increased by the presence of free fatty acid, which frequently occurs to the extent of from 1.0 to 4.6 p.c. When tung oil is heated with lead oxide or red lead, the oil

gelatinises within 15 mins. to a light brown mass.

If a saturated solution of iodine in chloroform or any other solvent be dropped on tung oil, the oil is immediately solidified; and if the oil has been previously dissolved in chloroform, a jelly is obtained. Bromine has no such action on the oil.

When a solution of 1 grm. of the oil in 5 c.c. of chloroform, is stirred with 5 c.c. of a saturated solution of iodine in chloroform, the whole is converted into a stiff jelly after about 2 mins. With 2 grms. of the oil the jelly is so stiff that it can be granulated.

Investigation of the effect of glycerol, oleic acid, resin, 'ester gum,' paracoumarone resin, and linseed oil on the rate of gelatinisation of tung oil shows that their efficiency in preventing this change falls in the order given. Tung oil containing 6 p.c. of glycerol can be 'bodied,' e.g. at 280°C., without difficulty. Tung oil containing lead linoleate equivalent to 0.02 p.c. of lead, when treated in this way and dissolved in turpentine, dried rapidly to a smooth tough, transparent film (F. H. Rhodes and T. J. Potts, Chem. and Met. Eng. 1923, 29, 533; J. Soc. Chem. Ind. 42, 1923, 1081 A).

In China and Japan tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, as a common adulterant of lacquer, and also for lighting. Large quantities are also consumed for water-proofing paper and all kinds of tissues. The oil is further employed in admixture with powdered lime as a mortar. The lampblack of the best kinds of Chinese ink are obtained by burning the oil with a regulated amount of air. The cold-drawn oil is stated to be used in medicine as an emetic and also as a purgative. It should be noted that the raw oil is poisonous.

J. L.

TUNGSTEN. Sym. W. At.w. 184.1. Although found in most of the tin deposits throughout the world, the mineral *wolfram* which furnishes the bulk of the tungsten of commerce and its products, appears to have been regarded, until the middle of the eighteenth century, rather as a constituent of *casiterite* than as an associated mineral. The term 'wolfram' was, in fact, apparently applied to it on account of its causing loss of tin in smelting, in the same sense that antimony was called 'the wolf' by the alchemist because it devoured the base metals when employed in the refining of gold.

The word 'tungsten' is of Scandinavian origin and signifies 'heavy stone,' in allusion to the high specific gravity of wolfram.

In 1781, Scheele obtained a yellow powder (which he termed tungstic acid) by acid treatment of the aqueous extract from the fusion of a certain heavy lime mineral with potassium carbonate. The production of a yellow colouring matter by direct acid treatment of this mineral (afterwards termed *scheelite*) had been previously noted by Woulfe, who did not, however, explain its nature. Scheele's work was confirmed and amplified by Bergman in 1782, and the following year, his former pupil, the brothers D'Ehuyart, are stated to have shown the presence of tungstic acid in wolfram and to have produced metallic tungsten from it.

Scheelite CaWO_4 (theoretically containing

80.55 p.c. of WO_3) is also an important tungsten mineral, but its common association with rare metals (molybdenum, &c.) and base metals (antimony, &c.), from which it is difficult to effect a separation, has resulted in a smaller output and a lower price as compared with wolfram. Among other minerals may be mentioned *reinite*, a variety of ferberite, FeWO_4 , *capro-scheelite* $\text{CaWO}_4 \cdot \text{CuWO}_4$, *stolzite* or *raspite* PbWO_4 , and *tungstite* (tungsten ochre) $\text{WO}_3 \cdot \text{H}_2\text{O}$ and *ferritungstite* $\text{Fe}_2\text{O}_3 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$. The last-named minerals are commonly found as an incrustation produced by the weathering of tungsten minerals, but occasionally occur massive, and the author has an interesting piece of the former which was sent to England as scheelite, but is almost pure tungstic acid, apparently of colloidal origin.

The principal countries where tungsten minerals are found are (in order of importance) United States (chiefly west of the Rocky Mountains), Burma (mainly from Tavoy, south of Rangoon), Bolivia, Portugal, Australia, Japan, South China, Spain, South Africa (including Rhodesia), Austria, Germany, France, and England (Cornwall). The world's production (mostly wolfram, although notable quantities of scheelite are mined in United States, Australia, New Zealand, and South Africa) is estimated at nearly 20,000 tons in 1917 against about 8,000 tons in 1913. The largest producers are United States (about 4,700) followed by Burma and Bolivia with about 3,000 and nearly 4,000 respectively. The British Empire produces about 30 p.c. of the total world's production. For a useful summary of the occurrence of tungsten ores, see S. J. Johnstone, J. Soc. Chem. Ind. 1918, 37, 29 R. and later.

Although their value mainly depends on the amount of tungsten which they contain, almost the whole of the output being absorbed in the manufacture of the metal and its alloys, the minerals are invariably sold on their tungstic acid content. The best concentrated or hand-picked material contains up to 74 p.c. WO_3 , but the usual value of that sold in bulk varies between 65 and 72 p.c., the latter being considered high grade. The sale of the ores was, before the war, more often a matter of private treaty, although schedules, covering ores of various percentages and showing limits for P, S, and other impurities, were published by several firms in the United States. The home consumption of ores of tungsten was comparatively small before the war, when most of the ore produced within the Empire was bought and smelted by the Germans, who separated it and exported to this country the manufactured tungsten metal. At the outbreak of war, the then existing makers of the commercial metal ('tungsten powder') and ferro-tungsten in England very largely increased their output, and other concerns commenced the manufacture, notably one organised by an association of the large steel interests. The price of wolfram and scheelite rapidly rose to more than double that obtaining before the war, until all ores of tungsten produced within the Empire were commandeered, by agreement between the Imperial and Colonial governments, and a maximum price fixed. The basis price fixed

was 55s. (afterwards raised to 60s.) for each unit WO_3 (i.e. for each 1 p.c. per ton of ore) at 65 p.c. or over, 3d. deduction being made by the buyer for each unit or part of a unit below 60 p.c., and 6d. per unit below 60 p.c. down to 55 p.c. Ore containing lower percentages is saleable at approximately the same rate of penalisation, and, if the impurity is chiefly tinstone, the tin is paid for if over 4 p.c., as it then usually pays for electro-magnetic separation and recovery of the tin. A large proportion of the wolfram ore imported into this country is 'concentrated' at the mine by hand-picking, but in some centres it is separated from the gangue by finer crushing and wet dressing. In the case of the Burmese and Bolivian production, the wolfram is more frequently associated with tinstone. Below 2 p.c. tin (metal) the concentrate is sold direct to the smelters; above that amount (and the ores or concentrates sometimes contain as much as 30 p.c. Sn and over) it is separated. For methods of analysis of ores and concentrates, see Hutchin, Analyst, 1911, 36, 398, and Inst. Min. and Met. 1918; also Frantmann, Zeitsch. angew. Chem. 1911, 24, 2142.

The treatment of the mined ore varies according to its nature and the associated impurities. In Cornwall, where the ores are frequently arsenical and the recovery of the wolfram is chiefly subsidiary to the tin, the treatment consists usually in wet-dressing the crushed ore on tables, roasting the first rough concentrates, re-grinding and concentrating, and finally dry-dressing by means of electro-magnetic separators. The last-named operation, which depends upon the fact that wolfram is weakly magnetic to an electro-magnet, provides the only available means of mechanically separating wolfram from tinstone and other heavy minerals which accumulate during the concentration. Three or four products are commonly produced, viz. fairly clean wolfram (from 60 to 65 p.c. WO_3), an intermediate or tinny wolfram, which is returned to the plant for re-treatment, a strongly magnetic iron oxide, which is valueless, although commonly containing 3 or 4 p.c. WO_3 , and a fairly clean tin concentrate containing usually less than 2 p.c. WO_3 . Much of the imported ore or concentrate from Burma or Bolivia contains wolfram in a less fine state of division, and electro-magnetic separation is carried out on the material with no preliminary treatment other than crushing and grading into various sizes. In this case, only two final products are obtained, viz. wolfram containing from 65 to 73 p.c. or even 74 p.c. WO_3 , and a non-magnetic 'reject' containing from $\frac{1}{2}$ to 2 p.c. WO_3 , and from 50 to 70 p.c. tin (metal), according to the concentration of the original material. In the United States most of the wolfram occurs free from tin and in a gangue of a comparatively low specific gravity composed chiefly of silicious matter. In this case a simple concentrating plant consisting of crusher, jigs, and shaking table is sufficient. Wolfram, is, however, extremely friable and liable to slime on crushing, and great care must be exercised to minimise the losses which are in any case considerable. No satisfactory method has yet been devised for the mechanical separation of an ore contain-

ing both wolfram and scheelite with tinstone, such as is found in the Shan States (Burma) and elsewhere. Scheelite is heavy and non-magnetic, and remains with the tinstone when either wet-dressing or electro-magnetic separation is employed. It is invariably present in wolfram ores, although frequently in more traces.

For the estimation of tin in wolfram, see O. F. Lubatti (Chem. Soc. Trans. 1923, 123, 1409-1411).

For estimation of molybdenum in tungsten, see W. J. King (J. Ind. Eng. Chem. 1923, 15, 350).

The composition of selected specimens of the principal tungsten minerals of the nature of wolfram is shown in the following table, compiled from published and private sources, including Dr. W. F. Hillebrand of the United States Geological Survey, and H. E. Wood of the Colorado Scientific Society, etc. :—

Wolfram.			Ferberite.			Hübnerite.		
Colo- rado	Burma	Siam	Corn- wall	Spo- kane	Colo- rado	Colo- rado	Wash- ington	
P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	P.c.	
WO ₃	74.10	75.41	75.00	73.16	75.0	75.9	75.53	
FeO	11.07	17.33	15.05	22.78	18.0	23.0	0.24	
MnO	14.35	7.13	8.20	3.06	8.0	0.6	23.40	

The above analyses are all those of picked specimens, any silica, lime, alumina and other gangue matter being ignored. Traces of columbium, tantalum and other rare metals, as well as of tin, copper, and bismuth, are commonly present in actual combination, even in selected crystals.

Estimation of tungsten in low-grade ores.—

Two grms. of ore are fused with 4 parts of sodium peroxide in a nickel crucible. The fused mass is leached with 100 c.c. of water, the liquid filtered, and the precipitate well washed. The filtrate is heated, acidified with nitric acid, and made alkaline with ammonia; the precipitate is left to settle and filtered off. The hot filtrate, faintly acidified with nitric acid, is treated with excess of mercurous nitrate solution followed by ammonia until the precipitate gets black; the liquid, however, should remain faintly acid and contain mercurous nitrate. The precipitate is filtered off, washed with boiling water and dried, and the paper ashed separately. The precipitate is ignited to constant weight in a platinum crucible and fused with potassium bisulphate, and the cold mass is treated with hot water and a fragment of ammonium carbonate; if the resulting solution is not perfectly clear, the flocculent precipitate (silica or alumina) is filtered off, ignited, and weighed, and the weight subtracted from the first, tungstic acid being obtained by difference (E. Jünger, Zeitsch. anal. Chem. 1923, 63, 438; Analyst, 1924, 49, 298).

Estimation of tungsten in tungsten-steels.—

Two to three grms. of the steel are dissolved in 80-100 c.c. of 1:1 hydrochloric acid and the solution is evaporated to 40 c.c. Nitric acid is added drop by drop until all the iron is oxidised and the insoluble material assumes a yellow colour. The solution is cooled below 40°, then gently evaporated to 15 c.c., and boiled with 5 c.c. of strong hydrochloric acid and 4 or 5 drops of strong hydrofluoric acid. 50 c.c. of cold water are added and the solution is boiled for 3 min. and filtered through a pulp filter.

The precipitate is washed with hot dilute hydrochloric acid till free from iron, ignited, and weighed as tungsten trioxide (K. Swoboda, *Oester. Chem. Ztg.* 1924, 37, 53; *J. Soc. Chem. Ind.* 1924, 43 B. 435).

Manufacture of tungsten.—The manufacture of tungsten (by the soda fusion method) and ferro-tungsten (by the thermit or electric furnace method) demands an ore or concentrate as free from impurities as possible, and, while makers' requirements differ in normal times, this is only because those whose requirements are less stringent are themselves prepared to carry out the necessary purification. Objectionable impurities, inasmuch as they affect either or both the quality of the resultant product and the yield, are Sb, As, Bi, Cu, Sn, P, S, and Si, and they should be removed, so far as possible, before the chemical or metallurgical treatment. In the sodium carbonate fusion method, arsenic, phosphorus, and silica are highly objectionable, owing to the formation of soluble tungstates; freedom from tin, copper, and bismuth is not so important as it is in the thermit process, when these metals, if present, appear in large proportion in the ferro-alloy. In the electric furnace method of reduction these metals are objectionable, but are to some extent volatilised in the process. Wolfram is preferred to scheelite by the users of the soda fusion method, but a mixture of the two minerals is an advantage in the thermit and electric furnace treatment. Some users object to hübnerite, or wolfram containing an excess of manganese over iron, but no discrimination is made in the market; wolfram, ferberite, hübnerite, and scheelite, all fetching the same price per unit of WO_3 .

The treatment of tungsten ores for the manufacture of metallic tungsten ('tungsten powder') or of its oxides or salts comprises a series of operations which, although chemically and metallurgically simple, require extreme care and experience, and result in heavy losses even under the best conditions. The first step is the production of sodium tungstate by the 'Oxland' process, patented in 1847 and still used with practically no modification. It consists in heating, in a reverberatory furnace, the finely powdered ore with from 5 to 10 p.c. more than the theoretical amount of sodium carbonate (sometimes with the addition of about 5 p.c. sodium nitrate). The charge is maintained at a bright red heat for from two to three hours and is rabbled occasionally by hand. The mass is not allowed to fuse beyond a pasty condition, in which state it is withdrawn when the reaction is completed. Sodium sulphate in place of the carbonate was proposed by Oxland, but its use necessitates a higher temperature and results in irregularity in the furnace and in the nature of the product, and has met with no general application. The fritted charge or 'melt' is broken up when cold, reduced to powder and dissolved by means of live steam in a boiler provided with stirrers. The tungstate solution and residual mud (consisting mainly of oxides of iron and manganese) is pumped through a filter press and the liquor concentrated to the required strength. For the preparation of pure tungstate the solution is crystallised and re-crystallised in vats.

For the manufacture of tungstic acid, the second step in the production of metallic tung-

sten, the hot concentrated solution of sodium tungstate is run direct from the evaporator into boiling hydrochloric acid (strongest commercial HCl, sp.gr. about 37 Tw.), the granular, yellow tungstic acid being washed by decantation, pressed and calcined. The strength of the solution of both tungstate and acid and the method of admixture and washing, require the most careful supervision. Under the best conditions, both temporary and permanent, losses are heavy, partly from the production of a soluble acid tungstate and partly from the formation of colloidal tungstic acid. The production of both is minimised by the use of pure ores, by precipitation with a large excess of acid at the highest possible temperature, and by washing rapidly with dilute acid. Any arseno- or phospho-tungstates which may have been formed are not decomposed by HCl, and silico-tungstates also result in loss of WO_3 , by remaining partly in solution or, if decomposed, hinder settlement and introduce SiO_2 into the precipitated WO_3 . In order to recover any tungstate or tungstic acid in solution, it is usual to treat all filtrates and wash waters with lime, the precipitated calcium tungstate being either mixed with a fresh furnace charge or put aside for special treatment.

The third and final step in the manufacture of tungsten consists in the reduction of the calcined tungstic acid with carbon, which is usually carried out in crucibles, either in coke wind furnaces or regenerative gas furnaces of the Siemens type. The calcined tungstic acid is finely ground and intimately mixed with the purest anthracite, in the proportion of slightly less carbon than is theoretically required for the reduction of the metal with production of carbon monoxide. The temperature is raised slowly until it reaches about $1100^\circ C$, at which it is maintained for some hours, when the crucible is cooled in a reducing atmosphere. The partly sintered mass is removed from the crucible, finely ground in a ball mill, washed free from undecomposed oxide, free carbon and particles of crucible, heated with a weak solution of sodium carbonate to remove remaining traces of oxide, and finally dried as a fine-grained but distinctly granular powder. Proposals have been made from time to time to carry out the reduction by means of producer gas, while hydrogen is always used when the pure carbon-free metal is required.

Metallic tungsten may also be prepared by the direct reduction of sodium tungstate with carbon at a heat sufficient to volatilise the sodium which is simultaneously produced, or by similarly reducing calcium tungstate and dissolving out the lime which remains with the resultant powdered metal, or by reducing tungstic acid with metallic zinc. The metal obtained thus and by many other apparently simple processes is, however, always impure, and the only commercial methods known consist in the reduction of tungstic acid by the processes already referred to.

The melting-points of tungsten-molybdenum alloys lie on a straight line connecting the melting-points of the elements, and the microstructures are all homogeneous. The two form a continuous series of mixed crystals. The electrical conductivity temperature coefficients

confirm this; this coefficient may be used to determine small proportions of molybdenum in tungsten (W. Geiss and J. A. M. van Liempt, *Zeitsch. anorg. Chem.* 1923, 128, 355-360; *J. Soc. Chem. Ind.* 1923, 42, 1227 A).

The accepted standard specification for tungsten powder in England is as follows:—

	p.c.	
Tungsten	96-99	
Carbon	0.6	
Silicon	0.3	
Manganese	0.3	
Sulphur	0.06	
Phosphorus	0.02	
Arsenic	Trace	combined not over 0.06 p.c.
Tin	0.05	
Copper	Trace	
Calcium	0.1	

and for ferro-tungsten:—

Tungsten	75-80
Carbon	1.0
Manganese	1.5
Silicon	1.5
Calcium	0.5

In the event of manganese and silicon not exceeding 1 p.c. each, calcium may be 1 p.c.

Copper	0.35
Tin	0.35
Sulphur	0.07
Arsenic	0.06
Phosphorus	0.06

The following table shows the composition of a number of typical varieties of tungsten powder and ferro-tungsten as made in England at the present time (iron omitted):—

	1 P.c.	2 P.c.	3 P.c.	4 P.c.	5 P.c.	6 P.c.	7 P.c.
Tungsten	83.36	84.82	80.74	85.72	81.79	98.51	96.45
Carbon	0.54	0.027	0.04	0.75	0.53	0.109	0.129
Silicon	1.06	1.96	0.99	0.130	0.49	0.25	0.28
Manganese	0.81	0.21	0.815	0.395	1.33	0.035	0.03
Copper	0.03	0.022	0.22	Nil	Trace	0.012	0.18
Tin	0.276	0.177	0.214	0.196	0.285	0.059	0.029
Phosphorus	0.019	0.055	0.031	0.009	0.016	0.003	0.004
Sulphur	0.005	0.007	0.035	0.005	0.022	0.004	0.046
Lime	0.02	0.134	0.0164	0.021	Nil	0.041	0.164

Nos. 1, 2, and 3. Ferro-tungsten produced by the aluminium or 'thermit' process. Balance, metallic iron.

Nos. 4 and 5. Ferro-tungsten produced by the electric furnace.

Nos. 5 and 6. Tungsten powder produced by reduction of WO_3 by carbon. Iron is usually about 0.5 or 0.6 p.c. (For analytical methods, see Arnold, *Zeitsch. anorg. Chem.* 1914, 88, 748, and R. Fieber, *Chem. Zeit.* 1912, 36, 334.)

Ferro-tungsten is an alloy usually containing from 80 to 85 p.c. W. It is made on a large scale by the 'thermit' process (*q.v.*) and in the electric furnace. By the former method two qualities are made by at least one English firm, viz. one very low in carbon and containing about 2 p.c. silicon, for the manufacture of magnet and other steel, and the other containing about 0.5 p.c. carbon and about 1 p.c. silicon for high-speed tool steels. In the electric furnace the ore is commonly smelted with carbon as a reducing agent, and the resulting alloy decarburised and refined. It is stated that one American firm smelts scheelite with iron sulphide and carbon in the electric furnace producing an alloy low in carbon.

The loss of tungsten is high in all methods of reduction. It is estimated that yields of 91½, 87, and 88½ p.c. respectively are obtained in the thermit, electric furnace, and soda fusion processes, but these figures vary considerably in different works and are probably not on the low side. In the case of ferro-tungsten, losses in the slags may be partly recovered by re-treatment. In the electric furnace there is also loss by volatilisation.

With the exception of a very small amount (probably under 1 p.c.), the whole of the world's output of tungsten is used in the manufacture of alloy steels; chiefly in those known as 'high-

speed' tool steels. The original 'self hardening' steel of Mushet, first made in 1857, contained about 6 p.c. W. The modern high-speed steels contain between 16 and 20 p.c. W. and from 2 to 4 p.c. Cr., and have the property of red-hardness, i.e. ability to retain their temper at the dull red heat which is reached when cutting metal at a high speed. Arnold and Read (*Proc. Inst. Mech. Engs.* March, 1914) attributed this property to the presence of tungsten carbide. They showed that with about 11½ p.c. W present in the steels they examined the whole was present as WC displacing Fe_3C . With less tungsten the two carbides Fe_3C and WC were present, and with more tungsten the excess was present as a tungside (Fe_2W). Tungsten may be introduced into steel in the form of metallic powder or ferro-tungsten alloy. The prejudice against ferro-tungsten, which formerly existed among high-speed steel makers, due in some measure to the impurities present (high carbon, &c.) and irregularity of the tungsten content, appears to be largely disappearing under the influence of the excellent products which are now being manufactured in this country, and the scarcity of the powder in the early days of the war certainly helped the manufacturer of the ferro-alloy. Tungsten powder is preferred by a number of the English steel makers, and to-day probably the use is equally divided between the two. There is considerable loss by oxidation in the case of both, but users of the ferro-tungsten claim there is less danger of loss than with tungsten powder, and that it is cheaper. For particulars concerning alloys and the effect of tungsten upon the hardening and tempering of high-speed tool steel, see R. A. Hadfield, *Iron & Steel Inst.* 1903, 64, 14; Edwards & Kikkawa, *ibid.* Sept. 1915; and C. A. Edwards, *The Physico-Chemical Properties of Steel*, 1916.

Pure metallic tungsten, such as is used for the production of ductile tungsten, &c., is produced on a relatively small scale but has some highly important uses. A very high degree of purity is required, and the usual method of manufacture is by reduction with hydrogen, in electric resistance furnaces, of tungstic acid, purified by solution in ammonia, crystallisation of the ammonium tungstate, and re-precipitation by hydrochloric acid. The reduction is carried out at a temperature between 1000° and 1100°C. The metal powder is pressed in a hydraulic press into the form of rods, which are then sintered at a temperature of 1300°C in a current of hydrogen. The metal bar, which is still extremely brittle, is worked by hammering and rolling at a temperature of 1600°C. in a special machine through which hydrogen is flowing. Owing to the ease with which tungsten oxidises at a high temperature, cooling must take place in hydrogen. In the case of wire, the bar is worked down to about 30 mils ($\frac{3}{16}$ in.), when it becomes ductile at the ordinary temperature. The finer sizes are drawn while red hot through diamond dies. For a description of the methods for preparing ductile tungsten and filaments, see R. E. Myers, *Trans. Amer. Inst. Chem. Eng.* 1911, 3, 172; R. W. Moore, *Met. & Chem. Eng.* 1914, 3, 186; also *Electrical Rev.* 1914, 74, 595.

Tungsten as ordinarily obtained is a powdered or semi-fused, crystalline, brittle metal, harder than glass, and having a sp.gr. of between 16.5 and 17. That obtained by Moissan in the electric furnace had a sp.gr. of 18.7 and was softer than glass. A method for causing small crystals of tungsten to grow into large single crystals by taking advantage of the thermal dissociation of tungsten hexachloride is described by van Arkel (*Physica*, 1923, 3, 76; *J. Soc. Chem. Ind.* 1924, 43, B. 427). The properties of pure wrought tungsten are entirely different from those of the powdered or ordinary cast metal. It is grey-white, lustrous, tough, and non-magnetic, and can be rolled into thin sheet, welded at a yellow heat, and drawn into wire considerably thinner than one-thousandth of an inch. It melts at $3100^{\circ} \pm 60^{\circ}$, Pirani and Meyer (*Ber. Deut. Phys. Ges.* 1912, 14, 326), $3640 \pm 30^{\circ}$, Langmuir (*J. Franklin Inst.*, 1915, 490), 3645° – 3665° , Worthing (*Zeitsch. Physik.* 1924, 22, 9; *Chem. Soc. Abstr.* 1924, 126, ii. 289). Its tensile strength increases as the drawing proceeds. Wire of 5 mils diameter has a tensile strength of 460,000 lb. per sq. in., that of 1.2 mils rises to 580,000; hard drawn piano wire having a tensile strength of 507,000 lb. The sp.gr. of the pure wrought metal is from 19 up to about 19.5 in the finest wire. Tungsten has the lowest coefficient of expansion of any known element except the diamond within the range of ordinary temperatures (Worthing, *Phys. Rev.* 1917, 638). The hard drawn wire has an electric resistance of 6.2 microhms per cubic centimetre at 25°, the temperature coefficient for 0° to 170° being 0.0051. The corresponding figure for annealed wire is 5.0. The spectrum of tungsten has been investigated, among others, by W. S. Gorton (*Phys. Rev.* 1916, 7, 203); Bayen (*Compt. rend.* 1925, 180, 57); Bloch (*ibid.* 133); and Lemon (*Nature*, 1925, 214, 802). The radiation of

heat and light from tungsten at high temperatures has been studied by Zwikker (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 409; *Chem. Soc. Abstr.* 1925, 128, ii. 1041; see also Worthing, *Zeitsch. Physik.* 1924, 22, 9; *Sci. Abstr.* 1924, 27, 628).

Emission of positive ions from hot tungsten.—Tungsten at temperatures approaching the melting-point emits positively charged ions. The positive ions are not due to the presence of residual traces of gas; they only appear at temperatures above 2600°, and they are very heavy or very slow-moving particles, little affected by a magnetic field of 400 gauss, and probably consist of charged atoms or molecules of tungsten. The positive emission is much smaller than the electron emission at the same temperature and, like the electron emission, increases rapidly as the temperature is raised. At the highest temperatures the positive emission decreases rapidly with time. A tungsten spiral which has been made to give a large electron emission gives a larger initial positive emission when the potential tube is reversed (W. A. Jenkins, *Phil. Mag.* 1924 [vi], 47, 1025–1047; *Chem. Soc. Abstr.* 1924, ii. 443).

Tungsten is unaffected by water or air at ordinary temperatures, but when heated in air above 300°C. it oxidises rapidly and burns at a bright red heat. Molten sulphur or phosphorus attacks it slowly, while at a red heat their vapours rapidly convert it into the sulphide or phosphide. It is attacked by fluorine at ordinary temperatures with incandescence, and by chlorine at 250° to 300°C. It dissolves very little hydrogen and shows no tendency to react with nitrogen at temperatures up to 1500° (Sieverts and Bergner, *Ber.* 1911, 44, 2394). Tungsten is readily attacked by fused oxidising salts, such as alkaline nitrates and peroxides. Fused bi-sulphates and alkalis or alkaline carbonate also attack it, but their solutions have no action. It is readily oxidised when heated with oxidising agents such as lead peroxide, potassium chlorate, &c. At ordinary temperatures it is unaffected by bromine, iodine, and sulphuretted hydrogen. Sodium hypochlorite has a considerable solvent action on the fine powder, which is also soluble in an ammoniacal solution of hydrogen peroxide. Strong or weak hydrochloric acid has no action upon it at ordinary temperatures, but the strong acid slowly attacks it at the boiling-point and produces a coating of black sub-oxide. Boiling dilute sulphuric acid has no action, but the hot strong acid attacks it slowly. Concentrated nitric acid has but little action, but the dilute acid produces a yellow coating of tungstic acid which, as is also the case with *aqua regia*, appears practically to prevent further action. Hydrofluoric acid does not affect the metal even when hot, but dissolves it readily when mixed with nitric acid.

Tungsten combines directly with silicon and boron at or near the melting-point. It has been alloyed with many metals such as aluminium, copper, manganese, and nickel, but the alloys are not yet in extensive use. It enters into the composition of 'steelite,' the new cobalt-chromium alloy used in cutting steel. Irman (*Metall. und Erz.* 1915, 12, 356) investigated nickel-tungsten alloys and found

that with 18 p.c. W the alloy was very ductile and very resistant to dilute sulphuric acid. An alloy of tungsten with 1 p.c. thorium and 0.2 p.c. platinum is said to produce a tough, ductile alloy (U.S. Pat. 1167827, 1916). Schirmeister (Stahl und Eisen, 1915, 996) finds tungsten increases the tensile strength of aluminium, and that the hardness of the hot-rolled alloys increases at first but becomes constant at 1 p.c., the ductility falling slowly. For properties of tungsten at high temperatures, see Langmuir, Phys. Rev. 1916, 7, 302.

As a winder for electric furnaces tungsten wire is cheaper and said to be superior to platinum. Owing to its high melting-point, heat conductivity and hardness, tungsten appears to be eminently suitable for electrical contact devices, and is superior to platinum as a material for the targets in Röntgen (X-ray) tubes. Owing to its high melting-point (over 3000° as compared with 1755° for platinum) it can be placed directly at the focus of the cathode rays, and radiographs of sharper definitions can be obtained with much shorter exposure than with platinum (Coolidge, J. Ind. Eng. Chem. 1912, 4, 2). Tungsten has been suggested as a catalyst for the production of ammonia from atmospheric nitrogen (Eng. Pat. 1161, Jan. 15, 1912, and U.S. Pat. 1910, 175693), and has also been used for valves of aeroplane engines and ultra-violet ray electrodes, and valves for wireless telegraphy. There is reason to think that a considerable future use for this metal lies in the manufacture of laboratory and other utensils, as, although not so resistant to certain reagents as platinum or tantalum, there are many purposes for which its special resistance to such reagents, coupled with its greater cheapness, will render it of special value.

It is now generally recognised that tungsten is one of the most important metals other than those commonly spoken of as commercial metals. The saving which has been introduced by its employment in the manufacture of high-speed steel and in the form of fine-drawn wire in the electric light industry shows very remarkable figures. A recent bulletin issued by the United States Geological Survey (F. L. Hess, Bull. 652), states that one man and one lathe can do as much work with high-speed tungsten steels as five men and five lathes could formerly do with simple carbon steels, and that hundreds of millions of dollars' worth of labour is saved annually by this means. The 'Mineral Resources,' 1910, estimated that, assuming the present lamp consumption to require 80 million 25-watt tungsten lamps per annum, the saving in current effected by employing tungsten lamps in place of the old carbon lamps would result in an annual saving of between £40,000,000 and £50,000,000. Since that time lamps filled with nitrogen have been placed on the market, and other improvements have been added which have made the incandescent electric lamp more efficient and the saving very largely increased. It is stated that in 1916 about 200,000,000 lamps were manufactured in the United States alone. For a description of the manufacture of filament lamps, see Coolidge, U.S. Pat. 6028933, 1913; also Elec. Rev. 1914, 74, 596, and J. Soc. Chem. Ind., 1914, 1083.

G. T. H.

COMPOUNDS OF TUNGSTEN.

Oxides.—Tungsten is said to form a number of oxides the separate existence of which is not definitely settled. Thus, when sulphuric acid acts on metallic tungsten under varying conditions, the blue oxides, WO , W_2O_3 , W_4O_{10} , W_5O_{15} , are formed; sulphurous acid acts on tungsten forming the oxide W_2O_3 , and a beautiful purple oxide with a yellow metallic lustre, W_2O_5 , is obtained by heating ammonium metatungstate to a bright red heat or by fusing tungstic acid with potassium iodide (Desi, J. Amer. Chem. Soc. 1897, 19, 213). On heating tungstic oxide with carbon a blue or purple oxide is produced at 650° to 850°, a chocolate-brown mixture of oxides at 900° to 1050°, and metallic tungsten above 1050° (Davis, J. Ind. Eng. Chem. 1919 11, 201).

The hydroxide $W_2O_5 \cdot H_2O$, a dark blue powder with a purple lustre, is formed when tungstic acid is reduced with stannous chloride and hydrochloric acid, or by heating the acid with hydrogen iodide in a sealed tube at 200°. With ammonia it yields ammonium tungstate and the hydroxide $W_2O_5 \cdot H_2O$ (Allen and Gottschalk, Amer. Chem. J. 1902, 27, 328).

The only oxides which are definitely known are WO_2 , W_2O_3 , WO_3 .

Tungsten dioxide WO_2 may be prepared by the reduction of the trioxide or an alkaline metatungstate with zinc and hydrochloric acid (Pfordten, Ber. 1883, 16, 508) or by heating the trioxide to a dull redness in hydrogen (Riche, Ann. Chim. 1857, [iii.] 50, 29; Greenwood, Chem. Soc. Trans. 1908, 1493). It may be obtained crystalline by reducing lithium paratungstate with hydrogen (Hallopeau, Compt. rend. 1898, 127, 512).

Tungsten dioxide may be formed by heating an intimate mixture of tungsten trioxide and $\frac{1}{10}$ its weight of glycerol, ethylene glycol or similar hydroxyl compound, to a bright red heat for some hours (Eng. Pat. 18922, 1907; J. Soc. Chem. Ind. 1908, 22; see also Van Liempt, Zeitsch. anorg. Chem. 1923, 126, 133).

Tungsten dioxide, prepared in the wet way is of a copper red colour, prepared in the dry way it is a brown powder. It is readily oxidised to the trioxide; heated in chlorine it yields a yellow oxychloride WO_2Cl_2 . When amorphous it is soluble in hydrochloric and in sulphuric acid, but is quite unacted on when crystalline.

Blue tungstic oxide W_2O_5 , formed when tungsten trioxide is reduced with hydrogen at 250°–300° (Malaguti, Compt. rend. 1835, 1, 292) or by electrolyzing fused sodium tungstate (Smith, Ber. 1880, 13, 753), is readily oxidised to the trioxide.

Tungsten trioxide (*tungstic oxide or anhydride*) WO_3 occurs naturally as *wolfuramine* and as *tungstite* or *meymacite* (Walker, Amer. J. Sci. 1908, [iv.] 25, 305), also in the form of tungstates in *wolfram* and *scheelite*. It may be prepared by calcining in contact with air, the lower oxides, the metal, a sulphide or its hydrate (*tungstic acid*), *v. below*.

Tungsten trioxide forms large bright yellow needles which may be obtained by heating the amorphous metal to a very high temperature in air or by fusion of tungstic acid with borax in a porcelain vessel (Nordenfalk, Pogg. Ann.

1881, 114, 612); or by passing hydrogen chloride over tungstic acid or a mixture of sodium tungstate and sodium carbonate at a white heat (Debray, Compt. rend. 1862, 55, 287). The green or blue colour which it occasionally exhibits is probably due to reduction at ordinary temperatures by traces of organic matter. The yellow colour may be restored by heating in oxygen. Its sp.gr., when amorphous, varies between 5.27-7.13, when crystalline between 6.30-6.38. It melts at 1473° and is insoluble in water. According to Matignon, tungstic oxide does not melt at 2130° (Compt. rend. 1923, 177, 1290; Chem. Soc. Abstr. 1924, 126, ii. 48). When heated in hydrogen it gives the blue oxide at 250°, the dioxide at a red heat, and the metal if the latter action is prolonged. It is also reduced when heated with zinc and certain other metals (Delépine, Bull. Soc. chim. 1900, [iii.] 23, 675). When heated with chlorine or sulphur monochloride, it is converted into a volatile oxychloride and in the former case also into the hexachloride (Smith and Fleck, J. Amer. Chem. Soc. 1899, 21, 1008; Bourion, Compt. rend. 1908, 146, 1102; Defacqz, *ibid.* 1319).

The oxide is soluble in hydrofluoric acid, but not in hydrochloric or nitric acids or in *aqua regia*. See also Ehrenfeld, J. Amer. Chem. Soc. 1895, 17, 381.

Plastic masses of tungsten oxide for incandescent lamp filaments may be prepared by treating the oxide or hydrated tungstic acid with ammonia at -20° or below, or when in alcoholic suspension with gaseous ammonia (Eng. Pat. 14850; J. Soc. Chem. Ind. 1908, 1198, 1104). According to J. A. M. van Liempt (Zeitsch. anorg. Chem. 1923, 127, 215-220), temperature has little effect on the precipitation of tungsten trioxide by mineral acid, but concentration of the acid has considerable influence. The oxide is precipitated as a mixture of the white and yellow forms, together with an absorption compound with water, and in order to obtain the precipitate in an easily manipulated form, it is advisable to use hydrochloric or nitric acid in high concentration and in excess (J. Chem. Soc. Ind. 1923, 42, 1174 A).

Tungstic acids.—Tungsten trioxide forms two well characterised acids, $\text{WO}_3 \cdot \text{H}_2\text{O}$ or H_2WO_4 and $(\text{WO}_3)_2 \cdot \text{H}_2\text{O}$ or $\text{H}_4\text{W}_2\text{O}_{13}$. In addition the salts of a number of polytungstic acids are known (Schaefer, Zeitsch. anorg. Chem. 1903, 38, 142).

For the hydrosols of tungstic acid, see Lottermoser (Verh. Ges. deut. Naturforsch. Aertze, 1910, ii. 70); Müller (Zeitsch. Chem. Ind. Kolloide, 1911, 8, 93). For the hydrates of tungsten trioxide, see Hüttig and Kurre (Zeitsch. anorg. Chem. 1922, 122, 44).

Tungstic acid H_2WO_4 may be obtained by precipitating a solution of a tungstate with excess of hot acid. If cold acid is used, the white hydrate $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ is formed, from which the acid may be obtained by boiling. The comparative rates of precipitation of tungstic acid from sodium tungstate by different acids has been investigated by van Liempt (Rec. trav. chim. 1924, 43, 30; Chem. Soc. Abstr. 1924, 126, ii. 194). It is prepared by digesting a tungsten mineral with hydrochloric acid, then with *aqua regia* until the brown powder has

become yellow, when the iron and manganese have been dissolved out. The residue is well washed and then shaken with ammonia which dissolves the free tungstic acid. On filtration and evaporation the tungstic acid crystallises out. The finely powdered mineral may be fused with calcium chloride or with alkali carbonates or sodium chloride. The mass is lixiviated and the calcium or other metallic tungstate residue is then decomposed with nitric or hydrochloric acid.

Tungstic acid may be prepared from wolfram or other mineral containing tungsten, by heating the mineral under pressure with a concentrated solution of potassium hydroxide, lime or baryta being added to form insoluble compounds with some of the impurities.

The tungstic acid is then separated from the solution either by fractional precipitation with acid, the impurities separating first, or the whole of the precipitate formed by adding sufficient acid is fractionally redissolved by alkali. The process is said to be economical, convenient, and to give very pure acid (Fr. Pat. 369040, 1908; J. Soc. Chem. Ind. 1908, 939).

A continuous process for the manufacture of sodium tungstate and tungstic acid from wolframite ore by fusion with soda-ash and sodium nitrate is described by Gordon and Spring (J. Ind. Eng. Chem. 1924, 16, 555; J. Soc. Chem. Ind. 1924, 43, B. 631).

Tungstic acid may be purified by treating tungsten trioxide with carbon tetrachloride vapour at a red heat. The resulting volatile chlorine compound is sublimed, condensed and treated with *aqua regia*; the tungstic acid formed is then further purified by solution in ammonia and reprecipitation with dilute nitric acid (U.S. Pat. 926084; J. Soc. Chem. Ind. 1909, 794).

Tungstic acid is a yellow powder insoluble in water and almost so in all acids except hydrofluoric acid, in which it dissolves to the extent of 44.7 p.c. at 25°, 55.3 at 50°, using 50 p.c. hydrofluoric acid (Rosenheim and Bernhardt-Grisson, 7th Inter. Congr. Appl. Chem., 1909, Sect. x. 120). It is readily soluble in alkalis.

A colourless alcoholic hydrochloric acid solution of tungstic acid when electrolysed by a graphite anode, first becomes deep blue (containing sexa- and quinquevalent tungsten), then green (containing only quinquevalent tungsten), which on further reduction changes to olive green (mixture of quinque- and quadrivalent), then to brown (quadrivalent). When polished platinum is used as cathodes only green solutions are produced; with mercury cathodes of 0.025 amp. per sq. cm. of cathode surface, quinquevalent tungsten is formed, whilst with 0.07 amp. and over, trivalent tungsten was produced. With lead cathodes the results were similar to those with mercury, except that the trivalent tungsten formed violet-red solutions. Zinc cathodes also give rise readily to the tervalent form (see also Collenberg and Racker, Zeitsch. Elektrochem. 30, 230; Sci. Abstr. 1924, 27, 775).

Freshly prepared tungstic acid dissolves in aqueous solutions of most aliphatic amines forming substituted ammonium tungstates such as $(\text{NMe}_3)_2\text{W}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, which crystallises on evaporation. When heated they are de-

composed forming the amine, tungstic acid and the blue oxide of tungsten (Ekeley, J. Amer. Chem. Soc. 1909, 31, 664). It also gives crystalline precipitates with pyridine and quinoline (Rosenheim and Bernhardt-Grisson, *l.c.*).

Colloidal tungstic acid may be prepared by adding hydrochloric acid to concentrated sodium tungstate solution until it has an acid reaction. The white gelatinous precipitate formed, protected from currents of air, is washed by decantation several times at 0° to 5°: 15 parts of the acid are then dissolved in 1 part of concentrated oxalic acid by gently warming, and the liquid is subjected to dialysis. If the outer water is changed frequently, the oxalic acid may be completely removed (Pappadā, Gazz. chim. ital. 1902, 32, ii. 22; see Sabanéeff, Zeitsch. anorg. Chem. 1897, 14, 354).

Colloidal tungstic acid may be obtained by dissolving 5 grms. of tungsten tetrachloride in about 50 c.c. of a mixture containing equal volumes of ethyl alcohol and ether; the filtered solution is diluted to 250 c.c. with alcohol and then mixed with an equal volume of water. The colloidal solution thus obtained behaves as a positive colloid; it may be kept for some days without appreciable opalescence being observed, but coagulation occurs more quickly by adding a larger quantity of water, and immediately when small quantities of neutral salts, hydroxides, or strong acids are added. Weak organic acids or rise in temperature exert no effect. If an electric current is passed through, a deep blue precipitate separates at the cathode (Müller, Zeitsch. Chem. Ind. Kolloide, 1911, 8, 93; Lottermoser, Verh. Ges. deut. Naturforsch. Aertze, 1910, 11, 70; Wöhler and Engels, Koll. Chem. Beihefte, 1910, 1, 454; Zeitsch. Elektrochem. 1910, 16, 693).

The colloidal acid is also prepared by dialysing a 5 p.c. solution of sodium tungstate to which sufficient hydrochloric acid has been added to combine with the sodium. Colloidal tungstic acid forms a gum-like mass which may be heated at 200° without becoming insoluble and which at a red heat is converted into the trioxide. The colloidal acid has, probably, the constitution of the *meta* acid.

Tungstic acid and sodium tungstate are used in the production of colour resists for aniline black. 200 grms. sodium tungstate dissolved in 1 litre of gum tragacanth paste constitutes a white resist which may be rendered more lustrous and opaque by passing the printed tissue, after steaming, through a solution of barium chloride. The compound thus formed may be coloured by pigments, such as vermilion, ultramarine blue and chrome green, a series of pale resist colours being formed, along with which the usual albumin and tannic acid colour mixtures may be printed (Scheurer, Bull. Soc. Ind. Mulhouse, 1900, 138; *ibid.* 1898, 122).

Tungstic acid may also be employed in the production of resist effects upon *p*-nitraniline red and of discharge effects upon indigo-dyed tissues. In the latter case, the tissue dyed with the indigo is padded in a solution of sodium tungstate, dried and printed with a steam discharge mixture containing barium chlorate, potassium ferrocyanide and a basic dyestuff able to withstand the oxidising action, such as rhodamine 6 G, ultramarine, or chrome yellow.

The colours are rendered faster by the addition of albumin together with an alkali citrate or tartrate.

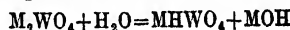
Metatungstic acid $H_2W_{12}O_{41} \cdot 7H_2O$, first isolated by Scheibler (J. pr. Chem. 1861, [i.] 83, 310), may be prepared by decomposing the lead salt with hydrogen sulphide or the barium salt with dilute sulphuric acid. It crystallises in small yellow octahedra, very soluble in water, giving a bitter solution, and loses its water of crystallisation at 100°. (*Cf.* Rosenheim and Kohn, Zeitsch. anorg. Chem. 1911, 69, 247; *ibid.* 1916, 96, 139). For its photochemical properties, see Vasilieva (J. Russ. Phys. Chem. Soc. 1912, 44, 819). For its behaviour on electrolysis, see Leiser (Zeitsch. Elektrochem. 1907, 13, 690).

Paratungstic acid, the acid corresponding to the salts of the formula $12WO_3 \cdot 5M_2O \cdot Aq$, has been prepared in dilute solution by mixing barium paratungstate with a quantity of dilute sulphuric acid not quite sufficient for complete decomposition. The solution cannot be concentrated even *in vacuo* without decomposition, and when boiled it yields tungstic acid (Hallopeau, Compt. rend. 1895, 121, 61).

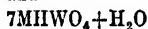
Tungstates.—Tungstic acid forms three series of salts: normal tungstates $R_2WO_4 \cdot xH_2O$; paratungstates $3R_2O \cdot 7WO_3 \cdot xH_2O$, or



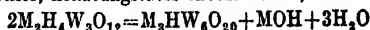
and metatungstates $R_2O \cdot 4WO_3 \cdot xH_2O$. Copaux (Compt. rend. 1913, 156, 1771) regards the paratungstates as hydrotungstates and represents them by $M_2[H(W_2O_7)]_3$. They may also be considered as compounds of 1 mol. of the tritungstate with 4 mols. of the hydrogen tungstate. Their derivation from normal tungstates may be expressed thus:



and



If, from analogy to the vanadates and molybdates, the action of hydrogen ions proceeds still further, hexatungstates should result, thus:



and the so-called metatungstates are in reality the hexatungstates (Prandtl, Ber. 1915, 48, 692). The alkaline tungstates $M_2WO_4 \cdot Aq$ are prepared by fusing a naturally occurring tungstate with sodium or potassium hydroxide or carbonate, preferably with the addition of a silicious or other flux. The alkali tungstate falls to the bottom and may be tapped off, or, after cooling, the slag may be removed (J. Soc. Chem. Ind. 1885, 116; *ibid.* 1900, 542; *ibid.* 1899, 171; Eng. Pats. 30053, 1897; 6045, 1900).

The **sodium salt** crystallises in thin prisms, soluble in 4 parts of cold, in 2 parts of hot water, the solution having a bitter taste and an alkaline reaction. It has m.p. 698° (Parravano, Gazz. chim. ital. 1909, 39, ii. 55).

The **potassium salt** forms large prismatic crystals, m.p. 894°. The ammonium salt is very unstable.

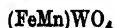
Calcium tungstate $CaWO_4$ occurs native as *scheelite* and may be prepared artificially by the interaction of calcium chloride and a normal tungstate. If the amorphous white precipitate so obtained is mixed with lime and heated in a current of hydrogen chloride, it is obtained

crystalline. The corresponding *barium tungstate* was prepared by Rousseau for use instead of white lead (Schoen, J. Soc. Chem. Ind. 1900, 740).

The so-called di- and tri-tungstates of sodium, barium, and calcium do not appear to exist.

Lead tungstate occurs native as *stolzite* and crystallises in red tetragonal pyramids.

Ferrous tungstate occurs as *wolfram*



forming dark grey or brownish-black prisms.

Manganese tungstate is found as *hobnerite*. Granger (Compt. rend. 1898, 127, 106; *ibid.* 1905, 140, 935) has proposed the employment of the tungstates in the ceramic industry.

Ammonio copper tungstate $\text{CuWO}_4 \cdot 4\text{NH}_3$, deep blue crystals, readily decomposed. A similar zinc salt is also known (Briggs, Chem. Soc. Trans. 1904, 675).

The copper compound



has been obtained by the interaction of an ammoniacal solution of copper sulphate and ammonium tungstate. It forms small blue needles (Briggs, *l.c.*).

Sodium paratungstate $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot \text{Aq}$ is known commercially as tungstate of soda and may be prepared on a large scale by roasting wolfram with soda ash and lixiviating the fused mass. The boiling solution is then nearly neutralised with hydrochloric acid and allowed to crystallise when large triclinic crystals of the salt separate. It is sometimes used as a mordant instead of sodium stannate in dyeing and calico printing. It also renders cotton, linen, &c., non-inflammable. The corresponding potassium salt is formed in glistening scales when normal potassium tungstate is boiled with a little water.

Sodium tungstate is much used both by itself and in conjunction with other fire-retarding compounds. In some experiments on its protective action recorded by Sibley (J. Ind. Eng. Chem., No. 8, 1921), impregnation of cotton fabrics with a 3 p.c. solution was found to be equally as efficacious as treatment with a more concentrated solution. For the protection of tulle, muslin, and other delicate fabrics impregnation with a solution containing 10 grms. tungstate, 125 grms. ammonium phosphate, and 7 grms. boric acid per litre has been proposed. This solution is added to the finishing medium (gum, starch, or dextrin) in the proportion 1 : 4. Ammonium chloride, ammonium sulphate, and aluminium acetate may also be combined with sodium tungstate. A medium particularly recommended for artificial silk can be prepared by diluting a mixture of the following solutions: 100 parts aluminium acetate (sp.gr. 1.13), 10 parts acetic acid (sp.gr. 1.06), and 200 parts sodium tungstate (sp.gr. 1.40). Water-resistance can be imparted by using an excess of the acetate (Eng. Pat. 175748 of 1920). According to Mond (Eng. Pat. 4457 of 1915) zirconium hydroxide may be applied to fabrics as a hydrogel, prepared by steeping in a solution of the aceto-nitrate containing magnesium sulphate, draining, heating to 65°C., and finally washing. One litre of the steeping medium

should contain 200 grms. magnesium sulphate and 20 grms. of the aceto-nitrate, prepared by evaporating zirconium nitrate with acetic acid. To enhance the fire-retarding effect, the treated fabric may be allowed to absorb phosphoric acid. Another method is to impregnate the material with a solution of precipitated zirconium phosphate in concentrated oxalic acid (Pharm. J. 1924, 691).

For various paratungstates, see Hallopeau, Ann. Chim. 1900, vii. 19, 92; Taylor, J. Amer. Chem. Soc. 1902, 24, 629.

Metatungstates $\text{M}_2\text{W}_2\text{O}_7 \cdot \text{Aq}$ were discovered by Margueritte (Ann. Chim. 1846, [iii.] 17, 475). The alkali salts are readily formed when the normal tungstates are boiled with tungstic acid until the filtrate no longer gives a precipitate on addition of hydrochloric acid. The other metatungstates are best prepared by double decomposition of the barium salt with the required sulphate or carbonate. The metatungstates have a bitter taste, are generally readily soluble in water and deposit tungstic acid on prolonged boiling. A large number of them are known but there is considerable difference of opinion as to their constitution (Copaux, Compt. rend. 1909, 148, 633; Zeitsch. anorg. Chem. 1911, 70, 297; Rosenheim, *ibid.* 418; *ibid.* 1911, 69, 247; 1912, 75, 141; Just, Ber. 1903, 36, 3619).

Pertungstates $\text{M}'\text{WO}_4 \cdot \text{Aq}$ are formed by boiling a paratungstate with hydrogen peroxide (Péchar, Compt. rend. 1891, 112, 1060); or by electrolysis of a slightly acid solution of sodium tungstate (Thomas, J. Amer. Chem. Soc. 1899, 21, 373). More highly oxidised compounds are formed by treating the pertungstates with hydrogen peroxide (McLiff and Pissarjewsky, Ber. 1898, 31, 632; Pissarjewsky, J. Russ. Phys. Chem. Soc. 1902, 34, 472).

Tungsten bronzes are compounds of the alkali metals with tungsten and oxygen, which, owing to their colour and insolubility in acids and alkalis have been employed as substitutes for bronze powders. Their exact constitution is not known, although they are generally regarded as compounds of the tungstates with tungsten dioxide. They may be obtained by the reduction of the tungstates heated to redness with hydrogen, coal gas, zinc, iron or tin.

Tungsten bronzes may be prepared electrolytically by fusing tungstic acid with the calculated amount of metallic carbonate and electrolysis the mass. A series of brightly coloured mixed alkali and alkaline earth tungsten bronzes of various compositions are described by Engels (Zeitsch. anorg. Chem. 1903, 37, 125) and Schäffer (*ibid.* 1904, 38, 148).

Four tungsten sodium bronzes are known. $\text{Na}_2\text{W}_2\text{O}_7$ of a golden yellow colour, $\text{Na}_2\text{W}_2\text{O}_{11}$ of a blue colour, $\text{Na}_2\text{W}_2\text{O}_9$ of a purple red colour, and $\text{Na}_2\text{W}_2\text{O}_{13}$ which forms red-yellow cubes and yields a brown-yellow powder (Philipp, Ber. 1882, 15, 499).

Potassium forms one bronze, $\text{K}_2\text{W}_2\text{O}_{11}$ (Knorre and Schaffer, *ibid.* 1902, 35, 3407).

Blue lithium bronzes are described by Hallopeau (Compt. rend. 1898, 127, 512).

Tungstates of the rare earths are described by Hitchcock (J. Amer. Chem. Soc. 1895, 17, 483).

TUNGSTEN AND THE HALOGENS.

Tungsten hexachloride WCl_6 , is prepared by heating metallic tungsten in excess of pure dry chlorine, particular care being taken to exclude all traces of air and moisture in order to avoid the formation of the oxychloride (Roscoe, *Annalen*, 1872, 162, 349). A small quantity of the latter is formed at the beginning of the reaction, however, in spite of all precautions. It should be driven off beyond the portion of the tube where the chloride is to be collected. Tungsten hexachloride forms dark violet opaque crystals, which are very stable when pure but are readily decomposed by moist air or water, if the slightest trace of the oxychloride is present. It has m.p. 275° , b.p. $346.7^\circ/759.5$ mm.

On heating the hexachloride in a stream of nitrogen with powdered aluminium and quartz, extracting the product with hydrochloric acid, concentrating the reddish-yellow extract and saturating it with hydrogen chloride, it yields $HW_2Cl_4 \cdot 4H_2O$ in slender yellow needles, which rapidly lose hydrogen chloride on exposure to air (Lindner, *Ber.* 1922, 55 [B], 1458).

The salt $K_2W_2Cl_6$, and a number of corresponding salts of tervalent tungsten form green solutions and are powerful reducing agents (Collenberg and Sandved, *Zeitsch. anorg. Chem.* 1923, 130, 1; *Chem. Soc. Abstr.* 1924, 126, ii, 51).

Tungsten pentachloride WCl_5 , is formed by the incomplete reduction of the hexachloride in a current of hydrogen. It is volatile and when redistilled forms long, pure black shining crystals, m.p. 248° , b.p. 275.6° . It is hygroscopic and dissolves in water forming an olive-green solution, but most of it decomposes into the blue oxide and hydrochloric acid (Roscoe, *l.c.*).

Tungsten tetrachloride WCl_4 , forms the non-volatile residue in the production of the pentachloride. It may also be prepared by the distillation of the latter or of the hexachloride, or better, a mixture of the two chlorides in a current of hydrogen. It forms a greyish-brown crystalline powder (Roscoe, *l.c.*). It is hygroscopic, infusible, is partially decomposed by water and is reduced by hydrogen to the metal.

Tungsten dichloride WCl_2 , is best prepared by heating the tetrachloride in a current of carbon dioxide at the temperature of a moderately hot zinc bath. It is a grey non-volatile powder partly decomposed and partly dissolved by water forming a brown solution (Roscoe, *l.c.*).

Tungsten dioxydichloride WO_2Cl_2 , obtained by passing chlorine over the dioxide, forms light lemon-yellow scales. Heated with ammonia it forms the compound $W_2O_5 \cdot N_2H_4$, (Smith and Shinn, *Zeitsch. anorg. Chem.* 1893, 4, 381).

Tungsten oxytetrachloride $WOCl_4$, beautiful red needle-shaped crystals, m.p. 210.4° , b.p. 227.5° , is formed by the interaction of the trioxide and phosphorus pentachloride (Schiff, *Annalen*, 1879, 197, 186); or by passing the vapour of the hexachloride over the heated trioxide.

Tungsten hexabromide WBr_6 , obtained by heating tungsten with dry bromine vapour in an atmosphere of nitrogen, forms blue-black needles which decompose when heated to a high temperature, give a colourless solution in aqueous ammonia, fume in air and give a royal

blue oxide when treated with water (Schaeffer and Smith, *J. Amer. Chem. Soc.* 1897, 18, 1008).

Tungsten pentabromide, prepared by passing dry hydrogen bromide over tungsten hexachloride at 300° , or better by the action of excess of bromine on tungsten, forms fern-like aggregates of dark needles with green reflex, m.p. 276° , b.p. 333° . It is very hygroscopic, yields the blue oxide when treated with water and dilute acids and is decomposed by alkalis, alkali nitrates, carbonates and bisulphates (Defacqz, *Ann. Chim.* 1901, [vii.] 22, 247).

Tungsten oxybromides WO_2Br_2 , $WOBr_4$, and the compounds WCl_2Br_4 , $WCl_4 \cdot 3WBr_4$, are also known (Defacqz, *Compt. rend.* 1899, 129, 515).

Tungsten tetriodide WI_4 , obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at 110° , is a black crystalline substance of sp.gr. 5.2 at 18° , decomposed by water, alkali-hydroxides and carbonates. Soluble in absolute alcohol (Defacqz, *Compt. rend.* 1898, 127, 510).

Tungsten diiodide WI_2 , obtained by the action of hydrogen iodide on tungsten hexachloride at 400° , is an amorphous, insoluble, infusible, non-volatile brown powder of sp.gr. 6.9 at 18° (Defacqz, *ibid.* 1898, 126, 962).

Tungsten hexafluoride WF_6 , may be obtained by the interaction of tungsten hexachloride with anhydrous hydrofluoric acid or with arsenic trifluoride, or, best of all, antimony pentafluoride. It has m.p. 2.5° and b.p. 19.5° . Is readily soluble in alkalis, attacks glass and most metals and forms double salts with alkali fluorides. When acted on by water it yields tungstic acid (Ruff, *Zeitsch. anorg. Chem.* 1907, 52, 256).

Tungsten oxytetrafluoride WOF_4 , obtained by the interaction of the oxytetrachloride and anhydrous hydrogen fluoride, forms small colourless hygroscopic plates, m.p. 110° , b.p. 185° – 190° , is decomposed by water forming tungstic acid and absorbs large quantities of ammonia in the cold (Ruff, *l.c.*).

Tungsten dioxydifluoride is known in an impure state. For various double fluorides, see Marnat (Ann. Chim. 1863, [iii.] 69, 63); Marchetti (*Zeitsch. anorg. Chem.* 1895, 10, 06); Miolati and Rossi (*Real. Accad. Lincei*, 1896, [v.] 5, ii. 223); Ephraim and Heymann (*Ber.* 1909, 42, 4456).

TUNGSTEN AND SULPHUR.

Tungsten disulphide WS_2 , may be prepared by passing hydrogen sulphide over tungsten hexachloride at 375° – 550° , or by fusing an intimate mixture of pure dry potassium carbonate, flowers of sulphur and tungsten trioxide. It is a grey-black crystalline powder, insoluble in water, fairly stable, and has sp.gr. 7.5 at 18° (Defacqz, *Compt. rend.* 1899, 128, 609).

Tungsten trisulphide WS_3 , best obtained by treating a sulphotungstate with excess of acid, is a brown powder which becomes black when dried, is slightly soluble in cold water, more so in hot water, and readily in alkali hydroxides and carbonates (Corleis, *Annalen*, 1883, 232, 244). It has been obtained in the colloidal state by Wunsinger (*Bull. Assoc. Sci. Belg.* 1888, 16, 390).

The compounds, $WCl_4 \cdot 3WS_2$ (Ann. Chim. 1901, [vii.] 22, 238) and WO_3 (Wunsinger,

(*i.e.*) and a number of metallic sulpho- or thio-tungstates, M_2WS_4 (Coriell, *l.c.*), have been described. A *di- and tri-selenide* (Uelsmann, J. 1860, 92) and a *trifluoride* are also known.

Tungsten nitrides W_2N_3 , W_3N_4 , a number of oxynitrides, nitretamido and oxynitretamido compounds, and also a hydroxylamine tungstate have been obtained (Wöhler, Annalen, 1850, 73, 190; *ibid.* 1858, 105, 258; Rideal, Chem. Soc. Trans. 1889, 41; Wöhler, *ibid.* 1851, 3, 171; Desl, *l.c.*; Allen and Gottschalk, *l.c.*).

Tungsten cyanides have also been prepared by Rosenheim and Dehn (Ber. 1914, 47, 392; Olsson, Ber. 1914, 47, 912).

TUNGSTEN AND PHOSPHORUS.

Tungsten combines directly with phosphorus when heated to redness, forming a dark green phosphide W_3P_4 .

Tungsten diphosphide WP_2 produced by heating tungsten hexachloride at 450° in a current of hydrogen phosphide forms a black crystalline mass insoluble in water, sp.gr. 5.8. The phosphorus is readily displaced by the halogens and by sulphur and nitrogen at high temperatures. It may be reduced by heating with hydrogen, zinc or copper (Defacqz, Compt. rend. 1900, 130, 915).

If tungsten diphosphide is heated with a large excess of copper phosphide in a graphite crucible in a wind furnace and the product treated with dilute nitric acid, it yields the *monophosphide* WP , grey lustrous prismatic crystals, sp.gr. 8.5 (Defacqz, *ibid.* 1901, 132, 32).

Another phosphide W_2P is formed by reducing a mixture of phosphorus pentoxide (2 mols.) and tungsten trioxide (1 mol.) in a charcoal crucible at a high temperature (Wöhler, Chem. Soc. Trans. 1853, 5, 94).

Phosphotungstic acid.—Tungstic acid combines with phosphoric and also with arsenic, antimonie and vanadic acids to form complex compounds of varying composition, $M_2O_5 : WO_3 = 1 : 7$ to $1 : 24$ analogous to the molybdates. Phosphotungstic acid is used as a reagent for the precipitation of alkaloids, proteins and some of their products of hydrolysis, also for the detection of potassium and ammonium salts with which it gives insoluble precipitates. It may be prepared by acidifying a solution of 4 parts of sodium tungstate and 1 part of sodium phosphate with sulphuric acid and extracting the phosphotungstic acid with ether (Winterstein, Chem. Zeit. 1898, 22, 539).

Some new series of phosphotungstates are described by F. Kehrman and R. Mellet (Helv. Chim. Acta, 1922, 5, 942), including the simple $3M_2O_5 \cdot P_2O_5 \cdot 6WO_3$, aq., of which the sodium, potassium, and ammonium salts have been prepared in the pure state.

Literature on phosphotungstic acids and the phosphotungstates: Kehrman, Zeitsch. anorg. Chem. 1891, 1, 428; Soboleff, *ibid.* 1896, 12, 16; Rogers, J. Amer. Chem. Soc. 1903, 25, 298.

Arsenotungstovanadates

$18(NH_4)_2O \cdot As_2O_5 \cdot 21WO_3 \cdot 4V_2O_5 \cdot 13H_2O$;
 $6Ti_2O_3 \cdot As_2O_5 \cdot 21WO_3 \cdot 5V_2O_5 \cdot 13aq.$; and
 $6BaO \cdot As_2O_5 \cdot 17WO_3 \cdot 5V_2O_5 \cdot 4aq.$

are described as red crystals by Cannevi (Gazz.

chim. ital. 1923, 53, 773; Chem. Soc. Abstr. 1924, 126, ii. 117).

Tungsten arsenide WAs_2 , prepared by heating tungsten hexachloride in a current of hydrogen arsenide at 150° – 360° , is a black crystalline insoluble powder of sp.gr. 6.9 at 18° .

Tungsten chloroarsenide W_2AsCl_4 , obtained by heating the above substances in a sealed tube at 60° – 70° , forms hygroscopic bluish-black crystals, decomposed by water and acids (Defacqz, Compt. rend. 1901, 132, 138).

For *arseniotungstic acids and tungstates*, see Kehrman and Rüttimann (Zeitsch. anorg. Chem. 1899, 22, 285). **Vanadotungstates** (Friedheim, *ibid.* 1894, 6, 11; Rogers, *l.c.*; Friedheim and Henderson, Ber. 1902, 35, 3242). **Antimoniotungstates** (Hallopeau, Compt. rend. 1896, 123, 1065). **Zirconotungstates** (*ibid.* 1896, 122, 1419). **Alumino- and aluminophospho- and arseno-tungstates** (Daniels, J. Amer. Chem. Soc. 1908, 30, 1846).

Tungsten boride WB_2 , prepared by fusing the two elements together in an electric furnace, crystallises in hard octahedra, sp.gr. 9.6 (Tucker and Moody, Chem. Soc. Trans. 1902, 16).

TUNGSTEN AND CARBON.

When tungsten trioxide is fused with calcium carbide in an electric furnace, it forms an iron-grey carbide, CW_2 , which is harder than corundum and has sp.gr. 16.06 at 18° . In the presence of a large excess of iron, the carbide CW , an iron-grey crystalline powder of sp.gr. 15.7 at 18° , is formed (Moissan, Compt. rend. 1897, 125, 839; Williams, *ibid.* 1898, 126, 1722).

Tungsten carbides are formed when the finely divided metal or its oxides are heated in carbon monoxide, or in a mixture of methane and hydrogen. At 1000° W_2C_4 is formed in carbon monoxide, and WC in a mixture of methane and hydrogen (1:1) at 80° (Hilpert and Ornstein, Ber. 1915, 48, 1669).

W_2C has been formed by heating tungsten in a carbon electric furnace; it melts above 2700° and solidifies as a homogeneous substance (Ruff and Wunsch, Zeitsch. anorg. Chem. 1914, 85, 292). Voigtländer and Lohmann (D. R. P. 286184, 1914) claim tungsten carbide to have a hardness of 9.8 compared with the diamond at 10.

Two carbides of tungsten, W_2C and WC , are formed when naphthalene vapour acts on incandescent tungsten filaments. These compounds at temperatures from $2400^\circ K.$ to $2790^\circ K.$ lose all their carbon, the tungsten filament regaining the same conductivity as before carbonisation. Incandescent tungsten may be carbonised by almost any hydrocarbon vapour. Alcohol will also carbonise the filament, but at only $\frac{1}{2}$ the rate at which acetylene effects the carbonisation. The electrical resistivity of cold W_2C is about 15 times that of tungsten, but the temperature coefficient of resistance is very much less. The conductivity of a partially carbonised filament at any temperature is in agreement with that calculated from the amounts of tungsten and W_2C present (M. R. Andrews, J. Phys. Chem. 1923, 27, 270).

Chromium tungsten carbide $CW_2 \cdot 3Cr_2O_3$, is formed by heating a mixture of chromic oxide, tungstic acid and carbon in a carbon crucible in

an electric furnace for five minutes with a current of 400 amperes at 75 volts and treating the product with warm hydrochloric acid, then with concentrated ammonia solution. It forms small hard stable crystalline grains of sp.gr. 8.41 at 22°. By the addition of tungsten to chromium steels, the formation of this stable hard carbide might give rise to the production of new steels with special qualities (Moissan and Kouznietzow, *Compt. rend.* 1903, 137, 292).

Iron tungsten carbide $3W_2C_2Fe_3C$, a magnetic substance, sp.gr. 13.4 at 18°, has also been prepared (Williams, *ibid.* 1898, 127, 410; Carnot and Goutal, *ibid.* 1899, 128, 207).

TUNGSTEN AND SILICON.

Tungsten silicide WSi_3 has been prepared by heating copper silicide with amorphous tungsten in an electric furnace, using a current of 800–900 amperes and 50 volts, the resulting product is then washed successively with nitric acid, caustic potash, warm hydrofluoric acid and water. It may also be prepared by reducing a mixture of silica and tungstic anhydride with sulphur and alumina. It forms brilliant, grey crystals, of sp.gr. 9.4, which are not magnetic and are very stable (Dofacqz, *Cempr. rend.* 1907, 144, 848; Hönigschmidt, *Monatsh.* 1907, 28, 1017).

The silicide W_2Si_3 is obtained by heating the trioxide with silicon in the electric furnace, after which the mass is suspended in dilute hydrochloric acid (1 in 10) and electrolysed. The excess of metal dissolves and the silicide is removed, washed with *aqua regia*, then with ammonia, and is finally separated from carbon silicide gravimetrically by suspension in methyl iodide (Vigouroux, *Compt. rend.* 1898, 127, 393). It forms beautiful steel grey crystals with a metallic lustre, sp.gr. 10.9. See also Friley, *Rev. de Metallurgie*, 1911, 8, 457; *J. Soc. Chem. Ind.* 1911, 1018.

Tungsten aluminium silicide forms black hexagonal crystals (Manchot and Kieser, *Annalen*, 1904, 337, 360).

Silicotungstic acids of the formulae,



$H_2W_{12}SiO_{42} \cdot 20H_2O$, $H_2W_{12}SiO_{42} \cdot 29H_2O$, &c., were discovered by Marignac (*Ann. Chim.* 1864, [iv.] 3, 5). The acid corresponding to the last formula is formed by precipitating its salts with mercurous nitrate and decomposing the mercurous salt with hot hydrochloric acid. It crystallises in large tetragonal prisms, is readily soluble in water, alcohol, and ether, and forms a valuable reagent for alkaloïds. The salts, most of which are soluble in water, are prepared by boiling gelatinous silicic acid with metallic polytungstates (Wyrouboff, *Bull. Soc. franc. Min.* 1896, 19, 219; Friedheim and Henderson, *l.c.*).

ORGANIC SALTS OF TUNGSTEN.

Esters of tungstic acid are described by Smith and Dugan (*J. Amer. Chem. Soc.* 1899, 21, 1916); *alkali tungsten tartrates* by Henderson and Barr (*Chem. Soc. Trans.* 1896, 1456); *citrate* by Henderson, Orr and Whitehead (*ibid.* 1899, 547); *tungsten oxalates* by Rosenheim (*Ber.* 1893, 26, 1191); *tungsten cyanides* by Rosenheim and Dehn (*Ber.* 1914, 47, 392; *ibid.*

1915, 48, 1167; Olsson, *Ber.* 1914, 47, 917; *Zeitsch. anorg. Chem.* 1914, 88, 49).

Tungsten forms ozosalts which are readily soluble and difficult to obtain free from the normal salts used in their preparation. The following have been described:—

Sodium ozotungsten oxalate



and also the corresponding ammonium and calcium salts which have only 1 mol. of water of crystallisation (Mazzucchelli and Inghilleri, *Atti. R. Accad. Lincei*, 1908, [v.] 17, ii. 30).

Complex compounds of the tungstic acids with organic acids have been obtained by Grossmann and Kramer (*Zeitsch. anorg. Chem.* 1904, 41, 43); and by Mazzucchelli and Bolghi (*Gazz. chim. ital.* 1910, 40, ii. 241); and additive compounds of the tetra-, penta-, and hexachloride with organic esters by Rosenheim and Loewenstamm (*Ber.* 1902, 35, 1115).

Oxalotungstites, *Chlorotungstites* and other derivatives of quinquivalent tungsten have been obtained by Collenburg (*Zeitsch. anorg. Chem.* 1918, 103, 247).

Gerber (*Mon. Scient.* 1917 [v.] 7, 73–219) finds evidence for the existence of a new element, *neotungsten*, at wt. 187, associated with tungsten, and which, as it is spectroscopically indistinguishable from tungsten, he suggested may be an isotope of that metal (*cf.* Barbe, *Mon. Sci.* 1919, [v.] 9, i. 73).

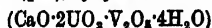
TUNGSTENITE. Tungsten sulphide WS_2 , corresponding with molybdenite (MoS_2), which it closely resembles in physical characters. It occurs in some quantity intimately intermixed with pyrites, fahlore, and galena in a compact ore at the Emma mine in the Little Cottonwood district, Salt Lake Co., Utah. Under the microscope it is seen in this ore as feathery flakes resembling graphite in appearance. It is lead-grey and opaque with a metallic lustre, and soft enough to mark paper; sp.gr. about 7.4. The mineral is not oxidised by roasting in air, and is not attacked by hydrochloric or nitric acids, but is decomposed by *aqua regia* (R. C. Wells and B. S. Butler, *J. Washington Acad. Sci.* 1917, 7, 596). L. J. S.

TUNGSTITE or TUNGSTIC-OCCHRE. A yellow, earthy mineral frequently observed in small amounts as an alteration product of wolframite and scheelite, and long supposed to be anhydrous tungsten trioxide WO_3 . The original tungstic-ochre of B. Silliman (1822) and the 'wolframine' from Cornwall were, however, never analysed, and in the text-books the characters of the artificial orthorhombic crystals of the anhydrous oxide have been assumed for the natural mineral. A mineral of similar appearance has been described under the name meymacite (A. Carnot, 1874) with the composition $WO_3 \cdot 2H_2O$. T. L. Walker (*Amer. J. Sci.* 1908, 25, 305) suggests that these are really identical and that the correct formula is $WO_3 \cdot H_2O$. He describes a golden-yellow mineral occurring with wolframite in veins of gold-quartz near Salmo in British Columbia. Minute crystals from cavities possess a perfect cleavage in one direction and are optically biaxial; sp.gr. 5.517; soluble in ammonia or sodium hydroxide, but not in acids.

Another 'tungstic ochre' occurring with

wolframite in the Germania tungsten mine, Deer Trail mining district in the State of Washington, was found by W. T. Schaller (Amer. J. Sci. 1911, 32, 161) to be a hydrated ferric tungstate, $\text{Fe}_2\text{O}_3 \cdot \text{WO}_3 \cdot 6\text{H}_2\text{O}$, for which the new name *ferritungstate* was proposed. This is pale-yellow to brownish-yellow and crystallised in minute hexagonal scales. L. J. S.

TURANITE. Hydrated copper vanadate, $5\text{CuO} \cdot \text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, forming compact, spongy, or radially fibrous aggregates and reniform crusts of an olive-green colour. It is found with alaite (*q.v.*), ferganite (*q.v.*), tyuyamunitite



malachite, &c., in the oxidation zone of the uranium and vanadium deposits which occur in limestone at Tyuya-Muyun in Fergana, Russian Central Asia. L. J. S.

TURANOSE. A sugar $\text{C}_{14}\text{H}_{22}\text{O}_{11}$ obtained by heating melezitose with acetic acid. Is not hydrolysed by any of the ordinary enzymes and is consumed very slowly by yeast. Rotatory power $[\alpha]_D = +71.8$ shows no birtotation (Tanret, Compt. rend. 1906, 1424) (*v. CARBOHYDRATES*).

TURBIDIMETRY. See NEPHELOMETRY.

TURF. *v. FUEL.*

TURGITE *v. TURITE.*

TURICINE *v. BETAINES.*

TURITE, TURGITE or HYDROHÆMATITE.

A hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, containing, according to the formula Fe_2O_3 , 94.7, (Fe 66.2), H_2O 5.3 p.c. It is sometimes soft and earthy with a bright red colour, being then included (together with earthy hæmatite) under red-ochre. It may also be massive and compact; with sometimes a radially fibrous structure and a smooth and brilliant mamillated or botryoidal surface, being then very similar to the kidney-iron-ore (more strictly the *Ger. Rother Glaskopf*) variety of hæmatite. Such material is dark red to black with a sub-metallic lustre. Sp.gr. 4.29-4.49; H. 6½ (harder than limonite). A characteristic feature is the dark cherry-red streak, which is of a lighter shade than that of hæmatite. Crystals are not known, but the fibrous material is birefringent with straight optical extinction. Few analyses show exactly the theoretical amount of water; there seems rather to be a gradual passage on one side to hæmatite (Fe_2O_3) and on the other to limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, with 14.5 p.c. H_2O). Compact or earthy red hæmatite often contains 1-2 p.c. H_2O . The existence of turite as a distinct mineral species has therefore been doubted, and it has been regarded as a colloidal material forming a stage in the hydration of hæmatite to limonite, or of the dehydration of limonite. Turite, however, when heated in a bulb-tube decrepitates with surprising violence, and in this respect it differs from both hæmatite and limonite. Its dehydration curve is quite distinct from those of limonite and goethite. Occurrences of fibrous mamillated turite and limonite at Salisbury in Connecticut and Bridgeville in Nova Scotia show a sharp line of demarcation between the two minerals. Turite was first described from the Turinaky¹ copper mines near Bogoslovsk in the Urals, and it has since

been recorded with iron ores from many other Russian localities. It is no doubt a mineral of common occurrence elsewhere with hæmatite and limonite ores (L. J. Spencer, Min. Mag. 1919, 18, 339). L. J. S.

See also *Iron oxides*, art. IRON.

TURKEY-RED OILS *v. OILS, FIXED, and FATS.*

TURMERIC (*Indian saffron; Terra merita*).

The so-called turmeric root of commerce is the underground stem or rhizome of *Curcuma longa* (Linn.), or of various species of *Curcuma*—e.g. *C. tinctoria*, *C. viridiflora* (Roxb.), &c. These plants, belonging to the *Scitamineæ*, are indigenous to Southern Asia, and are there largely cultivated, being exported from China, Madras, Bengal, Java, Malabar, Batavia and Barbadoes. Those varieties which are derived from the central rhizomes are more or less round (*Curcuma rotunda*, Linn.), while the lateral rhizomes are long and finger-shaped (*C. longa*). When of good quality these commercial varieties are hard, and possess a dull, waxy, resinous fracture, the external colour being yellowish-grey, and internally orange-brown, but producing, when ground, a somewhat bright yellow powder, having a strong characteristic odour and a peppery bitter taste.

The rhizome of *Canna speciosa*, a West African plant, is said to be exactly similar to East Indian turmeric in taste, smell, and chemical reactions (Daniell, Pharm. J. 19, 258). It is cultivated in Sierra Leone, and furnishes the so-called 'African turmeric.'

According to Pelletier and Vogel (Annalen, 44, 297), turmeric contains cellulose, gum, starch, mineral matter, a strong-smelling volatile oil, a brown colouring matter, and a characteristic yellow colouring matter named by them *Curcumin*. Pectin and pectic acid are also present (Schützenberger). Kachler (Ber. 3, 713) found a notable quantity of potassium binoxalate.

Pelletier and Vogel's method of isolating the curcumin consisted in first removing the fatty, resinous, and other impurities by extracting pulverised turmeric with water and carbon disulphide, then dissolving out the colouring matter with boiling alcohol, and purifying it by successive solution in ether and alcohol, precipitation with lead acetate, subsequent treatment with hydrogen sulphide and extraction of the product with ether. It was thus obtained as an amorphous yellow powder.

Lepage adopted a similar method, but after extraction with carbon disulphide the colouring matter was dissolved in alkali, precipitated with acid, and finally purified by means of ether.

Daube was the first to obtain curcumin in the crystalline state. He removed essential oil by passing a strong current of steam over the coarsely-ground turmeric, then thoroughly extracted it with hot water, and finally treated the dried residue with boiling benzene. On cooling the solution thus obtained, crude curcumin separated as bright orange-red crystalline crusts, which were pressed between blotting-paper, and dissolved in cold alcohol. After filtering off some yellow flocculent substance, the solution was precipitated with an alcoholic solution of neutral lead acetate, adding finally a little basic lead acetate in order to neutralise

¹ Hence the name, from the adjacent Tura river. The German spellings *turgite* and *turjit* are mistranslations of the Russian *тырма*, turite.

almost entirely the liberated acetic acid and prevent thereby any solution of the colour-lake. The brick-red precipitate was washed with alcohol, suspended in water, and decomposed with hydrogen sulphide. The liberated curcumin was extracted from the precipitate with boiling alcohol, from which it crystallised on slow evaporation.

Benzene is very suitable for the isolation of pure curcumin, for although it is very little soluble in this liquid, the resinous impurities are not dissolved thereby.

Gajewsky (Ber. 3, 265) obtained crystalline curcumin by first extracting turmeric root with carbon disulphide, then dissolving out the colouring matter with ether, and purifying it by fractional crystallisation from ether or benzene. He detected the presence of another colouring matter and also traces of an alkaloid. This chemist obtained an increased yield of colouring matter by washing the dry ethereal extract with dilute ammonia to remove resin, then dissolving the brittle residue in boiling concentrated ammonia solution and precipitating with carbon dioxide; 250 grms. ethereal extract gave 100 grms. flocculent curcumin, m.p. 140°. Jackson (Ber. 14, 485) also obtained crystallised curcumin by first removing the oil by long extraction with carbon disulphide (sixty hours), then thoroughly extracting (sixty hours) with ether, and after washing the orange-coloured product thus obtained with cold alcohol or ether, crystallising from hot alcohol.

Perkin (Chem. Soc. Trans. 1904, 85, 63) precipitates an alcoholic turmeric extract with lead acetate, washes the lead compound first with alcohol then with water, and decomposes it with dilute sulphuric acid. From the mixture of lead sulphate and curcumin the latter is removed with boiling alcohol and the extract evaporated and poured into ether, which causes the separation of tarry impurities. The ethereal solution, after evaporation to a small bulk, is treated with carbon disulphide and allowed to stand, the crystals which separate from time to time being removed. 0.56 p.c. of curcumin was thus obtained from turmeric.

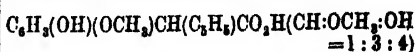
Curcumin crystallises from alcohol in orange-coloured prisms, m.p. 165° (Daube), 172° (Gajewsky), 178° (Jackson), and 183° (Ciamician and Silber, Ber. 30, 192), and is soluble in ether, forming a green fluorescent liquid. Alkaline solutions dissolve it with a reddish-brown colour, which when neutralised passes to yellow, and on this account it is useful in the form of 'turmeric paper' as a reagent for alkalis. Whereas Daube assigned to curcumin the formula $C_{18}H_{16}O_8$, Gajewsky ($C_{18}H_{16}O_8$), probably



Jackson considered that $C_{18}H_{16}O_8$ or $C_{18}H_{14}O_8$ were more reasonable expressions, and of these Jackson and Menke (Amer. Chem. J. 6, 78) preferred the former, and prepared the following derivatives harmonising with this view:—

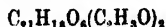
Dihydrocurcumin $C_{18}H_{18}O_8$, brownish-white powder, m.p. 100° ca.; *dihydrocurcumin anhydride* $C_{18}H_{16}O_8$, dirty white powder, m.p. 120° ca.; *diethylcurcumin* $C_{22}H_{28}O_8$, brownish tar; *p-bromobenzylocurcumin* $C_{21}H_{18}BrO_8$, pale yellow crystals, m.p. 76°–78°; *acetylcurcumin* $C_{20}H_{18}O_8$, brownish mass; *diacetylcurcumin* $C_{18}H_{14}O_8$,

yellow rhombic crystals, m.p. 154°; *curcumin-tetrabromide* $C_{18}H_{10}O_8Br_4$, powder, m.p. 185° ca.; *tetrabromocurcumin* $C_{18}H_6O_8Br_4$, red powder; *pentabromocurcuminindibromide* $C_{18}H_4O_8Br_6$, red powder, m.p. 120° ca.; *potassium curcumin* $KC_{18}H_{14}O_8$, red powder, and *dipotassium curcumin* $K_2C_{18}H_{12}O_8$, red needles. By fusion with alkali curcumin gives *protocatechuic acid*, when oxidised with permanganate *vanillin*, and the diethyl ether by similar treatment yields *vanillic acid ethyl ether*. Jackson and Menke represented curcumin by the following formula:—



Heller (Ber. 1914, 47, 2998) has obtained *dihydrocurcumin*, now shown to possess the formula $C_{21}H_{20}O_8$, by catalytic reduction, as colourless needles, m.p. 95°–96°.

Ciamician and Silber (Ber. 30, 192), as the result of methoxy determinations, assigned the formula $C_{21}H_{20}O_8$ or $C_{19}H_{14}O_8(OCH_3)_2$ to curcumin, and prepared *diacetylcurcumin*



needles, m.p. 170°–171°; and *curcumin dimethyl ether* $C_{19}H_{16}O_8(OCH_3)_2$, yellow needles, m.p. 135°. Digested with hydroxylamine hydrochloride in alcoholic solution curcumin gave the compound $C_{21}H_{19}NO_8$ (i.e. $C_{21}H_{20}O_8NOH-H_2O$), needles, m.p. 178°, whereas phenylhydrazine gave a substance crystallising in colourless needles.

Perkin (Chem. Soc. Trans. 1903, 83, 140; 1905, 85, 63), by means of alcoholic potassium acetate, obtained from curcumin the monopotassium salt $C_{21}H_{19}O_8K$, fine orange-red needles. A *benzoylcurcumin*, pale yellow needles, m.p. 176°–178°, was also prepared, and gave by the cryoscopic method numbers harmonising with Ciamician and Silber's formula.

Molecular weight determinations, according to Jackson and Clarke (Ber. 1905, 38, 2712), indicated the correctness of the formula



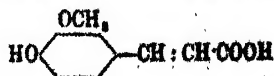
and again (*ibid.* 1906, 39, 2269) these authors pointed out that unless special care is employed, Zeisel's method gives erroneous figures with curcumin. When heated with hydriodic acid at 120° a correct result is given, but above this temperature curcumin gives a colourless oil rich in iodine (75.75 p.c.) which reacts with the alcoholic silver nitrate solution.

Von Kostanecki and Lampe (*ibid.* 1910, 43, 2163) consider that Ciamician and Silber's formula $C_{21}H_{20}O_8$ correctly represents curcumin, and describe *dicarbomethoxycurcumin*



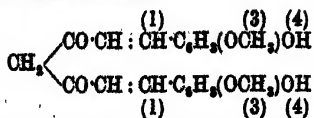
yellow prisms, m.p. 150°, and *dicarbomethoxycurcumin*, yellow leaflets, m.p. 140°–150°.

When curcumin is boiled with potassium hydroxide solution, *vanillic acid* and *ferulic acid*

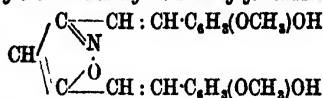


are produced. As a result these authors con-

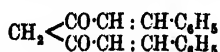
sider that the constitution of this colouring matter is as follows:—



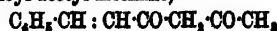
Further support for this formula is given by the fact that curcumin, like β -diketones, gives when treated with hydroxylamine an isoxazole derivative, and the compound prepared by Ciamician and Silber is probably 4,4'-di-hydroxy-3,3'-dimethoxy-1:1'-distyrylisoxazole—



Ryan and Dunlea (Proc. Roy. Irish Acad. 1913, 32, 9) attempted to obtain dicinnamoyl-methane—

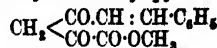


by condensing cinnamic ester with benzylidene-acetone in the presence of sodium without success, though with saturated ketones such a reaction proceeds normally. Thus cinnamic ester and acetone give cinnamoyl-acetone (cinnamoyl-acetyl-methane)—



a substance crystallising in yellow needles, m.p. 83°–84°, and capable of dyeing mordanted wool.

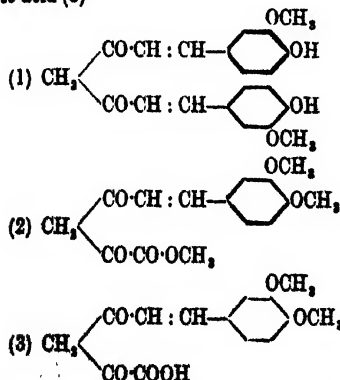
Ryan and Algar (*ibid.* 1913, 32, 9) again obtained methyl cinnamoyl-pyruvate—



from cinnamyl methyl ketone and methyl oxalate which crystallises in yellow prisms, m.p. 70°, also capable of dyeing mordanted wool. Numerous compounds of this type have been described by Ryan and his co-workers, and in a paper by Ryan and Plunkett (*ibid.* 1910, 199) a list of the dyeing properties of some of the compounds on wool is given, of which the following is an abstract:—

—	Chromium	Aluminium	Tin	Iron
Cinnamoyl-acetyl-methane . . .	Dark yellow	Light yellow	—	Bright red
Cinnamoyl-benzoyl-methane . . .	Dark yellow	Light yellow	—	Reddish-brown
Methyl cinnamoyl-pyruvate . . .	Russet-brown	Orange-yellow	Light orange-yellow	Reddish-brown
Cinnamoyl-pyruvic acid . . .	Brown	Orange	Orange	Deep reddish-brown
<i>p</i> -methoxycinnamoyl-pyruvic acid .	Chocolate-brown	Bright orange	Bright orange	Reddish-brown
3-4-dimethoxycinnamoyl-pyruvic acid	Chocolate-red	Orange-red	Orange-brown	Dark chocolate-brown
Curcumin	Brown	Orange-yellow	Orange-red	Brown-black *

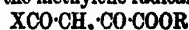
The shades given by these compounds are of a similar nature to those produced by curcumin itself, and the results of these authors thus support v. Kostanecki's formula for this compound. In comparing the three compounds, curcumin (1), methyl 3,4-dimethoxy-cinnamoyl-pyruvate (2), and 3,4-dimethoxycinnamoyl-pyruvic acid (3)



Ryan and Plunkett point out that in all these compounds the same double chromophore



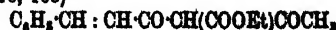
is present, together with the acidic methylene radical which is here the auxochrome. Though in curcumin the double chromophore occurs twice, its effect is to some extent balanced by the fact that the methylene radical in



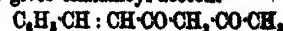
possesses much stronger auxochromic property than in the group $\text{XCO-CH}_2\text{-COX}$. In curcumin, again, the auxochromic effect of the hydroxyls in the vanillin nuclei can only be slight.

In 1913 Lampe and Milobedzka (Ber. 46, 2233) succeeded in synthesising dicinnamoyl-methane, the mother substance of curcumin, in the following manner:—

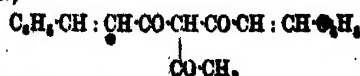
Cinnamoyl-aceto-acetic ester (Fischer, Ber. 1883, 16, 166)



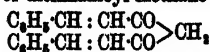
on hydrolysis and simultaneous loss of carbon dioxide gives cinnamoyl-acetone—



The monosodium derivative of this latter when condensed with cinnamoyl chloride gives dicinnamoyl-acetyl-methane (dicinnamoyl-acetone)—

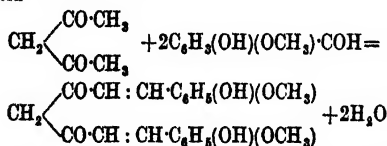


which on hydrolysis splits off acetic acid with formation of dicinnamoyl-methane—

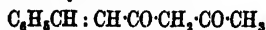


This compound, which crystallises in yellow prismatic needles, m.p. 144°, dissolves in sulphuric acid to form an orange-red solution possessing a yellow fluorescence. Both in its chemical and physical properties it closely resembles curcumin, and dyes cotton yellow shades which, however, are weaker than those given by curcumin itself.

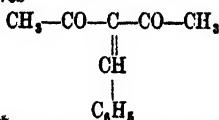
In 1914 (Ber. 47, 887) Heller described a stereoisomeride of curcumin which he named *iso-curcumin*, and this he obtained as a reddish-yellow crystalline solid, sintering at 140° and melting near 180°, by condensing vanillin with acetylacetone in the presence of hydrochloric acid—



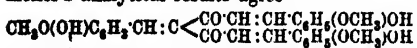
Ryan and Dunlea (Proc. Roy. Irish Acad. 1915, 32, B, 657), however, criticised this statement. They find that the first product of the action of benzaldehyde on acetyl-acetone in this way is not benzylidene-acetone



but a chlorinated compound which on heating *in vacuo* gives



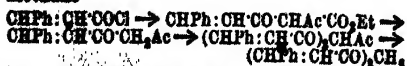
Iso-curcumin thus may be the trivanillin condensation product, with which indeed Heller's analytical results agree—



Heller (Ber. 1914, 47, 2998), however, states that this criticism of Ryan and Dunlea is unjustified in that *iso-curcumin* is a chlorine free colouring matter. *Iso-curcumin* shows a faint reaction with ferric chloride, and is to be regarded as a mixture of ketone with a little enol, whereas curcumin is decidedly enolic. *Ethyl-carbamato-iso-curcumin* melts at 142°. See also Ber. 1917, 50, 1244, and Ber. 1921, 54, 1118.

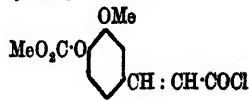
Ghosh (Chem. Soc. Trans. 1919, 292), by the simple conversion of curcumin into *iso-curcumin*, confirms Heller's view that the two substances are geometrical isomerides.

Curcumin has been synthesised by an application of the method employed for the synthesis of dicinnamoyl-methane (Lampe and Milobedzki, Ber. 1913, 46, 2235). In this cinnamoyl chloride was condensed with ethyl acetacetate and the product hydrolysed, when cinnamoyl-acetone resulted. Condensation of this product with a second molecule of cinnamoyl chloride and hydrolysis of the product gave dicinnamoyl methane



By employing carbomethoxyferuloyl chloride (J)

in the place of cinnamoyl chloride, the dicarbomethoxy-derivative of curcumin was obtained. It gave curcumin on hydrolysis (Lampe, Ber. 1918, 51, 1347)



(I)

It is well known that a mixture of boric and hydrochloric acids imparts to turmeric paper a red colour which is turned blue by alkalis. This reaction was investigated by Schlumberger (Bull. Soc. Chem. [ii.] 5, 194), who found that when an alcoholic extract of turmeric is heated in a sealed tube with boric acid, a red crystalline boric acid derivative is produced, soluble in alkaline solutions with a purple-violet colour. Boiling water decomposes this compound with elimination of boric acid, and formation of *pseudo-curcumin*, a yellow powder. If the alcoholic solution of the boric acid compound is digested with strong hydrochloric acid, a black substance separates, whereas boric acid remains in the liquid.

On extracting the black powder with a mixture of alcohol and acetic acid, the filtrate deposits green iridescent crystals of *rosocyanine*.

Rosocyanine is readily soluble in alcohol containing a trace of mineral acid and dissolves in ammonia solution with a blue colour. It is, according to Schlumberger, an unstable substance, and if boiled for a long time with alcohol, is converted into *pseudo-curcumin*.

Jackson and Clarke (l.c.) prepared *rosocyanine* by heating a solution of curcumin in dilute alcohol with boric and sulphuric acids, and describe it as a purplish-red powder, closely resembling powdered rosaniline. These authors considered it to be isomeric with curcumin $\text{C}_{21}\text{H}_{20}\text{O}_4$, and described an *ammonium salt* $\text{C}_{21}\text{H}_{21}\text{O}_4\text{NH}_4$, and a *potassium salt* $\text{C}_{21}\text{H}_{21}\text{O}_4\text{K}$, both of which possess an intense blue colour.

The tinctorial properties of curcumin are of special interest, for not only is it a strong colouring matter towards mordants, but with cotton, wool, and silk it behaves also as a substantive dyestuff. In the latter case it is only necessary to add the material to a boiling decoction of the colouring matter. Though considerably employed up to within recent years by the wool and silk dyer in the formation of olives, browns, and other compound colours, turmeric is now but rarely used for dyeing purposes in England. In India, however, it appears to be still in vogue.

Cotton is usually dyed in a decoction of turmeric rendered slightly acid by the addition of a little acetic acid, or alum may be employed. The colour does not resist either the action of light or of alkalis, and readily acquires a brownish-red tint. Wool may be dyed without any addition, keeping the temperature about 60°. By previously mordanting with alum a brighter effect is produced, whereas tin mordant gives a more orange colour. Potassium dichromate and ferrous sulphate employed in a similar manner yield respectively olive and brown-coloured shades.

Silk is preferably dyed in an acid bath, and is sometimes previously mordanted.

Turmeric oil is the thick orange-coloured aromatic oil present to the extent of 3.23 p.c. in turmeric from which it can be extracted by means of carbon disulphide. Bolley examined the portion distilling over at 230°-250°, and considered it to be identical with carvol, whereas Gajewsky (*l.c.*) found the portion distilling over at 220°-228° contains less carbon and more hydrogen than that which passes over at a higher temperature. On oxidising the latter portion with chromic acid, an acid oil is obtained which contains valeric, caproic, and terephthalic acids. Jackson and Menke (*l.c.*) analysed that portion which distills over at 285°-290°, and gave it the formula $C_{11}H_{14}O_4$, and the name *turmerol*, and obtained *turmeryl chloride* $C_{11}H_{17}Cl$, *sodium turmerol* $C_{11}H_{17}ONa$, and *turmerol iso-butyl ether* $C_{11}H_{17}O \cdot C_4H_9$. With permanganate turmerol gave *terephthalic acid*, *turmeric acid* $C_{11}H_{14}O_4$, and *apoturmeric acid* $C_{10}H_{12}O_4$ or $C_{10}H_{10}O_4$. According to Rüpe (Ber. 1907, 40, 4909), when turmeric oil is boiled with dilute sodium hydroxide solution a substance, b.p. 156°/12 mm., apparently not identical with Jackson and Menke's turmerol, is produced. Stronger alkali yields an optically active ketone $C_{11}H_{16}O$, *curcumone*, b.p. 119°-120°/8 mm., which gives a semicarbazone, m.p. 119.5°-120.5°, an oxime, b.p. 159°/11 mm., and condensation products with aromatic aldehydes. With permanganate the ketone gives *p-methylacetophenone* and *terephthalic acid*, and with alkaline hypobromite the acids $C_{12}H_{16}O_8$, m.p. 150°, and $C_{12}H_{16}O_8$, m.p. 33°-34°. By the further action of permanganate the latter yields a dicarboxylic acid $C_{12}H_{14}O_8$, m.p. 228°. Rüpe, Lüksch, and Steinbach (Ber. 1909, 42, 1515) were unable to isolate from turmeric oil the turmerol of Jackson and Menke, having sp.gr. 0.9388 at 20° and $[\alpha]_D^{20} = -27.46$. By digestion with alcohol and 30 p.c. potassium hydroxide solution the ketone $C_{11}H_{16}O$, *curcumone*, was obtained, which has b.p. 121°/10 mm., sp.gr. 0.9566 at 20°, $n_D^{20} 1.50526$, $[\alpha]_D^{20} 80.55$, and yields the *p-bromophenylhydrazone*, m.p. 71°. It condenses with benzaldehyde to form the compound $C_{12}H_{16}O : CH \cdot C_6H_5$, m.p. 106°, and with piperonal and anisic aldehydes similar compounds melting respectively at 86° and 77°-78° are produced.

The acid $C_{12}H_{16}O_8$ (*l.c.*), m.p. 33°-34°, is called *curcumatic acid*, and appears to be identical with Jackson and Menke's turmeric acid (Rüpe and Steinbach, Ber. 1910, 43, 3465). By oxidation with permanganate it gives terephthalic acid, *p*-tolyl methyl ketone, and the acid $C_{12}H_{16}O_8$, m.p. 226°-228° (*l.c.*), and this possibly consists of *apoturmeric acid* (Jackson and Menke). Although it was considered that curcumatic acid might be γ -*p*-tolylvaleric acid, the synthesis of this latter compound showed that the substances are similar but not identical (*ibid.* 1911, 44, 584). Again, curcumatic acid is not *p*-tolyl- α -methylbutyric acid (Rüpe and Bürgin, *ibid.* 1218). Rüpe and Steinbach (*l.c.*) consider that curcumone is to be regarded as a benzene derivative containing two parasubstituents, one being methyl, and the second, one or other of the groups



whereas in curcumatic acid the group COMe is replaced by COOH. See also Schimmel & Co. (Ber. April, 1911).

A. G. P.

TURMERIC ACID v. TURMERIC.

TURMERINE v. PRIMULINE AND ITS DERIVATIVES.

TURMERYL CHLORIDE v. TURMERIC.

TURNBULL'S BLUE. A variety of Prussian blue, probably a ferricyanide, v. CYANIDES.

TURNER'S YELLOW. *Patent yellow.* Lead oxychloride $3PbO \cdot PbCl_2$.

TURNIP. A biennial, cruciferous plant, producing in the first year a large root stock containing a store of carbonaceous and nitrogenous matter intended for the formation of flower-stem and seeds in the second year. This 'root' is the chief valuable product for which the crop is grown. Many varieties, differing in the shape, size, and colour of the root, are known, but they may all be classed as belonging to two species—the 'white turnip,' or simply 'turnip,' *Brassica rapa* (Linn.), or *B. rapa rapifera* (Metzger), and the 'Swedish turnip,' or 'Swede,' known often as 'ruta-baga' in America, *Brassica campestris rutabaga* (Linn.), or *B. napus esculenta* (DC.). There are many varieties of each, but as a rule 'turnips' have rougher leaves, of greener colour, and the root has white, or, in some cases, yellow flesh; whilst 'swedes' possess smoother leaves of a bluish-green colour, and the roots have yellow flesh. The leaves of the turnip spring directly from the root, whilst those of the swede arise from a distinctly marked 'neck.'

Both types grow best in cool, damp climates; in hot, dry countries the roots tend to become very woody and fibrous. Swedish turnips resist frost better, and can be grown in stiffer soils than the white varieties; they also keep better after gathering.

According to König, the following figures represent the average composition of the two types—

	Pro-	Other	
	Water	N-free	
	teln	Fat	Sugar ext. Fibre Ash
White turnips	90.67	1.12	0.24 2.55 3.55 1.11 0.76
Swedes	88.88	1.39	0.18 3.02 4.35 1.44 0.74

Great variations in composition, however, have been observed, the most important factors, in order of importance, being apparently, season, variety, size of root, district, and soil. Even with the same variety, grown under the same conditions, and with roots of approximately the same size, considerable variations in the composition of individual roots are found, especially in the amount of sugar. Thus, Collins (*J. Soc. Chem. Ind.* 1920, 20, 536) found in 25 individual roots of XL All swedes, the proportion of sugar varied from 4.5 to 7.8 p.c., with an average of 6.27 p.c.

The variation with season is considerable; Collins, as the average of 12 varieties of swedes grown in 1900, found a sugar content of 6.26 p.c., while the same varieties, in 1901, gave an average of only 4.05 p.c. of sugar. Analogous to the effect of season is that of local climate; even in Britain this effect is seen. In 1904 several varieties of swedes were grown simultaneously in Cambridgeshire, Norfolk (2 centres), and Ross-shire (4 centres), and the resulting

crops were examined for dry matter and sugar content.

The following figures show the sugar contents of 5 varieties, as grown at the various centres—

Variety	Cam-bridge				Norfolk				Ross-shire			
	1	2	3	4	1	2	3	4	1	2	3	4
Fell's Bronzotop.	6.5	6.1	8.0	7.0	7.2	7.3	7.1	8.0	7.4			
New Arctic	6.1	6.0	8.1	7.0	6.9	7.2	7.1	7.9	7.3			
Magnum Bonum	6.3	5.7	7.6	6.6	6.8	7.2	6.6	8.1	7.2			
XL All	6.0	6.0	7.4	6.7	6.8	6.8	6.7	7.5	7.0			
Carter's Elephant	6.3	5.6	7.0	6.3	6.7	6.9	6.8	7.4	7.0			
Average	6.2	5.9	7.6	6.7	6.9	7.1	6.9	7.8	7.2			

These results clearly show that the roots grown in the moist, cool climate of Ross-shire were, on the average, richest in sugar, while those grown in the hot, dry climate of Cambridgeshire were the poorest (Guide to Expts. 1906, Dept. of Agric. Univ. of Cambridge).

So, too, Hendrick (Bull. 1, Coll. Agric. Univ. of Aberdeen, 1904) found, as the average of analyses of 21 varieties of swedes, grown in Aberdeenshire, 11.7 p.c. of dry matter, and 5.15 p.c. of sugar, while 9 varieties of turnips yielded an average of 9.48 p.c. of dry matter, and 4.55 p.c. of sugar; and Wood (Guide to Expts. Dept. of Agric. Univ. of Camb. 1906) found as the mean of the analyses of 5 varieties of swedes, grown in Cambridgeshire (1 centre) and Norfolk (2 centres), 10.8 p.c. of dry matter and 6.6 p.c. of sugar, and for 7 varieties of white turnips 7.81 p.c. of total dry matter, and 4.24 p.c. of sugar.

The effect of soil upon the composition of the roots, although perceptible, is not great. That of manuring is very great upon the yield, but is comparatively small upon the composition, except in so far as it affects the size of the roots.

The effect of size of root, in any variety, is considerable, small roots being invariably richer in solid matter, especially sugar, than large ones. This is well seen from the following analyses by Hendrick (J. Soc. Chem. Ind. 1897, 16, 213) of two samples of 'Achilles' turnips—

Average wt.	Dry					
of 1 root	Water	matter	Sugar	Total N	Alb. N	Ash
5lb. 1oz.	92.8	7.2	3.93	0.192	0.108	0.56
2lb. 14oz.	91.3	8.7	4.62	0.148	0.076	0.64

In view of these many circumstances affecting the composition of the roots, it is obviously of little value to attempt to give any representative composition of turnips.

It may, however, be of interest to quote the figures given by Kellner and by Warrington as representing the average composition of turnips and swedes.

Kellner gives—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Swedes	87.8	1.5	0.2	8.2	1.3	0.9
Turnips	91.5	0.9	0.1	6.0	0.8	0.7

Warrington's figures are—

	Water	Amides, Proteids etc.	N-free Fat	Crude extract	fibre	Ash
Swedes	89.3	0.7	0.7	0.2	7.2	1.1
Turnips	91.5	0.5	0.5	0.2	5.7	0.9

The protein, i.e. total N \times 6.25, in the above analyses, contains a considerable and variable quantity of non-proteid substance. König states that from 35 to 55 p.c. of the total nitrogen is present, partly as amides or amino acids,

partly as nitrates. Warrington estimates the non-albuminoid nitrogen in turnips at 49 p.c. of the total nitrogen, but gives as the average digestible albuminoids 0.2 p.c. in swedes, and 0.1 p.c. in turnips. Collins (l.c.) found, in 'Monarch' swedes, the real albuminoids varied from 0.47 to 0.63 p.c., while the amides, &c., ranged from 0.34 to 0.61 p.c. Hendrick (l.c.) found the proportion of non-albuminoid nitrogen to total nitrogen varied from 27 to 42 p.c. in yellow turnips, and from 23 to 59 p.c. in 'Best of All' swedes. In the days when the 'nitrogenous substances' or 'albuminoids' in food-stuffs were estimated by multiplying the total nitrogen by 6.25, turnips, in common with other roots, gave results on analysis which indicated that they possessed greater feeding value than actual experience showed them to have. If, however, distinction is made between true proteids and amino compounds, amides, and nitrates, the nutritive value of turnips, as assessed by analysis, seems, in most cases, to be much less than their actual efficiency as foods (v. Ingle, Trans. High. & Agric. Soc. Scotland, 1910, 22, 178; also Hendrick, *ibid.* 150). It would seem, in fact, that either the true albuminoids in turnips are much more digestible than has hitherto been admitted, or, more probably, that the amino compounds may, under certain conditions, behave like albuminoids, in building up animal tissue.

For a study of the hydrolysis of the soluble protein of swedes, v. Williams (J. Agric. Sci. 1917, 8, 182).

The sugars present in turnips are dextrose, lævulose, and sucrose, the invert sugars largely predominating. The other N-free extractives include pectins, pentosans, and cellulose.

The ash of turnips varies greatly in composition and amount. According to figures compiled by König, the whole ash varies from 4.9 to 14.0 p.c. of the dry matter, while the potash in the ash may range from 26 to 62 p.c., the lime from 5.5 to 15.9 p.c., and the phosphorus pentoxide from 5.5 to 18.9 p.c. The mean of 32 analyses of the ash gave—

K ₂ O	Na ₂ O	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	Cl
45.4	9.8	10.6	3.7	0.8	12.7	11.2	1.9	5.0

The upper half of a root is richer in solid matter than the lower, and due allowance must be made for this fact in sampling turnips for analysis.

Turnip leaves are sometimes used for feeding purposes; according to Kellner they contain, on the average—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
88.4	2.2	0.5	5.3	1.5	2.1

Turnips, like other plants of the genus *Brassica*, contain this compounds, and when they decay or even suffer slight decomposition by boiling, they evolve unpleasant-smelling sulphur compounds, among which mercaptans are probably included.

Turnips require liberal supplies of phosphates, and phosphatic manures, generally superphosphates, are almost invariably used for this crop. For a study of the destination of phosphates and nitrogen when applied as a manure to turnips, v. Somerville and Smith (J. Soc. Chem. Ind. 1897, 16, 19).

TURPENTINE v. OILS, ESSENTIAL: also TERPENES.

The production of turpentine and rosin in France during the last 10 years has been as follows:—

Year.	Turpentine metric tons.	Rosin metric tons.
1913	25,000	85,000
1914	19,000	64,000
1915	15,000	51,000
1916	17,000	60,000
1917	17,000	60,000
1918	20,000	60,000
1919	25,000	85,000
1920	35,000	120,000
1921	31,000	105,000
1922	32,000	118,000

For the temperature coefficient of refractive index of American turpentine, see G. Thompson (Chem. News, Jan. 12, 1923, 126, 20-21).

About 75 p.c. of the world's supply of turpentine is produced in the United States, chiefly from the southern longleaf yellow pine (*Pinus palustris*), but other species, such as the Cuban or slash pine (*P. caribæa* or *heterophylla*), the rosemary pine (a variety of the Loblolly pine, *P. taeda*), and the western yellow pine (*P. ponderosa*) are also tapped; most of the remaining 25 p.c. is obtained in the south-western coast regions of France from the maritime or cluster pine (*P. pinaster* or *maritima*). The following States contribute to the American supply: Florida, 37 p.c.; Georgia, 19 p.c.; Louisiana, 15 p.c.; Alabama, 12 p.c.; Mississippi, 9 p.c.; Texas, 7 p.c.; North and South Carolina, which formerly produced the bulk of the world's supply, now furnish less than 1 p.c.

The oleo-resin is obtained by scarifying or 'chipping' the living trees. A V-shaped cut is made about once a week immediately above the last cut, thereby forming a 'face' down which the gum exuding from the cut flows, collects in galvanised iron or baked clay cups holding 1 to 2 quarts. The tapping season lasts from early spring to late autumn, the oleo-resin being removed from the cups about once a month and taken to the stills in barrels.

The distillation plant is simple and has not been improved materially during the last 50 to 60 years. It consists of a copper still of 500 to 1000 gallons capacity, with a still-head (generally removable) connected to a large copper condensing-coil cooled in water. From 7 to 14 barrels of oleo-resin go to make a charge, depending on the size of the still and the nature of the oleo-resin.

The oleo-resin contains some water and the distillate at the beginning consists of about 45 p.c. of turpentine and 55 p.c. of water. When the water decreases to about 30 p.c., a small stream of water is admitted to the still. The yield of turpentine varies from 16 to 22 p.c. It is mostly shipped in wooden casks holding 50 to 53 U.S. gallons (231 cub. in.), treated internally with glue to prevent absorption of turpentine by the wood. Tank cars of 5000 to 10,000 gallons capacity are used in the Western States (F. P. Veitch and V. E. Grotliach, U.S. Dept. Agric., Bureau of Chem. Bulletin No. 898, 1920, in abstract, J. Soc. Chem. Ind. 1921, 165 R.).

Ordinary American turpentine is able to

attack iron in the presence of air, thus acquiring a deep red colour. This appears to be due to organic acids of high molecular weight (Levy and Defries, J. Soc. Chem. Ind. 1923, 42, 472 T.; 1924, 43, B. 103).

Wood turpentine is obtained from stumps, sawmills slab, &c., by destructive distillation or by steam distillation; the crude product is redistilled over soda-ash, and when thus refined, can scarcely be distinguished from the volatile portion of the oleo-resin exuded from the living tree (spirits of turpentine.) Refined wood-turpentine has the following characteristics: sp.gr. at 15° 0.863; n_D^{20} 1.468; initial b.p. 153°; distillation range 91 p.c. below 170°; acidity, trace. About 70 p.c. distils below 160°, and this portion has been identified as α -pinene (Lambert, J. Ind. Eng. Chem. 1922, 14, 491; Analyst, 1922, 406).

The following are suggested by the U.S. Dept. of Agric. as specifications for three standard grades of turpentine:—

Standard or No. 1 turpentine should have a sp.gr. at 20° of from 0.862 to 0.870; a refractive index at 20° of from 1.468 to 1.476; 95 p.c. should distil below 170°, and a layer of not less than 200 mm. should be required to equal in colour the Lovibond yellow glass No. 1. On polymerisation with 38-normal sulphuric acid the residue should not exceed 1 p.c., should be reddish in colour and viscous, and its refractive index at 20° should be from 1.500 to 1.520. An unadulterated turpentine which does not agree with these requirements may properly be regarded as not of standard or No. 1 quality.

Second quality or No. 2 turpentine should have a sp.gr. at 20° of from 0.862 to 0.875; a refractive index at 20° of from 1.468 to 1.480; 90 p.c. should distil below 170°, and a depth of not less than 100 mm. should be required to equal the Lovibond yellow glass No. 1. The polymerisation residue must not exceed 1 p.c., and must have a refractive index of not less than 1.50.

Third quality or No. 3 turpentine should have a sp.gr. at 20° of from 0.865 to 0.880; a refractive index at 20° of from 1.468 to 1.485; 60 p.c. should distil below 170°, and a depth of not less than 50 mm. should be required to equal the Lovibond yellow glass No. 1. The polymerisation residue must not exceed 1 p.c., and must have a refractive index of not less than 1.500.

The following are the tests for adulteration:—

'Straight' wood turpentines are readily distinguished from gum turpentines by their odour, or when they have been very carefully refined by the odour of the first fraction, or of the residue from fractional distillation. One or both of these portions have the peculiar 'sawmill smell,' and the residue has a camphoric and somewhat nauseating odour characteristic of wood turpentine, which is quite different from the mild, sweet fragrance of gum turpentine.

Destructively distilled wood turpentine and also rosin spirits are more readily distinguished from gum spirits by their odour than is wood turpentine prepared by steam distillation, and they also give distinguishing colour reactions when mixed with sulphurous acid or with hydrochloric acid. When steam-distilled wood turpentine has been carefully refined so that 95 to

95 p.c. of it distils at from 155° to 170°, both of these colour tests are practically useless.

At the present time a number of highly refined grades of pine wood oil ("kienöl"), obtained as a by-product from the manufacture of sulphate wood pulp, are on the market and employed for the adulteration of true turpentine oil. An extremely simple test for this adulteration is obtained with the ferric ferricyanide reagent. Two solutions are made up (a) with 0.5 gm. of potassium ferricyanide in 250 c.c. of water and (b) 0.1 gm. of ferric chloride in 250 c.c. Four c.c. of each of the two solutions are mixed together and 3-5 drops of the sample to be tested are added. With impure turpentine oils the formation of Prussian blue is observed within a few minutes. Pure turpentine oil within 3 minutes produces only a faint green coloration, or at the most slightly blue colour at the line between the oil and aqueous layer (H. Wolff, Zeitsch. angew. Chem. 1923, 36, 233; J. Soc. Chem. Ind. 1923, 42, 730 A).

Turpentine adulterated with more than 10 to 20 p.c. of coal-tar oils, or of gasoline or kerosene which have not been deodorised, may usually be readily detected by the characteristic odour of the mixture. The odour of rosin spirits, while quite distinctive, is difficult to detect in mixtures with turpentine. The presence of petroleum oils is also indicated by bubbles or 'beads' persisting for a few moments on the surface of the turpentine shaken in a partly filled bottle.

The presence of more than 10 p.c. of kerosene or similar mineral oils is readily detected by the spot which a few drops of the sample placed on white paper leaves on drying. Gasoline and other light mineral oils do not leave this spot.

It is possible so to adulterate turpentine that neither the specific gravity, refractive index, or flash-point is materially altered. Such careful adulteration is rare, but as adulterants cannot invariably be detected by making these determinations, and further, as mineral oil is the most probable adulterant, it is more rational at once to polymerise the suspected sample, note the volume, colour and consistency of the unpolymerised residue, and determine its refractive index.

If rosin spirits is present in notable quantities, it may be detected by the amount of residue on polymerisation in conjunction with lowered initial boiling-point and the deep coloration produced by mixing portions of the original turpentine of the first fraction with sulphurous acid and with hydrochloric acid.

If the initial distilling temperature of the turpentine is less than 154° and the original sample gives a reddish colour with sulphurous acid and a greenish-red with hydrochloric acid, and the residue from polymerisation is less than 5 p.c., it is probable that the sample is adulterated with rosin spirits. An odour of rosin spirits in the sample, or in any fraction, would be confirmatory, and all tests should be repeated on the first fraction obtained with a fractionating column. At best the detection of small amounts of rosin spirits is very difficult, and the procedure outlined may often fail to detect its presence.

The presence of marked quantities of coal-tar oils, benzol, toluol, and xylol is detected by the odour, the lower initial distilling temperature,

i.e. between 80° and 155°, and by further examination of the first fractions which distil below 155°. The rise of temperature on shaking during polymerisation is also indicative of the nature of the sample. Coal-tar and petroleum oils do not raise the temperature more than 35° or 40° when mixed with sulphuric acid. When the temperature of turpentine mixed with 38-normal sulphuric acid does not rise above 50° or 60°, mineral oil, coal-tar oil, or some other oil than turpentine is present in large quantities. The older the sample of turpentine, the greater, or at least the more rapid, the rise of the temperature of the mixture.

Benzene in turpentine may also be detected by the precipitate of $\text{Ni}(\text{C}_2\text{NH}_2\text{C}_2\text{H}_5)_2$, which it forms with nickel ammonium cyanide (Pritakev and Jungkuz, Chem. Zeit. 1924, 48, 555; Analyst, 1924, 49, 450).

Non-volatile oils are easily detected by a distillation test (J. Soc. Chem. Ind. 1911, 30, 559).

For the constituents of Indian turpentine from *Pinus longifolia*, Roxb., see J. L. Simonsen and M. G. Rau (Chem. Soc. Trans. 1923, 123, 549-560); J. L. Simonsen (Chem. Soc. Trans. 1923, 123, 2642-2666).

Oil of turpentine from *Pinus laricio* of Spain contains over 90 p.c. of *l*-pinene (Dupont and Barraud, Bull. Soc. Chem. 1924, 35, 784; J. Soc. Chem. Ind., 1924, 43, B. 720).

Venice Turpentine.—The production of Venice turpentine (trementina) in Italy is confined to the Province of Venetia Tridentina, formerly Austrian Tyrol territory, in the northern part of Italy. In this region that species of pine known as larch is found in abundance on the slopes of the Apennines, and the distillation of turpentine from the wood of this tree forms an important industry. There seems to be no monopoly of the industry as, according to the Journal of the Royal Society of Arts, quoting a United States Consular report, the production of Venice turpentine (known to the producers as olio greggio di larice or Tyrol larch turpentine) is divided among a great number of individuals and small concerns. In some cases the municipal government owns and operates distillation plants for the production of turpentine—an unusual occurrence in Italy. Venice or Tyrol larch turpentine is sold by weight (Pharm. J. Sept. 8th, 1923).

TURPETH or TURBITH MINERAL. An old name for basic mercuric sulphate $\text{HgSO}_4 \cdot 2\text{HgO}$, sometimes called Queen's yellow, v. MERCURY.

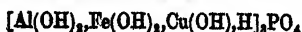
TURPETH or TURBITH ROOT. The root of the convulvulaceous plant *Ipomoea Turpethum* (R.Br.) [*Operculina Turpethum* (Peters)], found in India and Australia. It contains a volatile oil and a drastic resin, turpethin $\text{C}_{22}\text{H}_{36}\text{O}_{10}$, isomeric with jalapin and scammonin. When treated with dilute mineral acids this substance is hydrolysed into glucose and turpetholic acid $\text{C}_{14}\text{H}_{22}\text{O}_6$ (v. Boutron-Charlard, J. Pharm. Chim. 8, 131; Spigragia, J. pr. Chem. [i.] 92, 97).

TURPETHIN v. GLUCOSIDES.

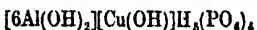
TURQUOISE or CALAITE (Tarkis, Ger.). A gem-stone which has often been regarded as a hydrated aluminium phosphate



accidentally coloured by copper and iron phosphates. It has been shown, however, by S. L. Penfield (Amer. J. Sci. 1900, 10, 346) that the latter enter into the constitution of the mineral, and he writes the formula as—



representing a derivative of orthophosphoric acid with the hydrogen atoms largely replaced by the univalent radicles $\text{Al}(\text{OH})_2$, &c. In some analyses approximately two-thirds of the hydrogen atoms are so replaced, and the formula becomes $\text{R}_2'\text{HPO}_4$. The amount of copper ranges from 2.0 to 8.5 p.c. CuO , and the iron from 0.1 to 4.0 p.c. Fe_2O_3 . The mineral is soluble in hydrochloric acid without discoloration; when heated it loses water and blackens. It is opaque (or translucent in thin chips) with a sky-blue to green colour, and on the polished surface shows a soft, waxy lustre; sp.gr. 2.6–2.8; H. 6. Turquoise occurs as cryptocrystalline masses, sometimes with nodular or stalactitic surfaces, in crevices in rocks, more especially in those of volcanic origin. The best quality of material has for centuries been mined near Nishapur in Persia, and being exported to the west through Turkey it came to be known as turquoise. Deposits in the Sinai Peninsula were worked by the ancient Egyptians. Ancient mines, worked in prehistoric times, are also known in Mexico and in the state of New Mexico. Considerable quantities (17 tons in 1909, and 8½ tons in 1910) are now obtained from Nevada, New Mexico, Arizona, California, and Colorado (D. B. Sterrett, Min. Res. U.S., Annual Reports for 1910 and earlier). Minute crystals of turquoise have been described from Campbell Co., Virginia; these are triclinic and isomorphous with chalcocislerite. Analysis of them gave the formula $\text{CuO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$; written in the form of Penfield's formula this becomes



(W. T. Schaller, Amer. J. Sci. 1912, 33, 35).

Turquoise has been imitated by subjecting to pressure a mixture of aluminium and copper phosphates. Very clever imitations are also made of glass; these may be detected by the bright, glassy, conchoidal fracture when chipped at the edges—the fracture of turquoise being dull and finely granular.

Bone-turquoise or *odontolite* is fossil bone or ivory coloured by the iron phosphate vivianite, or perhaps sometimes artificially stained by a copper solution. It can be recognised under the microscope by its organic structure. It effervesces with acid, and gives a smell of burning when heated.

L. J. S.

TUSSOL. Antipyrine mandelate.

TUTENAG or **TUTENAGUE.** Chinese silver. *Packfong.* An alloy resembling German silver.

TUTOCALINE. A local anæsthetic of the novocaine type (*cf.* Vol. vi. p. 637). Its action is more powerful than that of novocaine (Schulemann, Lancet, 1924, 206, 965; Pharm. J. 1924, 113, 46; Wagner, Arch. Exp. Path. Pharm. 1925, 109, 64; Chem. Soc. Abstr. 1925, 128, i. 1503).

TYLCAISIN (*kalmopyrin*). Trade name for calcium acetyl salicylate.

TYLALITHIN (*apryon*). Trade name for lithium acetyl salicylate.

TYLMARIN. Trade name for acetyl-o-

coumaric acid, used in the treatment of inoperable cancer.

TYLNATRIN. Trade name for sodium acetyl salicylate.

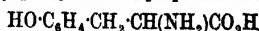
TYNDALLMETER. See NEPHELOMETRY.

TYPE METAL *v.* TIN.

TYRAMINE. Trade name for *p*-hydroxyphenylethylamine hydrochloride, *v.* ERGOT.

TYRIAN PURPLE *v.* PURPLE OF THE ANCIENTS. In Costa Rica a dyestuff apparently of the 'Tyrian purple' class is obtained from shell-fish, and is used for dyeing silk thread a fast purple colour.

TYROSINE. *p*-hydroxyphenylalanine, *p*-hydroxy-β-phenyl-α-aminopropionic acid



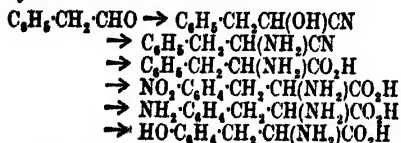
was so named by Leibig, who first obtained it by fusing freshly prepared cheese (*rupós*) with caustic potash (Annalen, 1846, 57, 127). It occurs widely spread both in the animal and vegetable kingdoms, forming one of the most common products of proteid hydrolysis, and occurring in the free state in the seedlings and young shoots of the vetch (*Vicia sativa*) (Gorup-Besanez, Ber. 1877, 10, 781); the gourd (*Cucurbita pepo*) (Schulze and Barbieri, *ibid.* 1878, 11, 710, 1233); the lupins (*Lupinus luteus*, *L. albus*) (Schulze, *ibid.* 1878, 12, 1924; Wassilieff, Landw. Versuchs Stat. 1901, 55, 45); in the tubers of potatoes (*Solanum tuberosum*) (Schulze, Ber. 1879, 12, 1924), the swede (*Brassica rapa*), the dahlia (*Dahlia variabilis*) (Borodin, Botan. Zeit. 1882, 590; Leitgeb, Chem. Zentr. 1888, 1397; Bertrand, Compt. rend. 1896, 122, 1215); in the tubercles of *Stachys tubifera* (Planta and Schulze, Ber. 1890, 23, 1698); in the juice of sugar beet (*Beta vulgaris*) (*v.* Lippmann, *ibid.* 1884, 17, 2835), in celery (*Apium graveolens*) (Bamberger and Landsiedl, Monatsh. 1904, 25, 1030); in the unripe seeds of the French bean (*Phaseolus vulgaris*) (Pfenninger, Ber. Deut. bot. Ges. 1909, 27, 227), the pea (*Pisum sativum*) (Schulze and Winterstein, Zeitsch. physiol. Chem. 1910, 65, 431); in the green pods of the broad bean (Bourquelot and Hérissé, J. Pharm. Chim. 1898 [vi.] 8, 385); in the juice of elderberries (*Sambucus nigra*) (Sack and Tollens, Ber. 1904, 37, 4115); in fungi (Winterstein, Zeitsch. physiol. Chem. 1899, 26, 438). In the animal kingdom, tyrosine is found in caterpillars, crabs, spiders, and beetles (*v.* Lippmann, *l.c.*) and in cochineal (Warren de la Rue, Annalen, 1848, 64, 1); in the larva of *Lucilia Caesar* (Gessard, Compt. rend. 1904, 139, 644); it occurs in Emmmenthaler and in Roquefort cheeses (Benecke and Schulze, Landw. Jahrbücher, 1887, 16, 317; Winterstein and Thöny, Zeitsch. physiol. Chem. 1902, 36, 28; Dox, J. Amer. Chem. Soc. 1911, 33, 423). Under normal conditions, tyrosine is not found in the liver or blood of men and animals, but occurs under certain pathological conditions (Frerichs and Staedeler, J. 1856, 703; Hoppe-Seyler, Zeitsch. physiol. Chem. 1881, 5, 348; Neuberg and Richter, Deut. med. Wochensh. 30, 499; Huber, Archiv. Heilkunde, 18, 485; Wyss, Schweiz. Zeitsch. Heilkunde, 1864). The presence of tyrosine in muscle and in all other organs which do not normally contain products of digestion suggests putrefaction (Pistre, Compt. rend. 1914, 158, 1934); *v.* Jugs (J. Pharm. Chim. 1913, [vii.] 8, 559) for its presence

in urine. It can be detected by the Frerichs-Städeler method in normal or pathological urines, in quantities of 0.2 gram in 400 c.c. of urine and by Lippich's method in quantities of 0.01-0.02 gram in 100 c.c. Tyrosine is sometimes present in cases of acute yellow atrophy (Schumm and Papendieck, *Zeitsch. physiol. Chem.* 1922, 121, 1).

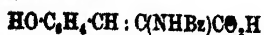
Preparation.—Tyrosine is most conveniently prepared from silk by hydrolysing with fuming hydrochloric acid, and evaporating the product under reduced pressure to dryness; the residue is dissolved in water and a stream of ammonia passed through the solution; it is then again evaporated to dryness, and the residue treated with cold water, when the tyrosine is left undissolved; or the whole residue may be boiled with water and animal charcoal, and from the filtrate pure tyrosine crystallises out quantitatively: one kilo of silk yielding 50-65 grms. of tyrosine (Abderhalden, *Zeitsch. physiol. Chem.* 1912, 77, 75; Abderhalden and Teruuchi, *ibid.* 1906, 48, 528). Marshall (J. Biol. Chem. 1913, 15, 85) recommends obtaining it from the pancreatic digestion of caseinogen; the liquid on cooling deposits an abundant crystalline yield of tyrosine.

For the preparation of tyrosine from peptones, see Beijerinck (*Chem. Weekblad*, 1919, 16, 1494).

Synthesis.—Städeler (*Annalen*, 1860, 116, 57) was the first to show that tyrosine was an aromatic compound, since it yielded chloranil (tetrachloroquinone) on treatment with chlorine; but its constitution as *p*-hydroxy- β -phenyl- α -aminopropionic acid was not established until 1882 when Erlenmeyer and Lipp (*Ber.* 1882, 15, 1544; *Annalen*, 1883, 219, 161) prepared racemic tyrosine from phenylacetaldehyde by the following series of reactions: phenylacetaldehyde on treatment with hydrogen cyanide gave phenyllactonitrile; this was converted by ammonia into the nitrile of phenylalanine which, on hydrolysis, gave phenylalanine; *p*-nitrophenylalanine on reduction gave the corresponding amino compound from which *p*-hydroxyphenylalanine (*r*-tyrosine) was produced by the action of nitrous acid.



A more convenient method of synthesis is that due to Erlenmeyer jun., and Halsey (*Annalen*, 1899, 307, 138), in which *p*-hydroxybenzaldehyde and hippuric acid condense in the presence of acetic anhydride and anhydrous sodium acetate to form the acetyl derivative of the lactimide of *p*-hydroxy- α -benzylamino-cinnamic acid, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C} \begin{smallmatrix} \text{NBz} \\ \diagup \\ \text{CO} \end{smallmatrix}$. This, on hydrolysis with alkali, gives *p*-hydroxy- α -benzylaminocinnamic acid

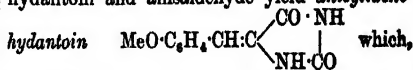


from which by reduction benzoyltyrosine

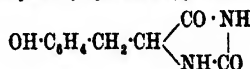


is obtained and converted by hydrolysis with

acids into *r*-tyrosine. Another method of synthesis which can also be extended to the preparation of halogenated derivatives of tyrosine is described by Wheeler and Hoffmann (*Amer. Chem. J.* 1911, 45, 368; cf. Wheeler, Hoffmann and Johnson, *Bio-Chem. J.* 1911, 10, 147; Johnson and Bengis, *J. Amer. Chem. Soc.* 1912, 34, 1061). This method consists in condensing a suitable aldehyde with hydantoin, reducing and hydrolysing the product; thus hydantoin and anisaldehyde yield *anisylidene*-



when boiled with hydrogen iodide is converted into tyrosine together with a small quantity of 4-*p*-hydroxybenzoylhydantoin (tyrosinehydantoin)

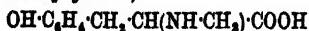


from which tyrosine can be obtained by boiling with baryta water; *dl*-tyrosine may also be synthesised by condensing ethyl phthalimino-malonate with *p*-methoxybenzyl bromide and hydrolysing the product (Stephen and Weizmann, *Chem. Soc. Trans.* 1914, 105, 1152).

Properties.—*L*-Tyrosine, the natural product, is also obtained by the resolution of *dl*-benzoyltyrosine through its brucine salt and subsequent hydrolysis of the *l*-benzoyltyrosine. It crystallises in long flexible silky needles, soluble in 2491 parts of water at 17° (Erlenmeyer and Lipp, *l.c.*), more readily soluble in hot water; dissolves in 13,500 parts of cold 90 p.c. alcohol (Städeler, *l.c.*), insoluble in acetone, ether or absolute alcohol. It melts and decomposes at 314°-318° (corr.) when rapidly heated (Fischer, *Ber.* 1899, 32, 3638); at 295° (Cohn, *Zeitsch. physiol. Chem.* 1896, 22, 166); at 272° (Habermann and Ehrenfeld, *ibid.* 1902, 37, 18); 287° (*Trans. Guinness Lab.* 1903, i, 57). *L*-Tyrosine is levorotatory both in acid and in alkali solution; the specific rotation varies with the concentration. For a 4 p.c. solution in 21 p.c. hydrochloric acid, the natural product has $[\alpha]_D^{16} = -7.98^\circ$ (Mauthner, *Monatsh.* 1882, 3, 345), $[\alpha]_D^{20} = -8.07^\circ$ (Landolt, *Ber.* 1884, 17, 2838); $[\alpha]_D = -8.48^\circ$ (Schulze, *Zeitsch. physiol. Chem.* 1884, 9, 98); the synthetic product has $[\alpha]_D^{20} = -8.64^\circ$ (Fischer, *Ber.* 1899, 32, 3638). In a 4.6 p.c. solution in 4 p.c. hydrochloric acid, the synthetic compound has $[\alpha]_D^{20} = -13.2^\circ$ (Fischer), and the natural product $[\alpha]_D^{16} = -14.6^\circ$ to -16.1° (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1902, 35, 299); in a 5.8 p.c. solution of 11.6 p.c. potassium hydroxide, the natural product has $[\alpha]_D = -9.01^\circ$ (Mauthner, *l.c.*). The molecular heat of combustion is 1071.2 Cal., heat of formation 150.4 Cal. (Berthelot and André, *Compt. rend.* 1890, 110, 884). The affinity constants of tyrosine are: first acid dissociation constant $K_1 = 4 \times 10^{-3}$, second acid dissociation constant $K_2 = 4 \times 10^{-10}$, basic dissociation constant $K_3 = 2.6 \times 10^{-10}$ (Kanits, *Pflügers Archiv.* 1907, 118, 539). The single band ultra violet absorption spectrum exhibited by solutions of tyrosine, is practically identical with that of proteids containing tyrosine;

gelatin, and other proteids that contain no tyrosine show continuous spectra (Blyth, Chem. Soc. Trans. 1899, 1164). Tyrosine is not affected by diazomethane (Geake and Nierenstein, Bio-Chem. J. 1915, 9, 309). For the oxidation of tyrosine, v. Denis (J. Biol. Chem. 1911-12, 10, 73).

L-N-methyltyrosine,



may be obtained from natural *l*-tyrosine by means of the monotonuene sulphonyl derivative; it has $[\alpha]_D^{21} + 19.75$, and it is identical with natural ratiline (Fischer and Lipschitz, Ber. 1915, 48, 360).

d-Tyrosine, obtained by the resolution of *dl*-benzoyltyrosine through its cinchonine salt and subsequent hydrolysis, has $[\alpha]_D^{20} + 8.64^\circ$ in 4.6 p.c. solution of 21 p.c. hydrochloric acid (Fischer); the dextrorotatory tyrosine obtained by v. Lippmann from the white shoots of sugar beet gave $[\alpha]_D = +6.85^\circ$ in 25 p.c. hydrochloric acid; a feebly dextrorotatory tyrosine was found by Winterstein and Thöny (Zeitsch. physiol. Chem. 1902, 36, 28) in a very old Emmenthaler cheese.

dl-Tyrosine prepared by hydrolysis of the synthetic benzoyl derivative crystallises in stout needles, melting and decomposing at 316° (corr.) when rapidly heated (Fischer, l.c.); its hydrochloride is much less soluble in concentrated hydrochloric acid than are the salts of the optically active forms, and the racemic compound can thus be separated from admixture with *d*- and *l*-tyrosine. By fermentation with large amounts of yeast in the presence of sugar and nutritive salts, tyrosine is converted to the extent of 60-80 p.c. into *p*-hydroxyphenylethanol (tyrosol) $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, m.p. 93° , b.p. 310° (compare also Hirai, Acta Scholae Med. Univ. Imperial, Kido, 1918, 2, 425). The *dibenzoyl* derivative melts at 111° ; tyrosol is also obtained by the action of yeast on *p*-hydroxyphenylethylamine (Ehrlich, Ber. 1911, 44, 139; Ehrlich and Pischtschimuka, *ibid.* 1912, 45, 1006). According to Tsudji (Acta Schol. Med. Kyoto, 1917, 1, 439, from Physiol. Abstr. 1917, 2, 320; 1918, 3, 165) *Bacillus proteus vulgaris* attacks *r*-tyrosine, and 65.7 p.c. of *d*-tyrosine can be isolated. Tyrosine is converted to *p*-hydroxyphenylethylamine to the extent of 78.7 p.c. by the action of *B. coli* in a suitable medium (Sasaki, Biochem. Zeitsch. 1914, 59, 429). Bacterial action degrades tyrosine to phenol by removal of the alanine side-chain. Sieke (Z. Hyg. 1921, 94, 314) describes experimental conditions for the culture of phenol-forming bacteria and the morphological, cultural, and serological behaviour of *Bacillus coli phenologenes* and *B. paracoli phenologenes*. Varieties of *B. coli* capable of forming phenol are widely distributed.

By putrefactive decomposition, tyrosine is successively broken down into hydro-*p*-coumaric acid $\text{HO}\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *p*-hydroxyphenyl-acetic acid $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, *p*-cresol and phenol (Baumann, Ber. 1880, 13, 279; Zeitsch. physiol. Chem. 1880, 4, 304). The administration of tyrosine to normal animals causes the production of phenol in the urine, but no excess of hydroxy acids (Blendermann, *ibid.* 1882, 6,

234; Bied. Zentr. 1883, 209; Cohn, Zeitsch. physiol. Chem. 1894, 14, 189), except in one case when a man took 50 grms. of tyrosine in 24 hours, and this produced alcaptonuria, homogentisic acid being found in the urine (Abderhalden, *ibid.* 1912, 77, 454). Inactive tyrosine administered to cats undergoes selective decomposition, so that the urine contains more of the dextro- than of the naturally occurring laevo- variety, and on evaporating the neutral or alkaline urine containing the tyrosine, it is converted into the corresponding uramino acid which, on subsequent treatment with acid, readily loses water, yielding tyrosine hydanitoin (Dakin, J. Biol. Chem. 1910, 8, 25). In the case of alcaptonurics, the administration of tyrosine or certain derivatives of tyrosine, such as mono-palmityl-*l*-tyrosine, distearyl-*l*-tyrosine, *p*-aminotyrosine, causes an increase in the amount of homogentisic acid excreted (Abderhalden and Massini, Zeitsch. physiol. Chem. 1910, 66, 140; Wolkow and Baumann, *ibid.* 1891, 15, 228).

Detection and estimation.—Tyrosine develops a red colour when warmed with Millon's reagent, and can be estimated by means of this reaction (Weiss, Biochem. Zeitsch. 1919, 97, 170). When tyrosine is dissolved in a few drops of warm concentrated sulphuric acid, and the diluted solution neutralised with barium carbonate, the filtrate gives a beautiful violet colour with ferric chloride (Pirea, Annalen, 1852, 82, 252). If a few drops of a solution of tyrosine are added to 2 c.c. of sulphuric acid containing 3 to 5 drops of a solution of aldehyde in twice its volume of alcohol of 90° , the liquid acquires a gooseberry red colour, the intensity of which is proportionate, between certain limits, to the quantity of tyrosine present (Denigès, Compt. rend. 1900, 130, 583). When tyrosine is added to a reagent consisting of 1 part of formalin, 45 parts of water and 55 parts of concentrated sulphuric acid, a green coloration is developed on boiling the mixture (Mürner, Zeitsch. physiol. Chem. 1902, 37, 86). Cf. Totani (Bio-Chem. J. 1915, 9, 391).

Tyrosine develops a rose-red colour under the influence of *tyrosinase*, the colour changing to a dirty violet, and finally a black precipitate of *melanin* is deposited (v. *Tyrosinase*, art. FERMENTATION). See also Raper and Wormal (Bio-Chem. J. 1925, 19, 84); Happold and Raper (Bio-Chem. J. 1925, 19, 92); Gortner (Proc. Soc. Exp. Biol. Med. 1924, 21, 543; Chem. Soc. Abstr. 1925, 128, i. 474).

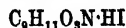
Tyrosine is readily estimated by titration with *N*/5 sodium bromate in the presence of hydrochloric acid and sodium bromide, the liberated bromine being absorbed by the tyrosine with formation of dibromotyrosine (Millar, Trans. Guinness Lab. 1903, I. Part 1; Brown and Millar, Chem. Soc. Trans. 1906, 145). For the estimation of tyrosine in proteins, v. Plummer and Eaves (Bio-Chem. J. 1913, 913, 7, 297); Johns and Jones (J. Biochem. 1918, 36, 319).

For the estimation of tyrosine in the presence of uric acid, see Herzfeld and Klinger (Biochem. Zeitsch. 1918, 88, 283; Fürth and Fleischmann (Biochem. Zeitsch. 1922, 127, 137); Folm and Looney (J. Biol. Chem. 1922, 51, 421).

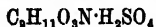
For a microchemical method of estimating

tyrosine, see Hanke and Koessler (J. Biol. Chem. 1922, 50, 235).

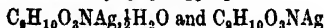
Salts and derivatives.—1-Tyrosine forms crystalline salts with mineral acids which dissociate in water, the *hydrochloride* $C_9H_{11}O_3N \cdot HCl \cdot 2H_2O$, *hydrobromide* $C_9H_{11}O_3N \cdot HBr$, *hydriodide*



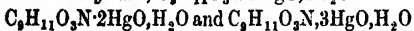
nitrate $C_9H_{11}O_3N \cdot HNO_3$, and *sulphate*



are described (Haushofer, J. 1883, 1177; Aloy and Rabaut, Bull. Soc. chim. 1908, [iv.] 3, 391; Staedeler, Annalen, 1860, 116, 64); the *platinichloride* ($C_9H_{11}O_3N \cdot HCl$), $PtCl_4$ forms yellowish-brown readily soluble crystals (Gintl, Zeitsch. Chem. 1868, 704); the *picrolonate* blackens and sinters at 260° (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127). The following metallic salts have been prepared, those of the heavy metals and the alkaline earth metals are sparingly soluble; the *copper salt* ($C_9H_{11}O_3N$), Cu dissolves in 1230 parts of cold or 240 parts of boiling water (Hofmeister, Annalen, 1977, 189, 24); the *silver salts* $C_9H_9O_3N \cdot Ag_2$, H_2O



the *mercury salts*, $C_9H_{11}O_3N \cdot 2HgO \cdot 2H_2O$

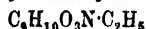


the *barium salt* ($C_9H_{10}O_3N$), Ba; *calcium salt* $C_9H_9O_3N \cdot Ca$, the *mercury-calcium salt*

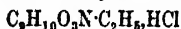


and the *sodium salt* $C_9H_9O_3N \cdot Na_2$ (Vintschgau, J. 1869, 895; Baumann, Zeitsch. physiol. Chem. 1880, 4, 320; Causse, Compt. rend. 1900, 130, 1196). Certain mercury salts are of therapeutic application, v. Dr. Bayer & Co., D. R. PP. 267411, 267412, and Hoffmann-La Roche & Co., D. R. P. 279957).

1-Tyrosine *methyl ester* $C_9H_{10}O_3N \cdot CH_3$ forms colourless prisms, m.p. 135°–136° (corr.); $[a]_D^{20} = +25.75^\circ$ in methyl alcohol solution; the *hydrochloride* $C_9H_{10}O_3N \cdot CH_3 \cdot HCl$ forms colourless needles; 1-tyrosine *ethyl ester*



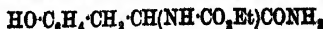
has m.p. 108°–109°, $[a]_D^{20} = +20.4^\circ$ in 5 p.c. alcoholic solution; the *hydrochloride*



has m.p. 166° (Fischer and Schrauth, Annalen, 1907, 354, 21; Fischer, Ber. 1908, 41, 850; Lilienfeld, Archiv. Physiol. 1894, 383, 555; Rohmann, Ber. 1897, 30, 1978; Fischer, *ibid.* 1901, 34, 433). Tyrosine *anil ester*, m.p. 68°–70°, yields a hydrochloride, m.p. 181°–182° (Curtius and Donselt, J. pr. Chem. 1917, [ii.] 95, 327).

1-Tyrosine *anhydride* $C_{18}H_{18}O_4N_2$ has m.p. 277°–280° (corr.), $[a]_D^{20} = -223.8^\circ$ in N/1 sodium hydroxide (Fischer and Scrauth); cf. Graziani (Atti R. Accad. Lincei, 1916, [v.] 25, 1, 500); an *anhydride* ($C_9H_8O_3N$), slender white crystals, m.p. 278°–279° (uncorr.), and an isomeric *anhydride*, a powder, m.p. 279°, are described. d-Tyrosine *anhydride*, m.p. 273°, has $[a]_D = +37.59^\circ$ in alkaline solution, and $[a]_D = +93.87^\circ$ in acid solution (Fränkel and Feldsberg, Biochem. Zeitsch. 1921, 120, 218).^a 1-Tyrosine *amide* $C_9H_{10}ON \cdot CONH_2$ has m.p. 153°–154° and

$[a]_D^{20} = +19.47^\circ$, condenses readily with ethyl chlorocarbonate to form the *monocarbethoxyl*

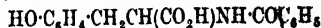


m.p. 155°–157°, and the *dicarbethoxyl*

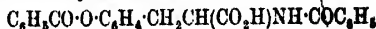


m.p. 185° (corr.), derivatives; the *dinaphthalene-sulphonyl derivative* $C_{22}H_{22}O_4N_2S_2$ has m.p. 204° (corr.) (Koenigs and Mylo, Ber. 1908, 41, 4427).

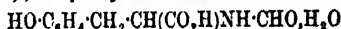
The following *acyl derivatives* of 1-tyrosine are described: N-acetyl-1-tyrosine, m.p. 165°, by methylation with methyl sulphate gives N-acetyl-O-methyl-1-tyrosine, m.p. 147°–148°, which on hydrolysis yields O-methyl-1-tyrosine, m.p. 243° (Karrer, Gisler and others, Helv. Chim. Acta, 1922, 5, 469); the *benzoyl derivative*



m.p. 165°–166° (corr.), $[a]_D^{20} = +19.25^\circ$ in 8 p.c. alkali solution, the *brucine salt* is crystalline; the *dibenzoyl derivative*



has m.p. 211°–212° and forms a *potassium* and a *cadmium salt* (Fischer, Ber. 1899, 32, 3638, 2454); the *formyl derivative*



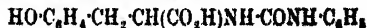
m.p. 171°–174° (corr.), $[a]_D^{20} = +84.8^\circ$ in 6 p.c. alcoholic solution (Fischer, *ibid.* 1907, 40, 3704); the *palmityl derivative*



m.p. 133°, $[a]_D^{20} = +24.35$ in 1.8 p.c. alcoholic solution; *palmityl-1-tyrosine-palmitylether* $C_{41}H_{71}O_4N$, m.p. 95°–96°, $[a]_D^{20} = +15.28^\circ$ in 1.7 p.c. alcoholic solution; *stearyl-1-tyrosine-stearylether* $C_{48}H_{79}O_4N$, m.p. 98°–108° (Abderhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61); *glycyl-1-tyrosine methyl ester*, m.p. 123°–124° (Geake and Nierenstein, Bio-Chem. J. 1915, 9, 309); the β -naphthalene-sulphonyl derivative forms a *hydrochloride* $C_{19}H_{19}O_4NSCl$, m.p. 170°, a *sodium salt* $C_{19}H_{18}O_4NSNa$, that decomposes at 175°, an *ethyl ester* $C_{21}H_{21}O_4NS$, m.p. 140°–143° (Abderhalden and Funk, *ibid.* 1910, 64, 436); the *di- β -naphthalenesulphonyl derivative* $C_{19}H_{18}SO_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2H) \cdot NH \cdot SO_2 \cdot C_{10}H_7$, m.p. about 120°, forms a *sodium salt*



m.p. 252°–254°, an *ammonium* and a *barium salt* (Fischer and Bergel, Ber. 1903, 36, 2592); the *phenylisocyanate derivative*



has m.p. 104°, and forms a *barium*



and a *silver salt* $C_{19}H_{19}O_4N_2 \cdot Ag \cdot H_2O$ (Paal and Zitelmann, *ibid.* 1903, 36, 3337); the α -naphthylisocyanate derivative melts at 205°–206° (Neuberg and Manasse, *ibid.* 1905, 38, 2359).

For the *hydrazides* of the esters of tyrosine and benzoyltyrosine, see Curtius and Donselt (J. pr. Chem. 1917, [ii.] 95, 327).

di-Tyrosine *carbamide*

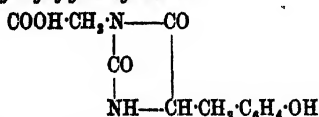


decomposes at 240° (Hugouveny and Morel,

Compt. rend. 1906, 142, 48); *l*-tyrosinehydantoin acid $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\text{NH}\cdot\text{CONH}_2$, m.p. 218° , forms a crystalline silver salt (Jaffé, Zeitsch. physiol. Chem. 1882, 7, 306).

l-Tyrosinehydantoin $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}$ $\begin{matrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{matrix}$ melts and decomposes at $242^\circ\text{--}245^\circ$ (Blendermann, l.c.).

Tyrosyl-glycinehydantoin



has m.p. $217^\circ\text{--}218^\circ$ (Johnson and Hahn, J. Amer. Chem. Soc. 1917, 39, 1255).

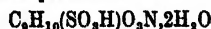
The alkaloid *surinamine* or *geoffroyne* from *geoffroya* bark is a *methyltyrosine*, in which the methyl has replaced one of the hydrogens of the amino group (Hiller-Bombien, Arch. Pharm. 230, 513; Blau, Zeitsch. physiol. Chem. 1908, 58, 153; Walpole, Chem. Soc. Trans. 1910, 97, 94).

O-Methyltyrosine *choline* forms a crystalline iodide, m.p. $137^\circ\text{--}139^\circ$, the *aurichloride* has m.p. $112^\circ\text{--}115^\circ$; the *platinichloride*, m.p. 204° .

Tyrosine-choline yields a crystalline iodide, m.p. 176° , and *chloride* (Karrer, Gisler and others, l.c.).

Derivatives of *l*-tyrosine containing substituents in the aromatic nucleus are: *3-nitro-l*-tyrosine $\text{C}_6\text{H}_4\text{O}_2\text{N}_2$, obtained by nitration of *l*-tyrosine, forms yellow needles, m.p. $222^\circ\text{--}224^\circ$ (decomp.); $[\alpha]_D^{15} +3\cdot21^\circ$, *hydrochloride*, m.p. 237° (decomp.); cf. Johnson and Kohmann (J. Amer. Chem. Soc. 1915, 37, 1863 and 2598); Waser and Lewandowski (Helv. Chim. Acta, 1921, 4, 657). The *barium* and *silver* salts have been prepared, also the *nitrate* and *sulphate* (Strecker, Annalen, 1850, 73, 70; Casimir Funk, Chem. Soc. Trans. 1912, 1004). *3-Amino-l*-tyrosine $\text{C}_6\text{H}_4\text{O}_2\text{N}_2$, needles, m.p. $287\cdot5^\circ$ (decomp.), $[\alpha]_D^{15} -3\cdot61^\circ$; *hydrochloride*, prisms, m.p. 175° (decomp.) (Waser and Lewandowski, l.c.), prepared by reducing nitrotyrosine. *3:5-Dinitrotyrosine* $\text{C}_6\text{H}_2\text{O}_2\text{N}_4$, golden yellow crystalline plates, the *ammonium* and *mercury* salts, also the *hydrochloride* and the *hydantoin* and *thiohydantoin* derivatives have been prepared (Johnson and Kohmann, l.c. 2164).

Tyrosine sulphonic acid



is strongly acidic and gives a beautiful violet colour with ferric chloride. The *ammonium*, *calcium* and *barium* salts are described (Staedeler, l.c.).

3-Bromotyrosine



has a sweet taste, decomposes at $247^\circ\text{--}248^\circ$; the *hydrobromide* decomposes at $190^\circ\text{--}191^\circ$, the *picrate* and *platinichloride* are very soluble in water (Johnson and Bengis, J. Amer. Chem. Soc. 1912, 34, 1061).

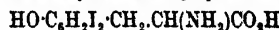
3:5-Dibromo-l-tyrosine, m.p. about 245°

(decomp.), prepared by the action of bromine vapour on the finely divided tyrosine (Mörner, Zeitsch. physiol. Chem. 1913, 88, 124), is obtained in anhydrous, long, slender needles grouped into bundles or in thin plates hydrated with two molecules of water; it has $[\alpha]_D^{20} +1\cdot3^\circ$, dissolves in 218 parts of water at 16° or 26 parts of boiling water; the *silver* salt, the *hydrochloride*, *hydrobromide* and *sulphate* are crystalline, and it forms an unstable *perbromide* (Gorup-Besanez, Annalen, 1863, 125, 281; Millar, Trans. Guinness Lab. 1903, I. Part 1). *3:5-Di-bromo-dl*-tyrosine crystallises with one molecule of water in transparent four-edged prisms or thick plates, m.p. about 245° (decomp.); it is nearly twice as soluble in water as the *l*-isomeride, it is not decomposed by concentrated sulphuric acid even on heating (Mörner, l.c.).

Chlorotyrosine, formed by the action of sulphuryl chloride on tyrosine suspended in acetic acid, melts at 257° and forms a benzoyl derivative, m.p. 195° , and a formyl derivative, m.p. 198° (Zeynek, Zeitsch. physiol. Chem. 1925, 144, 246).

3:5-Dichlorotyrosine, m.p. 252° (decomp.), prepared by chlorinating tyrosinehydantoin and decomposing with barium hydroxide the resulting *3:5-dichlorotyrosinehydantoin*; the *hydrochloride* has m.p. $260^\circ\text{--}265^\circ$ (Wheeler, Hoffmann and Johnson, J. Biol. Chem. 1911, 10, 147). *3:5-dichloro-l*-tyrosine, prepared by the action of chlorine on tyrosine in the presence of glacial acetic acid, has m.p. $256^\circ\text{--}260^\circ$ (decomp.), and the anhydrous hydrochloride gives in 5 p.c. aqueous solution $[\alpha]_D^{20} -7\cdot8^\circ$ (Zeynek, Zeitsch. physiol. Chem. 1921, 114, 275).

3:5-Di-iodotyrosine, iodo-gorgonic acid



is not found free in nature but is one of the constituent amino acids of certain proteids; it was first obtained by Dreschel (Zeitsch. Biol. 1896, 33, 85) from *gorgonia*, derived from the horny skeleton of *Gorgonia cavolinii*. This, on hydrolysis with barium hydroxide, yielded an iodo amino acid, hence name *iodogorgonic acid*. It was shown by Wheeler and Jamieson (Amer. Chem. J. 1905, 33, 365) that iodo-gorgonic acid is a di-iodotyrosine and can be prepared by the direct action of iodine on tyrosine. That it is the *3:5-di-iodotyrosine* was shown later by Wheeler and Johns (ibid. 1910, 43, 11), for on treatment with methyl iodide and potassium hydroxide it yields the methylether of a di-iodotyrosinetrimethylammonium iodide

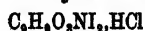


which on boiling with sodium hydroxide yields *3:5-diiodo-p*-methoxytyrosine. Iodo-gorgonic acid occurs in a large number of proteids, and has been isolated from *iodo-albacid*, *iodogelatin*, *iodocasein*, *gorgonin* and *spongion* (Oswald, Zeitsch. physiol. Chem. 1911, 70, 319; 71, 200; 74, 290; 75, 353).

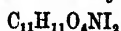
3:5-Di-iodo-dl-tyrosine, prepared by hydrolysis of the above-mentioned proteids, crystallises from hot water in glassy right-angled plates, from alcohol in hexagonal plates, dissolves in 2164 parts of water at 15° , melts and decomposes at 200° .

3:5-Di-iodo-l-tyrosine, prepared by the

action of iodine on *l*-tyrosine, melts at 204° (Oswald), 196°-205° with decomposition (Wheeler and Jamieson); it has $[\alpha]_D^{20} = +2.27^\circ$ in 4.5 p.c. solution of 25 p.c. ammonia (Abderhalden and Guggenheim, *Zeitsch. physiol. Chem.* 1907, 54, 331). The *hydrochloride*



forms colourless needles, decomposed by water; the *sulphate* $\text{C}_9\text{H}_9\text{O}_2\text{NI}_2\cdot\text{H}_2\text{SO}_4$ is readily soluble; the *silver salt* $\text{C}_9\text{H}_9\text{O}_2\text{NI}_2\cdot\text{Ag}_2$ and *copper salt* $(\text{C}_9\text{H}_9\text{O}_2\text{NI}_2)_2\cdot\text{Cu}_2\text{H}_2\text{O}$ form amorphous precipitates. The *acetyl derivative*



decomposes at 225° (Wheeler and Jamieson, *Amer. Chem. J.* 1905, 33, 365). The *methyl ester* $\text{C}_9\text{H}_9\text{OI}_2\cdot\text{CH}_3\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{Me}$ decomposes at 192°; its *hydrochloride* forms colourless needles that decompose at 211° (corr.), and yields the *nitrate* on treatment with dilute nitric acid (Abderhalden and Guggenheim, *Ber.* 1908, 41, 1237). *Palmityl-3:5-di-iodo-tyrosinepalmityl ether* $\text{C}_{46}\text{H}_{89}\text{O}_6\text{NI}_2$ melts at 55°-60° (Abderhalden and Slavů, *Zeitsch. physiol. Chem.* 1909, 61, 405).

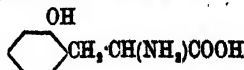
Tyrosinebisazobenzenearsenic acid



is a yellow microcrystalline powder which is insoluble in the usual organic solvents (Pauly, *Zeitsch. physiol. Chem.* 1915, 94, 284).

For the synthesis of *o*-tyrosine, v. Johnson and

Scott (*J. Amer. Chem. Soc.* 1915, 37, 1846). Starting with 2-thiohydantoin *o*-tyrosine-hydantoin is prepared, and this on hydrolysis with barium hydroxide yields *o*-tyrosine



m.p. indefinite; the hydrochloride crystallises from dilute hydrochloric acid in prismatic crystals which decompose at 180°.

A full account of the chemistry and physiological properties of tyrosine will be found in *Biochemisches Handlexikon*, von Abderhalden, vol. iv. part 2, 681-702. M. A. W.

TYSONITE. Fluoride of cerium metals (Ce, La, Di)F₃, crystallised in the hexagonal system. It is pale wax-yellow with resinous lustre, and a perfect pearly cleavage parallel to the basal plane. Sp.gr. 6.13. The mineral alters very readily to the fluo-carbonate bastnäsite, and the chestnut-brown crystals as usually found are really pseudomorphs of bastnäsite after tysonite with sometimes still a nucleus of the original mineral. Crystals and irregular masses up to several pounds in weight are found at several places in the coarse-grained granite of the Pike's Peak district in El Paso Co., Colorado. P. Geijer (*Geol. Förh. Stockholm*, 1921, 43, 19) suggests that tysonite is identical with the Swedish fluorite. L. J. S.

TYUYAMUNITE v. TURANITE.

U

UARANA v. GUARANA.

ULCO. An alloy of lead with small amounts of barium and calcium, used as a substitute for antimonial lead in the manufacture of shrapnel. It is suggested that it may be employed as a bearing metal on account of its high melting-point, excellent structure, and low coefficient of friction.

ULEXINE v. CYTTISINE.

ULEXITE (*Boronatrocalcite* of G. L. Ulex, 1849; *Natroborocalcite*). A hydrated borate of sodium and calcium $\text{NaCaB}_5\text{O}_9\cdot 8\text{H}_2\text{O}$, containing 43.0 p.c. B_2O_3 ; sp.gr. 1.65; H. 1; slightly soluble in hot water, and readily soluble in acids. It forms rounded, white masses, 2-3 ins. in diameter, consisting of a loose aggregate of fine, silky fibres; hence the popular name 'cotton-ball.' It occurs abundantly in the borate deposits of Nevada and California, and forms the main mass of those near Iquique in Chile, and Jujuy province in Argentina. L. J. S.

ULLMANNITE. Nickel sulph-antimonide NiSbS , crystallised in the cubic system with tetrahedral symmetry. The antimony is sometimes partly replaced by arsenic; and in the *willyamite* variety, from Broken Hill in New South Wales, half the nickel is replaced by cobalt. The mineral is easily mistaken for galena, since it has a good cubical cleavage. The cleavage is, however, less perfect than in galena, and the colour is steel-grey rather than bluish-grey; further, ullmannite (H. 5½) readily scratches galena. Sp.gr. 6.6-6.7. The mineral is decomposed by nitric acid with separation of antimony oxide and sulphur. It occurs in mineral

veins at several places in the Rhineland, at Lölling and Waldenstein in Carinthia, Mount Ar in the Pyrenees, and as good crystals at Monte Narba in the Sarrabus district of Sardinia. It has been found in small amount in a barytes vein in the New Brancepeth Colliery near Durham. L. J. S.

ULMARENE (*menoten*). Trade name for salicylic methoxymethyl ester.

ULMITE. A term applied to a form of humus covering grains of a black friable sandstone found along the coast of New South Wales (Steel, *Proc. Linnæan Soc. N.S.W.* 1921, 46, 213).

ULTRAMARINE. Ultramarine was first artificially made on a commercial scale in 1828, by Guimet, who earned the prize of 6000 francs offered by the 'Société d'Encouragement' of France for its production at a cost not exceeding 90s. per lb. About the same time, Gmelin (*Ann. Chim.* 1828, [ii.] 37, 409) independently discovered how to prepare ultramarine on a laboratory scale. According to Heintze (*J. pr. Chem.* 1891, [ii.] 43, 98), ultramarine was being made by Kottig, director of the laboratory of the Königl. Porzellan-manufaktur in Meissen, at the time when Guimet and Gmelin were claiming the priority of the discovery.

Until 1828 ultramarine was obtained by powdering and washing *lapis-lazuli* (q.v.); its composition was first determined by Clément and Désormes (*Ann. Chim.* 1806, [i.] 57, 317).

Properties.—Artificial ultramarine blue occurs in commerce as a bright, azure blue, impalpable powder, insoluble in water. Its constituent elements are sodium, aluminium, silicon,

sulphur, and oxygen. Heated to 200°-300° with water in a sealed tube, it leaves a colourless residue free from sulphur, while sodium sulphide passes into solution. It also loses its sulphur when heated with mercuric oxide (Chabré and Levallois, *Compt. rend.* 1906, 143, 222). Ultramarine is quite stable towards alkalis, but is readily decomposed by dilute acids, some sulphur being precipitated and hydrogen sulphide evolved. It is also decomposed by alum solution, owing to the formation of an aluminium derivative. Yellow phosphorus reduces it to a leuco compound, which again becomes blue when heated in air. The preceding reactions seem to indicate the presence of some kind of polysulphide in ultramarine; but it is unaltered by concentrated and fuming sulphuric acid, and also by a mixture of glacial acetic acid and acetic anhydride (Hoffmann and Metzner, *Ber.* 1905, 38, 2482), reagents which instantly decompose polysulphides and thiosulphates. Ultramarine withstands a red heat fairly well, although it loses its brilliancy, and becomes greenish; hence it is difficult to imagine that the blue colour is due to free sulphur, as has been suggested (Paterno and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.] 16, i. 465). Ultramarine blue when strongly heated in hydrogen loses some of its sulphur, but still retains its blue colour. It becomes violet when heated to dull redness in chlorine. It possesses hydraulic properties and increases the binding power of cement (Rohland, *Zeitsch. angew. Chem.* 1904, 17, 609).

When heated with aqueous silver nitrate at 120°-140° in a sealed tube for 15 hours, no silver sulphide is produced, but a dark yellow *silver ultramarine* is obtained, together with silver nitrite and other products (Unger, *Dingl. poly. J.* 1874, 212, 232; Heumann, *Ber.* 1877, 10, 991, 1345, 1888; 1897, 12, 60, 784; *Bull. Soc. chim.* 1877, [ii.] 28, 570; 1878, 30, 326, 327; 1880, 33, 60, 302; *Annalen*, 1879, 199, 253; 1880, 201, 262; Philipp, *Ber.* 1877, 10, 1227; Forcrand and Ballin, *Bull. Soc. chim.* 1878, [ii.] 30, 112; Chabré and Levallois, *l.c.*). Silver ultramarine is produced by replacement of the sodium in ordinary ultramarine by silver; when fused with various metallic chlorides or iodides the silver is replaced by other metals, and in this way have been obtained *potassium* (blue), *lithium* (blue), *barium* (yellowish-brown), *zinc* (violet), *manganese* (grey), *ultramaries*, &c. Heated with the requisite organic iodide, silver ultramarine is decomposed, yielding *ethyl*, *amyl*, *benzyl*, and *phenyl ultramarines*, and silver iodide (Forcrand, *Compt. rend.* 1879, 88, 30; *Bull. Soc. chim.* 1879, [ii.] 31, 161). Mercurous nitrate solution heated with ultramarine yields a greyish-blue mercurio-ultramarine, which loses mercury on heating and leaves a pure blue residue, which becomes yellow on heating and again blue on cooling, this change being capable of indefinite repetition. Cadmium yields an olive-green product. Lead replaces the sodium completely. Ammonium and calcium ultramarines have also been prepared. Ferrous ultramarine is dark greyish-blue and is readily decomposed by acids. These substances regenerate ultramarine when heated with sodium chloride. They do not evolve hydrogen sulphide when treated with cold hydrochloric acid

(Chabré and Levallois, *l.c.*). *Selenium* and *tellurium* ultramarines have also been produced, in which sulphur is substituted by either selenium or tellurium (Guimet, *Ann. Chim.* 1878, [v.] 13, 102; Plicque, *Bull. Soc. chim.* 1877, [ii.] 28, 518; 1878, 29, 522; 1878, 30, 51; Morel, *ibid.* 28, 522). Light blue *boron ultramarine* has been prepared by fusing together anhydrous borax, boric oxide, and either sodium or potassium sulphide, sulphite, or thiosulphate (Hoffmann, *Zeitsch. angew. Chem.* 1906, 19, 1089; 1907, 20, 568; *Chem. Ind.* 1911, 34, 699).

Ultramarine blue crystallises in the regular system, isomorphous with the minerals *kavyn*, *sodalite*, and *nosean*.

Green ultramarine is formed as an intermediate product in the manufacture of ultramarine blue, and is converted into the latter by roasting with sulphur. According to Philipp (*Ber.* 1876, 9, 1109), sulphur is not taken up in the change from green to blue, which can be effected by heating with water in a sealed tube at 100°; a small amount of sodium compound is removed by the water. Heated in chlorine, green ultramarine turns bluish-violet; sodium sulphide solution turns it grey.

White ultramarine is obtained by completely excluding air during the roasting of the materials in the manufacture of ultramarine, and is converted into blue ultramarine when heated in either chlorine, oxygen, or sulphur dioxide (Philipp, *Ber.* 1876, 9, 1109; 1877, 10, 1227; Böttger, *Annalen*, 1876, 182, 311; Hoffmann, *ibid.* 1878, 194, 1).

Red ultramarine was first obtained by Scheffer in the course of preparing the ordinary substance, by heating the materials very strongly in a muffle freely exposed to air; it contains less sodium and more aluminium than the blue variety (Scheffer, *Ber.* 1873, 6, 1450; Büchner, *Dingl. poly. J.* 1879, 231, 446; Zettner, *Ber.* 1875, 8, 259, 353).

Red ultramarine has been prepared by passing chlorine and steam over heated ultramarine blue. It is also obtained by the action of nitric oxide on the blue compound, sulphur being removed in the process. It is decomposed by acids without evolution of hydrogen sulphide, but evolves sulphur dioxide, and is not changed by alum solution. Heated out of contact with air it is changed into a blue product. It now yields hydrogen sulphide with acids.

Yellow ultramarine is obtained by heating the red variety in air for a short time at 360°, or at a little higher temperature (Hoffmann, *Annalen*, 1878, 194, 1). According to Büchner (*Ber.* 1874, 7, 990), both the yellow and red forms are produced by heating blue ultramarine to 300°-400° in oxygen or sulphur dioxide; the colour changes to red and then to yellow. If chlorine is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green and then reddish-yellow (Zettner, *Ber.* 1875, 8, 259, 353).

Violet ultramarine is obtained when the reddish-yellow product previously mentioned is heated with sodium hydroxide (Zettner, *l.c.*). It becomes blue when heated to dull redness or when further heated with an alkali hydroxide, and nitric acid vapours turn it red.

The violet variety was first prepared by

Leykauf in 1859 by allowing moist calcium chloride to react with warm ultramarine blue. In 1872 Wunder prepared it by heating the blue form in chlorine at 300° and treating the product with water. It has been manufactured from ultramarine blue by heating the latter, in thin layers, on earthenware trays at 280°, and passing steam over it to remove sulphur. The temperature was then lowered to 160°, and a mixture of chlorine and steam led over it for 3 hours. For further details, and other methods, *v. Wunder*, Chem. Zeit. 1890, 14, 1119; *ibid.* Zeitsch. anorg. Chem. 1912, 77, 209.

Composition.—The various varieties of ultramarine have not yet been satisfactorily shown to possess uniform compositions. In fact, commercial blue ultramarines are manufactured in three different grades, containing different proportions of silica and sulphur. Moreover, it is not possible to obtain products of identical composition even when, in repeated operations, the relative amounts of the different raw materials are maintained constant and the working conditions duplicated as exactly as possible. The following analyses of different samples of ultramarine blue rich in silica indicate its variable composition:—

	Rawlins			Parry and Coste		
	1	2	3	4	5	6
H ₂ O						0.7
SiO ₂	38.9	39.6	42.7	42.3	41.7	42.4
Al ₂ O ₃	29.5	24.0	24.5	26.8	25.2	24.0
Na ₂ O	21.0	19.2	20.0	19.5	18.8	18.7
S	10.8	13.1	13.0	12.0	14.2	15.4

The differences in composition between ultramarines of different colours are shown by the following numbers, taken from Jordan (*Zeitsch. angew. Chem.* 1893, 684):—

	White (Hoffmann)	Green (Philipp)	Blue (Philipp)	Blue (Philipp)	Violet (Wunder)	Red (Wunder)	Light blue (Wunder)
Na	21.5	17.02	15.66	14.66	11.7	8.1	11.9
Al	16.6	15.81	15.39	12.55	13.1	13.3	13.1
Si	17.0	17.51	16.87	17.29	19.4	19.3	19.7
S	6.4	7.91	5.69	11.38	13.3	15.2	12.7
O	38.4	—	—	—	42.1	43.4	42.0
H	—	—	—	—	0.4	0.7	0.6

The two analyses of ultramarine blue (Philipp) in the table refer to the varieties poor and rich in silica respectively.

The constitution of ultramarine is naturally a matter of great uncertainty, in view of what has been said concerning its composition. It is commonly regarded as a combined silicate and polysulphide of sodium and aluminium, but objections to this view have already been mentioned. For the numerous formulae that have been proposed for ultramarines, *v. Rawlins*, J. Soc. Chem. Ind. 1887, 6, 791; Szilasi, *Annalen*, 1889, 251, 97; Guckelberger, *ibid.* 1882, 213, 182; Dingl. poly. J. 1883, 247, 343; Clarke, *Amer. Chem. J.* 1888, 10, 126; Brögger and Hückström, *Jahresber. Tech.* 1891, 454; Rohland, *Zeitsch. angew. Chem.* 1904, 17, 609; Abegg's *Handbuch der Anorganischen Chemie*, vol. III, pt. i.

The blue colour is considered to depend on (1) the presence of an alkali metal; (2) the

direct union of a part of the sulphur with metal; (3) the presence of a part of the sulphur in a lower state of oxidation. Neither aluminium nor silicic acid is essential (*Wunder*, *Zeitsch. angew. Chem.* 1915, 28, 147; 1917, 30, i. 161; 1920, 33, 23).

The similarity in composition exhibited by ultramarines of quite different colours suggests that the actual colouring material may represent only a small fraction of the total mass; it has been supposed that such a small amount of a coloured substance is present, disseminated throughout a colourless body in a state of solid solution (*Rohland, l.c.*). *J. Hoffmann* (*Chem. Zeit.* 1910, 34, 823) has suggested that this coloured substance is sulphur; the comparative stability of ultramarine at a red heat does not lend support to this assumption. It is noteworthy, however, that were it not for the presence of sulphur, ultramarine would be expected to be colourless.

Alkali fusion of ultramarine converts the blue colour into a dark red. Since, according to Ostwald, alkali appears to enhance the dispersion of disperse sulphur systems, and since, as in the case of colloidal gold, greater dispersion is accompanied by a change in colour from blue to red, it is considered that the above experimental result is in support of the theory that the colour principle of ultramarine is colloidal sulphur (*I. T. Keine*, *Chem. Zeit.* 1923, 47, 513).

The silicon dioxide in ultramarine may be displaced by boron trioxide without the disappearance of the blue colour, and the amount of this substance may greatly vary without much alteration in colour. Other solvents for colloidal sulphur manifest a blue colour; thus potassium thiocyanate if dehydrated and heated to redness becomes blue, but it becomes colourless on cooling; phosphoric oxide also acquires a deep blue colour on fusing with sodium sulphide at 900°, but the colour disappears on cooling. The blue colour of the solution obtained by dissolving disulphur trioxide in concentrated sulphuric acid is probably due to the presence of colloidal sulphur.

Uses.—Ultramarine is extensively used in a variety of manufactures. Its large consumption is due to two characteristics: brilliancy as a body colour, and high colouring power. As a body colour it is used in calico-printing, and wall-paper printing, for colouring writing paper and printing-ink, preparing blue pigments, and blueing mottled soap. As a 'whitening' agent it is very valuable, its great strength and purity of tone correcting the yellow tinge in writing and printing papers, cotton and linen goods, paper pulp, whitewash, soap, starch, and even sugar. It is extensively used in the manufacture of square and ball blue for laundry use.

Tests and analysis.—(i) Dilute 0.1 gm. of a standard sample of ultramarine with 0.6 gm. of pure powdered chalk, and determine the amount of chalk that must be added to 0.1 gm. of the sample under examination in order to match the colour of the diluted standard; this gives an indication of the value of the sample. (ii) Heat a sample in hydrogen to 400°. A good ultramarine becomes grey and then green, the change taking about half an hour; a bad specimen changes in a few minutes. (iii) Stir

a little of the powder under examination in a cold saturated solution of alum, and note the length of time required for decolorisation; compare with a standard sample ground equally fine (iv.) Shake up with water and alcohol to detect adulteration with coal-tar dyes.

For the quantitative analysis, the substance may be treated as a silicate readily attacked by dilute hydrochloric acid (*v. ANALYSIS*); in the filtrate from the aluminium the sodium may be determined as the sulphate. The determination of sulphur should be effected on a separate portion, by oxidation to sulphuric acid with *aqua regia* or fuming nitric acid, and subsequent estimation as barium sulphate. See also Andrews, Analyst, 1910, 35, 157.

MANUFACTURE OF ULTRAMARINE.

The only ultramarines prepared on a large scale are the blue and green sodium-sulphur-ultramarines. Three chief varieties of ultramarine blue are found in commerce:—

Glauber salt or sulphate ultramarine, the palest variety. It has a slight greenish tinge, small covering power, and is the form most readily attacked by alum.

Soda ultramarine low in sulphur, a pure blue variety, darker than the preceding, and having more covering power.

Soda ultramarine rich in sulphur and silica, the darkest variety, with a reddish tinge. It has high covering power, and is the form most resistant towards alum; consequently it finds extensive use in paper blueing.

Ultramarine is produced when aluminium silicate is calcined with sodium sulphide; the silicate is employed in the form of china clay, or a similar material, with the addition of silica if necessary; sodium sulphide is produced during the manufacture, either from sodium carbonate, carbon, and sulphur, or from sodium sulphate, carbon, and sulphur. The relative proportions of the ingredients is an important factor in the manufacture of ultramarine, but different authorities recommend different mixtures. With materials of the best quality, the following mixtures are said to be the best for producing the three varieties mentioned above:—

Ultramarine blue	Pale	Medium	Dark
China clay	100	100	100
Soda	9	100	103
Glauber salt	120	0	0
Carbon	25	12	4
Silica (Kieselguhr)	0		16
Sulphur	16	60	117

If the clay employed differs in composition from china clay, the relative proportions of clay and silica must, of course, be suitably adjusted.

The manufacture of ultramarine blue is carried out either by (i.) the *direct* or (ii.) the *indirect* process. All ultramarines rich in silica and a certain amount of the other varieties poorer in silica are made by the former method; but the majority of the ultramarines poor in silica are prepared by the latter method, in which ultramarine green is found as an intermediate product. Both these are dry processes; wet methods have been described and patented, but

do not seem to have been adopted on a large scale (Knapp, J. pr. Chem. 1885, [ii.] 32, 375; 1888, 38, 48; Melvor, Eng. Pat. 9200, 1890; Melvor and Cruickshank, Eng. Pat. 19411, 1892).

For general accounts of the manufacture of ultramarine, *v. Rawlins*, J. Soc. Chem. Ind. 1884, 6, 791; Pichot and Grangier, *ibid.* 1888, 7, 573; Röhrig, Chem. Zeit. 1883, 567; Wunder, *ibid.* 1890, 14, 1119; Jordan, Zeitsch. angew. Chem. 1893, 684.

Raw materials.—*China clay*, and French, German, and Bohemian *pottery clays* are used, and always require levigation. The clay must be very finely divided, and free from excessive amounts of iron and manganese oxides. For *soda*, the best soda ash, known as carbonated ash, is employed; it must be stored in a dry place. The *Glauber salt* must be free from acid and iron, and well calcined; it should be ground in stone edge-runner mills before use. *Rod or stick sulphur*, containing very little non-volatile matter, is usually employed, since poorer forms of sulphur produce dirty shades of colour; like the Glauber salt, it is reduced to a fine powder before use. *Carbon* should not contain more than 4 p.c. of moisture; that made from pine trunks is preferred, and is ground in ball mills

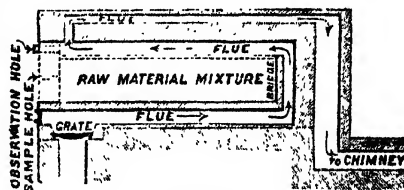


FIG. 1.

and stored in a dry place. Charcoal is sometimes replaced by pitch, tar, colophony, &c. If coal is used, it must be of good quality, and free from sand, stones, and pyrites. *Silica* is usually employed in the form of kieselguhr, but sometimes quartz is used; the latter is ignited and then quenched in water to cause it to break up, being finally dried and ground to powder. Silicious carbon, such as charred rice husks, may partly or wholly replace the carbon and silica (Cross, Eng. Pat. 3174, 1903).

Direct process.—The formation of ultramarine blue by this process is effected by roasting the well-mixed raw materials, allowing access of air during the operation. The successive operations involved are mixing, roasting, lixiviating, wet-grinding, levigating, pressing, drying, and sifting.

The most intimate and cheapest mixture is obtained when the various raw materials have been ground first in edge-runner mills, and then in balance mills. With mixtures containing much sulphur, the other ingredients should first be well mixed, the sulphur then added, and further mixing effected. The mixtures should, in any case, be calcined as soon as they are prepared.

The 'mass' oven, so called from the mixture being treated in a mass, produces directly very good ultramarine if carefully managed. Fig. 1 gives an idea of the arrangement. The raw materials, well mixed and ground, are shovelled

on to the floor of the oven, pushed up to the end with a broad rake, and, after being piled up to nearly the level of the bridge, are nearly flattened, and covered with thin tiles, the joints being filled in with a very thin mortar made with china clay and sand. The oven having been thus filled with about 1 ton of raw material, the front is built up, leaving a hole just above the level of the tiles for observation, fitted with a loose brick. A small hole below this and about opposite the centre of the mass, fitted with a clay stopper, affords a means of taking samples as the burning proceeds. The heat is slowly raised to a bright red, and as it rises small jets of sulphur dioxide are seen to come from the cracks between the covering tiles and burn with feathery flames, increasing in length as the heat becomes greater, and gradually dying away as the reaction is completed. The heat is maintained at its highest point for from 12 to 18 hours, or until the process appears to be finished, when a sample is taken through the small hole by means of a long auger inserted right into the middle of the mass. The sample presents, if sufficiently burnt, a greenish-blue appearance, gives off sulphur dioxide freely without actually burning, and on being spread upon a clean tile quickly loses its heat, and appears a blue colour with a tinge of green. The changes experienced by the mixture are interesting and remarkable. As introduced it is a yellowish-grey, and becomes successively brown, green, and blue. The brown, a dark rich colour, is very unstable, and burns on exposure to air to a greenish half-formed ultramarine, and, even if not exposed, slow combustion goes on until oxidation has taken place. The green is almost equally unstable.

When the drawn sample is found to be sufficiently burnt, the operation is concluded by closing the oven, plastering up cracks, and excluding the air as far as possible. It is then left to cool down, which takes a week or 10 days. On opening, the mass should appear dark blue, the bottom portion not being quite equal in brilliancy to the top owing to the greater degree of heat to which it has been subjected. A loss of about one-third of the original weight occurs, and the mass shrinks considerably.

Charges amounting to 5 tons are treated in stone troughs, 17-20 ft. long and 10-13 ft. wide, placed in a furnace in such a way that they can be reached on all sides by the flame. The troughs are filled to a depth of 12-16 ins. covered with firebricks, and calcined for about 3 weeks.

Ultramarine blue is also prepared directly in shaft furnaces (Fig. 2), described later on (p. 259). Various special furnaces have been patented (Fr. Pata. 410055, 1909; 407098, 403247, 399211, 400103, 1908; 403077, 1909; 425585, 1910).

A rapid process for the direct preparation of the blue has been patented (Fr. Pata. 391770, 391780, 1908). A mixture of china clay (35 parts), carbon (10 parts), sodium alum (40 parts), rosin (8 parts), and sulphur (7 parts) is heated rapidly to 600°-700°, and maintained at that temperature for about 3 hours; the temperature is then raised to 900°, and the mass stirred well for an hour to oxidise it. Powdered sodium

chlorate is then added and the mass stirred for 15 mins.; a further 30 mins. heating then follows. Ultramarine of very superior quality is said to be thus obtained.

Curtius has patented a continuous process. Cast-iron retorts, similar to gas retorts, are employed, lined inside with fire-proof cement. They are set in brickwork, and connected with flues for removing the gases and receivers for condensing sulphur vapour. The charged retorts are closed back and front, but arrangement is made for the admission of air from behind, in order to quickly convert the green ultramarine initially formed into blue. In a modified form of the process, green ultramarine is first produced, discharged into brickwork receptacles beneath the retorts, and directly oxidised to blue (Eng. Pat. 18527, 1890).

The lixiviating, &c. is described later (p. 259).

Indirect process.—The successive stages in

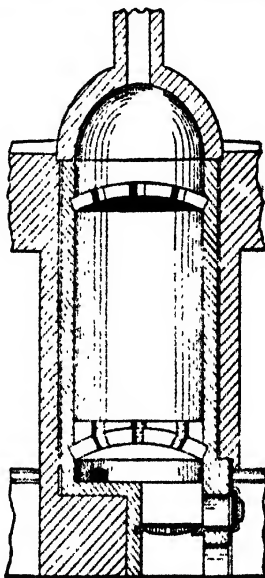


FIG. 2.

this process are mixing, calcining for ultramarine green, crushing, roasting to ultramarine blue, and lixiviating, &c., as in the direct process.

The preparation of the ultramarine green is carried out in either a crucible furnace or a shaft furnace. The former is a kind of muffle furnace, similar to those used in porcelain works, of square (seldom round) section and lined with firebrick. The ground mixture is filled into tapered crucibles of 12-16 ins. high, the lids are fixed on with a mortar of clay, and the crucibles piled in regular rows in the furnace. A furnace will hold several hundred crucibles, the aggregate charge being 6-8 cwt. of mixture. The temperature is slowly raised until the crucibles are at a bright-red heat, and this temperature is then maintained until the formation of ultramarine green is completed; from 7 to 10 hours are required. It is essential to maintain a uniform temperature throughout the furnace.

When the reaction is finished all openings into the furnace are shut tightly and the furnace allowed to cool down, a process that takes several days.

Shaft furnaces are used for calcining larger quantities, up to 2 tons, of material. These are large, cylindrical, vertical furnaces, lined with firebrick. The furnace is situated at the bottom of the shaft; it is covered in by a firebrick vault, the flat top of which forms the floor upon which the bottom layer of crucibles rests. Numerous openings in the vault allow the heating gases from the furnace to pass up into the shaft. The shaft is filled with crucibles charged with the ground mixture, and arranged layer upon layer. Another vault forms the roof of the shaft proper, and through openings in this the gases pass into a dome and thence into the chimney. Fig 2 shows such a furnace. These furnaces possess many advantages; they require no special fuel, accommodate large charges and permit the heat to be equally distributed in a very satisfactory manner. Soda mixtures low in sulphur must be heated slowly at first in these furnaces, a bright-red heat being only attained in 4 hours.

The green ultramarine thus produced exhibits a blue tinge on the surface, and if required to be sold as such, the blue outer portions must be

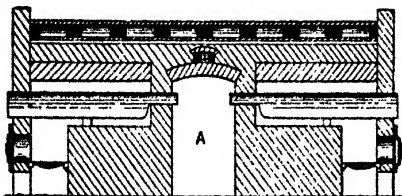


FIG 3.

removed. This is unnecessary if the product is to be directly converted into blue; it must, however, be crushed and ground to powder.

The material is crushed in roller mills to pieces about the size of peas. Glauber salt greens are then ground in dry mills to a degree of fineness that must be determined by preliminary trials, since if ground beyond a certain degree, the brightness of the final ultramarine blue suffers. Soda greens are much softer than Glauber salt greens, and the application of further pressure during the final grinding must be avoided as much as possible. They are usually ground in ball mills, which may be so constructed as to render the preliminary crushing of the raw green superfluous.

The crushed ultramarine green is converted into blue by roasting it with sulphur; the change is completed in a shorter time by this process than if ammonium chloride, hydrochloric acid, chlorine, &c., are used in the place of sulphur. During the process part of the sodium contained in the green becomes converted into sodium sulphate. Two types of furnace are in extensive use (i.) *cylindrical or retort* furnaces, and (ii.) *muffle* furnaces.

The former type consists of an arrangement of strong cast-iron tubes, not exceeding 80 in. long by 16 in. diameter, generally arranged in

sets of three, so that the flame entirely surrounds them. They project about 2 in. from the furnace, both at the back and front, and the ends are closed by tight-fitting sheet-iron caps. The arrangement adopted in large works is indicated in Fig. 3; the furnaces are mounted in pairs, back to back. All the gaseous products pass into the narrow corridor A, closed at both ends by doors; through openings in the roof they pass into the flue B, and thence to the chimney.

In the other type of furnace, the muffle is built into the furnace. The hearth is made of strong fireclay plates with lap joints, luted together, the whole surface being then smoothed. The hearth of the muffle forms the cover of the heating chamber; the products of combustion pass from the grate upwards through flues arranged on the sides of the muffle-walls, thence over the arched roof to the chimney. If the muffle is constructed entirely of fireclay, it is built in completely at the back, and a semi-circular hole left in the front, the base of which is on a level with the hearth. This opening, through which the muffle is charged and discharged, can be closed when necessary by a counterpoised iron slide; and since sulphurous gases escape from this opening, it is arched over with a hood for leading these gases to the chimney, an arrangement that is far less convenient and safe than that employed in the cylindrical furnaces. Sometimes the muffle is built with an iron top, and the front of the muffle closed with an iron cap.

The actual roasting process is carried out either (i.) by adding sulphur to the ultramarine green before heating, or (ii.) by heating the green and gradually adding the sulphur during the process. The requisite amount of sulphur is 7 p.c. with soda green, and 9-10 p.c. with Glauber salt green, of the weight of the crude green taken. In carrying out process (i.), the empty retorts or muffles are heated to a medium red heat for soda green, or to bright redness for Glauber salt green. The mixture of green and sulphur is then quickly introduced, and the containing vessels closed. After half an hour, the product is thoroughly mixed and levelled down, a process that is repeated at half-hourly intervals, until all the sulphur has been burnt off. This is indicated by the manner in which the green colour changes to blue. A further 45 mins. heating is given, and then the fire slowly reduced. The retorts and muffles are then tightly closed and allowed to cool. When method (ii.) is employed, the retorts or muffles are charged with ultramarine green, which is raked over and levelled. The successive portions of sulphur added amount to about 1½ lbs. each with retorts (¼ cwt. charge), and 4½ lbs. each with muffles (1½ cwt. charge). The first addition of sulphur may be made when a lump of that substance ignites as soon as it is thrown on the ultramarine; the charge is then raked over, and the sulphur allowed to burn away. This operation is repeated until a bright blue product is obtained; samples are withdrawn at intervals and spread out with a steel spatula to examine the colour. The product is then cooled as described under (i.).

The filtering boxes employed in the *lixiviating* process are made of pins, 5-7 ft. long, and

40-60 in. wide. About 6 or 8 in. above the solid bottom a false bottom is mounted, perforated with many $\frac{1}{4}$ -in. holes, and covered with strong cotton filtering cloth. The cold, calcined ultramarine blue is mixed with a small quantity of hot water (75°-80°) in a vat, thoroughly mixed, and transferred to a filtering box. In this manner all the numerous filtering boxes are charged. The clear filtrates are united, and if sufficiently concentrated (15°B. or more) the liquid is run into crystallising tanks for the recovery of sodium sulphate. Weaker solutions, and the first two or three washings, are concentrated by utilising waste heat from the furnaces. The ultramarine is washed with hot water until quite free from soluble sulphate, of which the crude blue contains about 15 p.c. It is then ground wet in upright mills between hard stones until the requisite fineness is obtained. During this operation sodium silicate passes into solution, and it is therefore necessary to use soft water for the grinding. The whole is then run into a large wooden vat and allowed to settle for 36-48 hours.

The *levigating process* follows next. The top blue liquor is baled out into another vat and left until the extremely finely divided particles of colour have settled; the product is afterwards added to other preparations. The paste remaining in the large vat is distributed in quantities of about 2 cwt. into levigating tanks, three-fourths filled with soft water, and the colour equally distributed throughout the water. The larger particles settle rapidly, and after 2 hours standing the liquids are run into other tanks. The next deposition of ultramarine takes 5 or 6 hours; the liquid is then baled into other tanks, and a further settling of colour for 12 hours is allowed. The liquid now baled off contains extremely finely divided particles; they are precipitated in a fourth series of tanks by the addition of alum, dilute mineral acid, milk of lime or other saline solutions, and the resulting blue paste is pressed. Passing from the first to the fourth series of tanks, the ultramarine becomes successively lighter, finer, bluer, and stronger. The different grades of product are then dried in sheds exposed to air, or on drying hearths heated by waste furnace heat, or in special drying rooms, &c.

The product dries in hard lumps, which must be powdered and sifted; for this purpose ball mills fitted with a continuous sifting device are employed. Very fine brands of ultramarine are sifted in centrifugal sifters or else in a Jasse sifter. It then remains to mix together the various shades and sorts in order to produce the standards of sale; this part of the work is of great importance, as the tinctorial power, fineness of division, depth and purity of colour in each standard, have to be exactly reproduced in bulk.

In making the cheaper brands of ultramarine blue, the pure material is mixed with from 10 to 50 p.c. of gypsum. The latter has an extremely bad effect upon the brightness of certain kinds of ultramarine, which is minimised by incorporating a little glycerol or vaseline into the mixture.

The development of the manufacture of ultramarine has been remarkable. The price in the year of its discovery was about 16s. per lb., but

competition soon brought this down, and created a demand. Guimet commenced the manufacture in 1828. Between 1830 and 1840 manufactures were established at Cologne and Nuremberg; between 1840 and 1850 nine more were started; 1850-1860 saw nine more; 1860-1870 at least a dozen, and from 1870-1888 four or five, while an equal number of the others had closed down. At the present day there are about a hundred factories, mainly in Germany and France, although a few are in England, Austria, and the United States, and the annual production of ultramarine is between ten and fifteen thousand tons.

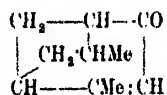
For further information on ultramarine, v. Zerr and Ribencamp's *Treatise on Colour Manufacture*, translated by Mayer (Griffin & Co.); Bersch's *Mineral and Lake Pigments*, translated by Wright (Scott, Greenwood & Son); and Hoffmann's *Ultramarine* (Vieweg u. Sohn, Braunschweig).

ULTRAMARINE, GREEN, v. ULTRAMARINE; also CHROMIUM.

ULTRAMARINE, YELLOW, v. ULTRAMARINE. The term is also applied to *Barium Chromate*, v. BARIUM; also CHROMIUM.

UMBELLIFERONE v. GUM RESINS.

UMBELLULARIA CALIFORNICA (Nutt). An evergreen tree indigenous to California, known locally as 'California Laurel,' 'Mountain Laurel,' 'California Bay-tree,' 'Spice-tree,' 'Pepper-wood,' &c. The essential oil is an aromatic liquid possessing a peculiar pungency due to the presence of a ketone *umbellulone* $C_{10}H_{14}O$



which forms 60 p.c. of the essential oil; the other constituents are eugenol, 1.7; eugonol methyl ether, 10; *l*-pinene, 6.0; cineol 20.0 p.c.; safrole and fatty acids, traces (Power and Lees, *Chem. Soc. Trans.* 1904, 85, 629; Tutin, *ibid.* 1906, 89, 1104; 1908, 93, 252).

UMBELLULIC ACID v. HENDECATOIC ACIDS.

UMBELLULONE v. LAURUS NOBILIS.

UMBER. A brown mineral pigment, consisting of a mixture of the hydrated oxides of iron and manganese, mechanically associated with a large proportion of earthy matter of variable character. The material is prepared for the market by grinding and levigation. Raw umber is exported from Cyprus, Turkey, and Umbria in Italy (hence the name). It is also worked to a limited extent in Derbyshire and Pennsylvania.

Sir A. H. Church (*The Chemistry of Paints and Painting*, London, 1901) gives the following analysis of a choice sample of raw umber from Cyprus; water, given off at 100°C., 4.8 p.c.; water expelled at a red heat, including organic matter, 8.8; Fe_2O_3 , 48.5; MnO_2 , 19; CaO , 1.4; MgO , 0.5; Al_2O_3 , 2.1; P_2O_5 , 0.9; SiO_2 , 13.7; CO_2 , &c., 0.3. Part of the manganese probably exists as Mn_2O_3 . For other analyses of umbers, siennas, and ochres, v. G. H. Hurst in *Chem. News*, 1889, 59, 172. He found crude Derby-

shire amber to yield the following results: hygroscopic water, 13.47 p.c.; combined water, 5.17; BaSO_4 , 30.10; SiO_2 , 4.43; CaSO_4 , 2.15; CaCO_3 , 2.61; Al_2O_3 , 8.08; Fe_2O_3 , 22.50; MnO_2 , 11.53. A sample of amber, from Caldbeck Fells, Cumberland, as prepared for market by grinding and washing gave: Fe_2O_3 , 47.14; MnO_2 , 11.17; CuO , 3.23; Al_2O_3 , 7.66; SiO_2 , 24.70; combined water, 6.18; CaO , MgO , traces=100.08 (J. Soc. Chem. Ind. 1890, 953, where are given details of the method of preparation).

Hurst regards most ochres as alteration products, formed mainly by the oxidation and hydration of pyrites *in situ*, and mechanically mixed with silica, clay, and other earthy matter. Umbers may have been washed as a fine sediment from deposits of iron and manganese ores. The pigment termed *burnt amber* is merely amber which has been exposed to heat, whereby its colour becomes somewhat reddened. *Cologne amber* is an earthy lignite.

References.—G. P. Merrill, *The Non-Metallic Minerals*, 2nd ed., New York, 1910, 104; chapter on Mineral Paints in *Min. Res. U.S. Geol. Survey*, annual volumes; v. OCHRE.

L. J. S.

UNAL. Trade name for solid hydrochloride of *p*-aminophenol, used as a photographic developer. Rodinal is a concentrated solution of the same compound.

UNDECATOIC ACIDS and UNDECYLIC ACID v. HENDECATOIC ACIDS.

UPAS ANTIAR v. ANTIAR RESIN.

UPAS TIEUTE v. NUX VOMICA.

URACIL v. ERGOT and PYRIMIDINES.

URALITE. A name proposed by G. Rose in 1831 for pseudomorphs of hornblende after augite from the Ural Mountains. (For a *résumé* of the literature, v. A. Wilmore, *Geol. Mag.* 1910, [v.] 7, 357.) Also used as a trade-name for a preparation of serpentine-asbestos, made into the form of boards for fire-proof partitions (v. ASBESTOS).

URAMIL v. PYRIMIDINES.

URANINITE v. PITCHBLENDE.

Alfred Schoep (*Bull. Soc. chim. Belg.* 1923, 32, 274-281) has analysed specimens of Katanga pitchblende, estimating total uranium as U_3O_8 and UO_2 in presence of UO_2 by Hillebrand's method of heating the mineral in a sealed tube with dilute sulphuric acid in an atmosphere of carbon dioxide, and volumetric estimation of the dioxide with potassium permanganate. The results lead to the conclusion that the purified mineral (i.e. uraninite) has the formula $(\text{UO}_2)_2(\text{UO}_3)_2$ (cf. Blomstrand, *Chem. Soc. Abstr.* 1884, 1102). This is discussed in comparison with results obtained by other workers for pitchblende from Katanga and other sources, and also for thorianite, and reasons are given for regarding the UO_2 as an oxidation product of the UO_3 , of which the original mineral consisted. Thus the author maintains that the formula of uraninite is UO_3 , as that of thorianite is ThO_3 , the two minerals being isomorphous and analogous in chemical composition. The percentage of the dioxide is greater in fresh specimens of the mineral; some consist of $\text{ThO}_3 \cdot \text{UO}_2$, in which all the uranium compound has undergone oxidation. Thorianite contains

various proportions of UO_2 , and isomorphous mixtures of the two dioxides may be prepared artificially (*Chem. Soc. Abstr.* 1923, 124, ii. 647).

URANITE. An early name for the 'uranium micas' in use before these had been separated into the following species, the most important of which are autunite (calco-uranite) and torbernite (cupro-uranite) (*qq.v.*).

Torbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, tetragonal.

Zeunerite $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, tetragonal.

Autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic.

Uranospinite $\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic.

Uranocircite $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, orthorhombic. L. J. S.

URAMINO ANTIPYRIN. Trade name for antipyrilurea.

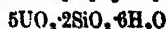
URANIUM. Sym. U. At.wt. 238.2 (238.17 Hönigschmid; 238.5 Richards and Merigold; Lebeau). In 1789 Klaproth prepared from *pitchblende* some compounds of a new element, which he called *uranium* (Crell's *Ann.* 1789, [ii.] 400). The compounds of uranium were studied by Richter, Arvedson, Berzelius, and others. In 1840 Pélégot showed that what had previously been thought to be uranium was really one of its oxides; he prepared the metal by reducing uranous chloride with potassium (*Ann. Chim.* 1842, [iii.] 5, 5). The work of Pélégot was confirmed and extended by Ebelmen (*ibid.* 1842, [iii.] 5, 189), Wertheim (*ibid.* 1844, [iii.] 11, 49), Rammelsberg (*Pogg. Ann.* 1842, 55, 318; 56, 125), and Hermann (*Ueber einige Uranverbind.* Göttingen, 1861).

Occurrence.—Uranium is not very abundant; its chief ore is *pitchblende* or *uraninite*, which consists of impure U_3O_8 , and is found in Cornwall, at Joachimsthal (Bohemia), and other localities. It contains from 40 to 90 p.c. of U_3O_8 (Hermann, *J. pr. Chem.* 1859, [i.] 76, 326; Ebelmen, *Ann. Chim.* 1843, [iii.] 8, 498; Whitney, *Amer. J. Sci.* 1849, [ii.] 7, 434; Genth, *ibid.* 1857, 23, 421; Zimmermann, *Annalen*, 1886, 232, 300). *Clevite* and *bröggerite* are varieties of *pitchblende* rich in rare earths. *Carnotite* is a vanadate of potassium and uranium, found in Utah and Colorado (Friedal and Cumenge, *Bull. Soc. chim.* 1899, [ii.] 21, 328). *Samaraskite* is a uranotantalite of iron and yttrium, found in Siberia (Miaak) and North Carolina (Rammelsberg, *Pogg. Ann.* 1877, 160, 658); *fergusonite* is a complex columbate of yttrium, cerium, uranium, calcium, and iron (Rammelsberg, *ibid.* 1873, 150, 200).

Schoep, of the University of Ghent, has identified several new uranium minerals, to which he has assigned the following formulae: *curite*, $\text{PbO} \cdot 5\text{UO}_2 \cdot 4\text{H}_2\text{O}$; *kasolite*



dewindtite, $\text{PbO} \cdot 2\text{UO}_2 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; *soddite*



becquerelite, $\text{UO}_2 \cdot x\text{H}_2\text{O}$. A uranotitanocolumbate of calcium containing small amounts of rare earth has been designated as *mendeleeffite*; the chemical formula has not been established definitely, but the mineral contains approximately U_3O_8 23.6 p.c., and CaO 15 p.c. It is considered as a variety of *betafite*, but contains

no water of crystallisation (J. Soc. Chem. Ind. 1923, 42, 1061).

Nearly all the phosphates, silicates, and zirconates of the rare earths contain small quantities of uranium, notably *zenotime*, *öschelite*, *columbite*, *cerite*, and *monazite*. *Thorianite* (a THORIUM) contains from 10 to 20 p.c. of uranosouranic oxide. See also Szilárd, *Le Radium*, 1909, 6, 233.

Naturally occurring uranium minerals are radioactive; it was from the pitchblende of Joachimsthal that radium was first prepared, whilst helium was originally obtained from cleveite.

Treatment of uranium minerals; preparation of uranium.—The chief source of uranium compounds is pitchblende, which, after a preliminary roasting, is heated in a reverberatory furnace with sodium carbonate. The product is extracted with warm dilute sulphuric acid and filtered, the residue being used in the preparation of radium salts. The filtrate is worked up commercially for uranium compounds as described under sodium diuranate (p. 265). The following method is due to Wöhler; the liquid is treated with hydrogen sulphide to remove arsenic, antimony, copper, lead, and bismuth, and after oxidising the filtrate with nitric acid, excess of ammonia is added. The washed precipitated iron hydroxide and ammonium uranate are digested at 100° with concentrated ammonium carbonate, containing ammonia in excess, to dissolve the ammonium uranate. The double salt, ammonium uranyl carbonate, crystallises out on cooling the filtered liquid. From the mother liquor a quantity of ammonium uranate can be obtained by precipitating any zinc, nickel, and cobalt with ammonium sulphide, and evaporating the filtrate. Both ammonium uranate and ammonium uranyl carbonate leave the green oxide U_3O_8 when ignited in the air.

Carnotite is fused with potassium hydrogen sulphate and the mass extracted with water; from the solution the double sulphates of uranium and vanadium with potassium sulphate are crystallised out. The crystalline product is reduced with zinc and sulphuric acid, and the vanadium then precipitated with ammonia and ammonium carbonate. From the filtrate the uranium is thrown down as ammonium uranate by boiling (Gin, *Chem. Zentr.* 1906, ii, 1172; cf. Haynes, *Mines and Minerals*, 1909, 30, No. 3, 139).

Separation of uranium from thorium and rare earths in pitchblende.—The mineral is dissolved in nitric acid and the silica removed in the usual manner. The filtrate is repeatedly evaporated to dryness for the elimination of free acid. The residue is dissolved in water; the solution in a beaker is neutralised exactly with a few drops of very dilute ammonia, strongly diluted, and boiled for 10 minutes with excess of thiosulphate. After standing 24 hours the precipitate is filtered off, well washed with water containing a little thiosulphate, dissolved in hydrochloric acid, and re-precipitated, after elimination of free acid, as before. If properly performed, the second precipitation removes the last of the cerium. The precipitate, which contains part of the uranium, is dissolved in hydrochloric acid, and the thorium precipitated as oxalate. The

filtrate is evaporated to dryness in a porcelain dish, and the residue cautiously heated with strong sulphuric acid for the decomposition of the oxalic acid; the acid is finally heated until strong fumes appear, and the uranium precipitated with ammonia after cooling and diluting the solution. The filtrate from the thiosulphate precipitate, containing the balance of the uranium is freed from rare earths by means of oxalic acid. The excess of precipitant is destroyed as before, and the iron separated from uranium by precipitation with ammonium carbonate, uranium being again precipitated with ammonia. The united uranium precipitates are ignited and weighed (W. Riss, *Chem. Zeit.* 1923, 47, 765-766; Analyst, 1923, 48 626).

Metallic uranium was first prepared by Pélégot (l.c.) by reducing the tetrachloride with potassium. Zimmermann (Annalen, 1883, 216, 1) replaced the potassium by sodium (cf. Lely and Hamburger, *Zeitsch. anorg. Chem.* 1914, 87, 209). It is better to employ the double chloride of uranium and sodium, and magnesium may be used in place of potassium (Moissan, *Compt. rend.* 1896, 122, 1088). These methods are unsatisfactory, since uranium tetrachloride is extremely hygroscopic. Uranium is best prepared by heating 500 parts of the oxide U_3O_8 with 40 parts of sugar carbon in the electric furnace in a carbon tube. The product, which contains a little carbon, is purified by heating it in a crucible brasqued with uranium oxide, and embedded in another crucible brasqued with titanium, to prevent access of nitrogen to the uranium (Moissan, *Compt. rend.* 1893, 116, 349). Reduction of uranium dioxide by carbon begins at 1500° (Greenwood, *Chem. Soc. Trans.* 1908, 93, 1492). The oxides of uranium may also be reduced by heating with aluminium powder (Aloy, *Bull. Soc. chim.* 1901, [iii.] 25, 153; Stavenhagen, *Ber.* 1899, 32, 3065; Stavenhagen and Schuchard, *ibid.* 1902, 35, 900; Giolitti and Tavanti, *Gazz. chim. ital.* 1908, 38, ii, 239; cf. E. Rideal, *J. Soc. Chem. Ind.* 1914, 33, 673). Uranium may also be prepared by the electrolysis of the fused double chloride of uranium and sodium, in an inert atmosphere, using carbon electrodes (Moissan, *Compt. rend.* 1896, 122, 1088); and is obtained in the pyrophoric state by heating its amalgam in a vacuum (Férée, *Bull. Soc. chim.* 1901, [iii.] 25, 622).

According to R. W. Moore (*Trans. Amer. Electrochem. Soc.* 1923, 95), metallic uranium is conveniently prepared by reducing with metallic sodium the green crystalline tetrachloride, obtained by heating the oxide U_3O_8 to 500°C. for several hours in a current of sulphur chloride vapour, and subliming the product in a current of chlorine. The resulting mass is broken up in an atmosphere of nitrogen and mixed with metallic sodium that has been distilled *in vacuo* and cut into small pieces under anhydrous benzene. The mixture is heated in a steel bomb in a vacuum, and the reaction product is extracted first with absolute alcohol to remove excess of sodium, then with water to remove sodium chloride, and finally with 2 p.c. acetic acid. The heavy brownish residue of metallic uranium is washed with acetone and dried *in vacuo*. A yield of 90 p.c. of the theo-

retical quantity of metal containing 99.8 p.c. U is readily obtained. The powder is very pyrophoric, but may be pressed into discs in a hydraulic press in an atmosphere of nitrogen, and is then no longer pyrophoric. These discs may be melted by the arc in an atmosphere of rarefied argon to bright, steel-grey, ductile, metallic buttons, which readily tarnish on exposure to the air (J. Soc. Chem. Ind. May 11th, 1923, 406).

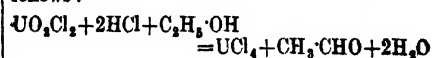
Properties.—Pure uranium is a white metal, which takes a high polish; its density is 18.7, and its specific heat 0.02765 (Zimmermann, *Annalen*, 1886, 232, 310; Ber. 1882, 15, 851). It melts at a white heat, and can be distilled in the electric furnace (Moissan, *Compt. rend.* 1906, 142, 425; cf. *ibid.* 1893, 116, 1429; 1896, 122, 1088). The most prominent lines in the emission spectrum are in the yellow (Thalén, *Ann. Chim.* 1869, [iv.] 18, 239; Hasselberg, K. Svenska. Vet-Akad. Handl. 1910, 45, 3; Pollok, *Sci. Proc. Roy. Dubl. Soc.* 1909, 11, 331). Most uranium compounds possess marked absorption spectra (Morton and Bolton, *Chem. News*, 1873, 28, 47, 113, 164; Jones and Strong, *Phil. Mag.* 1910, [vi.] 19, 566; Strong, *Zeitsch. physikal. Chem.* 1910, 11, 668) and are fluorescent, the fluorescence spectra having been studied by E. Becquerel (*Ann. Chim.* 1872, [iv.] 27, 539) and H. Becquerel (*Compt. rend.* 1886, 101, 1252; 1907, 144, 459); v. also Becquerel and Kamerlingh-Onnes (*ibid.* 1910, 150, 647) for phosphorescence at low temperatures.

Uranium in the form of powder is unaltered in dry air at ordinary temperatures; it burns in oxygen at 170°. It unites directly with fluorine in the cold, and with chlorine, bromine, and iodine when gently heated. At 500° it combines with sulphur and selenium, and at 1000° unites readily with nitrogen. It forms a crystalline carbide decomposed by water (Moissan, *Compt. rend.* 1896, 122, 1088). It forms alloys with certain metals; that with iron is pyrophoric, this property varying directly with the content of uranium.

Uranium powder decomposes water slowly at ordinary temperatures, more rapidly at 100°. It dissolves readily in hydrochloric, sulphuric, and nitric acids.

Uranium is closely allied to the elements chromium, molybdenum, and tungsten; they all exhibit a maximum valency of six, yield acidic trioxides, and form numerous halogen derivatives in which their valencies vary from two to six. These halogen derivatives in general bear little resemblance to well-defined salts, as is indicated by their volatility, solubility in numerous organic media, and the ease with which they are hydrolysed by water. There are two principal series of uranium salts: (i.) the *uranous* compounds, corresponding to the basic oxide UO_2 ; and (ii.) the *uranyl* compounds, in which the group UO_2 functions as a bivalent metallic radiole. Besides these, there exist *uranates*, *diuranates*, and *peruranates*, analogous to the corresponding chromium derivatives (v. O. de Coninck, *Bull. Acad. roy. Belg.* 1909, 175). The *uranous* salts are usually green or blue, and in solution are readily oxidised to uranyl compounds, even by air, the rate of oxidation being

proportional to the concentration of the solution and inversely proportional to the square of the concentration of the hydrogen ions present (McCoy and Bunzel, *J. Amer. Chem. Soc.* 1909, 31, 367.) They are obtained by the reduction of uranyl compounds (v. Aloy and Anber, *Bull. Soc. chim.* 1907, [iv.] 1, 569; Colani, *Ann. Chim.* 1907, 12, 59). The *uranyl* salts are generally yellow, with a greenish fluorescence. They are highly sensitive to light, and are employed in photography (Niepce de Saint Victor, *Compt. rend.* 1858, 46, 448, 489; Titlestad, *Zeitsch. physikal. Chem.* 1910, 72, 287; Bacon, *Philippine J. Sci.* 1910, 5, 281). Under the influence of light, uranyl salts are converted into uranous salts in the presence of the acid entering into the constitution of the salt and a readily oxidisable substance such as alcohol. The reaction which occurs is as follows:—



Two molecules of acid are necessary for each molecule of uranyl salt. In this way, the fluoride, chloride, bromide, iodide, and sulphate have been prepared, and an aqueous solution of the nitrate. If an insufficient amount of acid is present, basic salts are obtained. If the reaction is allowed to proceed further, a black precipitate of uranous hydroxide is obtained (Bauer, *Schweiz. Chem. Zeit.* 1918, 2, 40; Hatt, *Zeitsch. physikal. Chem.* 1918, 92, 513). Oxidations and reductions brought about by uranium compounds under the influence of light are closely related to the changes which the uranium salt itself undergoes. Thus when alcohol or dextrose is added to a 1 p.c. solution of uranium acetate the former is oxidised and the latter is reduced to the violet oxide $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$. If in addition methylene blue is added to the above solution the dextrose is oxidised and the methylene blue is reduced, the uranium salt playing the rôle of an oxido-reducing catalyst. Aldehydes and lower fatty alcohols can all be similarly oxidised, and the progress of the reaction can be followed by the reduction of the uranium salt or of methylene blue; the phenols, although readily oxidisable under ordinary circumstances, behave anomalously, owing to the antioxygen character of these substances, and they are not oxidised themselves, nor do they allow the oxidation of other substances to proceed. A red coloration is produced on adding the uranium compound to the phenol solution, but no other apparent change occurs. The solution does, however, contain a certain amount of uranous salt, and the violet oxide can be precipitated from it by heating to 100°C. (Aloy and Valdigné, *Compt. rend.* 1923, 176, 1229; J. Soc. Chem. Ind. 1923, 42, 574 A). Uranyl salts are somewhat analogous to basic salts, but they are stable in solution, being only hydrolysed to a slight extent. On electrolysis the uranyl ion UO_2 migrates to the cathode. Uranyl salts form numerous complex derivatives, especially with salts of organic acids (Dittrich, *Zeitsch. physikal. Chem.* 1899, 29, 249; Ley, *ibid.* 1900, 30, 193; Ber. 1900, 33, 2658; Kohlschütter, *Annalen*, 1900, 311, 1).

Uranium salts are radioactive, emitting γ -rays, and producing a radioactive element

called *Uranium-X* (v. *infra*, URANIUM-X and RADIOLOGY).

For the relation of uranium-X to uranium-Z, see Hahn (Zeitsch. physikal. Chem. 1923, 103, 461).

Atomic weight.—This was taken as *circa* 120 until Mendeléeff pointed out the similarity of uranium to chromium, molybdenum, and tungsten, and proposed the value 240 (Annalen, Suppl. 1872, 8, 178; Chem. News, 1880, 41, 39), which assigned to uranium a position in the Periodic Classification in the same Group as the elements just mentioned. The determination of the specific heat of the metal and the vapour densities of uranous chloride and bromide (Zimmermann, Annalen, 1882, 216, 1) confirmed the views of Mendeléeff. The actual value at present adopted (238.5) rests mainly on the work of Zimmermann (Annalen, 1886, 232, 299), Aloy (Ann. Chim. 1901, [vii.] 24, 418); of Richards and Merigold (Proc. Amer. Acad. 1902, 37, 365; Zeitsch. anorg. Chem. 1902, 31, 235); of Lebeau (Compt. rend. 1912, 155, 163); and of Hönigschmid (Compt. rend. 1914, 158, 2004).

OXIDES AND OXYACIDS.

Uranium dioxide or *Uranous oxide* UO_2 is obtained by heating the green oxide or uranyl oxalate in a stream of hydrogen (Berzelius, Péligot, Ebelmen); or by electrolyzing uranyl nitrate solution (O. de Coninck and Camo, Bull. Acad. Roy. Belg. 1901, 321); these methods yield a brown pyrophoric powder of sp.gr. 8.2. The reduction of uranyl chloride solution with magnesium or aluminium yields uranous oxide as a black powder (de Coninck, *ibid.* 1909, 744). It is obtained as black, microscopic crystals by reducing crystalline uranic hydroxide in hydrogen (Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368); and as jet black octahedra by fusing the amorphous form with borax, and washing the product with dilute hydrochloric acid (Hillebrand, Zeitsch. anorg. Chem. 1893, 3, 249). It is a basic oxide, and dissolves in concentrated acids to form green uranous salts. It combines directly with chlorine and bromine, forming uranyl chloride and bromine, and burns when heated in air, the oxide U_2O_5 being produced.

On a technical scale it is prepared for the production of ferro-uranium by fusing 35 parts of sodium chloride, 20 parts of sodium uranate, and 1 part of powdered charcoal in a cast-steel pot. The cooled mass is lixiviated with water and the uranium oxide washed by decantation, and is freed if necessary from iron and aluminium by treatment with 5 p.c. hydrochloric acid.

Uranous hydroxide $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ is precipitated by adding an alkali to a solution of a uranous salt and boiling; it forms black flakes, and readily dissolves in dilute acids (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranium trioxide, uranic oxide, uranic anhydride, or uranyl oxide UO_3 is a chamois yellow powder, obtained by heating uranyl nitrate to 250° ; also by heating the hydroxide or double uranyl ammonium carbonate to 250° (Ebelmen, Ann. Chim. 1842, [iii.] 5, 199; de Coninck, Compt. rend. 1901, 132, 204; Bull. Acad. Roy. Belg. 1904, 363, 448; Lebeau, Compt. rend. 1912, 154, 1806). It oxidises to

the green oxide when heated in air, and is reduced by hydrogen to uranous oxide. In contact with water it is transformed into uranic acid $\text{UO}_2(\text{OH})_2$. When heated *in vacuo* at 502° it forms the oxide U_2O_5 .

This oxide is slightly basic, but only one-third of its oxygen can be replaced by acidic radicles; the salts thus produced are of the type UO_2R_2 , and are called *uranyl* compounds. Towards strong bases, uranic oxide behaves as an acid anhydride, similar to chromic anhydride.

For heat of formation see, Mixer, Amer. J. Sci. 1912, [iv.] 34, 141.

Uranic hydroxide or *uranic acid* $\text{UO}_2 \cdot \text{H}_2\text{O}$ or $\text{UO}_2(\text{OH})_2$ is best prepared by heating a solution of uranyl nitrate in alcohol until no more brown fumes are evolved, and washing the yellow precipitate with boiling water (Malaguti, Ann. Chim. 1843, [iii.] 9, 463). It may also be obtained, mixed with the dihydrate, by evaporating a solution of uranyl nitrate to complete dryness (de Coninck, Compt. rend. 1909, 148, 1462). The *dihydrate* $\text{UO}_2 \cdot 2\text{H}_2\text{O}$, which is obtained as a yellow precipitate by boiling the double uranyl ammonium carbonate with water, loses water at 100° , and yields the hydroxide $\text{UO}_2 \cdot \text{H}_2\text{O}$ (Ebelmen, *l.c.*; for other methods, v. Jacquelin, Ann. Chim. 1842, [iii.] 5, 199; Riban, Compt. rend. 1881, 93, 1140; Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368). Uranic hydroxide has a sp.gr. of 5.9; it does not alter in air, and when heated to 300° it is dehydrated. For the preparation of the colloidal hydroxide, v. Szilárd, J. Phys. Chem. 1907, 5, 488, 636.

Uranosouranic oxide or *Green oxide of uranium* $\text{U}_3\text{O}_8 (= \text{UO}_2 \cdot 2\text{UO}_3)$ occurs more or less pure as *pitchblende*. It can be obtained by heating any of the other oxides to a red heat in air, also by igniting ammonium uranate or any uranium salt of a volatile acid. It forms a dark-green, lustrous powder of sp.gr. 7.2, insoluble in water; in concentrated acids it dissolves, forming a mixture of uranous and uranyl salts. This oxide is employed for producing a black glaze on porcelain. It is radioactive, and has been suggested as a suitable standard of α -ray radioactivity (McCoy and Ashman, Amer. J. Sci. 1908, 26, 521).

A violet hydroxide can be obtained by the action of light on aqueous uranyl oxalate or alcoholic uranyl acetate (v. Aloy, Bull. Soc. chim. 1900, [iii.] 23, 368; cf. Aloy and Rodier, *ibid.* 1920, [iv.] 27, 101). A large number of violet compounds of uranium exist, all of which, by loss of their acid radicles, tend to become transformed into the green hydrated oxide $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$. When heated in a current of hydrogen the oxide U_3O_8 shows signs of reduction at 625° , the reduction being complete at 650° , the product being UO_2 . In a vacuum U_3O_8 may be heated to 2000° before it dissociates to UO_2 .

Uranium pentoxide is a black powder, used for producing a black glaze on porcelain. According to Zimmermann (Annalen, 1886, 232, 273) it is a mixture of U_2O_5 and UO_3 .

Uranium peroxide UO_4 is only known in the hydrated form as *peruranic acid* $\text{UO}_4 \cdot 2\text{H}_2\text{O}$. It is obtained by adding hydrogen peroxide to a mixture of uranyl and uranous sulphate in aqueous solution, and drying the precipitate

over concentrated sulphuric acid (de Coninck, *Bull. Acad. Roy. Belg.* 1909, 692; cf. Fairley, *Chem. Soc. Trans.* 1877, 31, 133; Zimmermann, *Annalen*, 1886, 232, 273; Alibegoff, *ibid.* 1886, 233, 123). It forms a yellow powder, which loses oxygen when heated; when treated with alkali hydroxides it yields a mixture of alkali uranate and peruranate.

Other hydrates are also known (Hüttig and von Schroeder, *Zeitsch. anorg. Chem.* 1922, 121, 243). These substances are probably compounds of uranium trioxide and hydrogen peroxide. It is doubtful if uranium tetroxide exists.

URANATES.

The alkali uranates are formed by precipitating uranyl salts with alkali hydroxides; those of the other metals by adding ammonia to a mixture of a uranyl and a metallic salt. They are yellow, insoluble in water, but soluble in acids. The majority are of the type $M_2O \cdot 2UO_3$, analogous to the dichromates (v. Drenkmann, *J.* 1861, 255; Patera, *J. pr. Chem.* 1850, 51, 125; Debray, *Ann. Chim.* 1861, [iii.] 61, 514; Grandeau, *ibid.* 1886, [vi.] 8, 224; Zimmermann, *Annalen*, 1882, 213, 290; Ditte, *Compt. rend.* 1882, 95, 988; de Coninck, *Bull. Acad. roy. Belg.* 1909, 173, 835).

Ammonium uranate. This is obtained as a yellow, voluminous precipitate by adding ammonia to a solution of a uranyl salt. It is prepared by boiling a solution of uranyl sodium carbonate with ammonium sulphate; or by boiling sodium diuranate (*q.v.*) with concentrated ammonium chloride solution, and forms a fine, deep yellow-coloured powder, that is sometimes used commercially, under the name *uranium yellow*, in the preparation of uranium glass (v. Stolba, *Zeitsch. anal. Chem.* 1864, 3, 74) and sodium diuranate.

Potassium uranate K_2UO_4 , obtained by fusing uranyl chloride with a mixture of potassium and ammonium chlorides (Zimmermann, *l.c.*), forms yellow, rhombic crystals.

Potassium diuranate $K_2U_2O_7$, is obtained in the form of a trihydrate by precipitating a uranyl salt with potassium hydroxide and drying the product at 100° (Patera, *l.c.*).

Sodium uranate Na_2UO_4 may be obtained by fusing the green oxide with sodium chloride and sodium carbonate (Ditte, *l.c.*; Zimmermann, *l.c.*).

Sodium diuranate $Na_2U_2O_7$, is prepared commercially from pitchblende, which is powdered and roasted to remove the greater part of the sulphur, arsenic, and molybdenum. The ore is then heated in a reverberatory furnace with sodium carbonate and a little sodium nitrate. The product is washed with water, when soluble arsenate, molybdate, tungstate, and vanadate of sodium are removed; sodium uranate is insoluble in water. The insoluble residue is dissolved in dilute sulphuric acid, the solution evaporated to remove excess of acid, diluted and filtered from silica, lead sulphate, and basic sulphate and arsenate of bismuth, and an excess of sodium carbonate solution added. A solution of uranyl sodium carbonate is thus obtained, while the basic

carbonates of iron, aluminium, nickel, and cobalt are precipitated and removed. The uranium is then precipitated as sodium diuranate by adding sodium hydroxide, or by neutralising with sulphuric acid and boiling. The yellow precipitate is thoroughly washed, dried, and pulverised (Patera, *J. pr. Chem.* 1849, [i.] 46, 182; 1850, 51, 122; Gieseke, *J.* 1852, 779; Anthon, *J.* 1860, 698; Kessler, *J.* 1857, 199; Hofmann and Strauss, *Ber.* 1900, 33, 2316; cf. Metzger and Heidelberger, *J. Amer. Chem. Soc.* 1909, 31, 1040).

Sodium diuranate is found in commerce as the hexahydrate $Na_2U_2O_7 \cdot 6H_2O$. It is a fine yellow powder, known as *uranium yellow*, and is used in painting and staining glass and porcelain, and for making the fluorescent 'uranium glass.'

PERURANATES.

These salts are formed by the action of hydrogen peroxide and alkali hydroxides on uranyl salts, and are usually precipitated by means of alcohol as orange-yellow crystals. The sodium salt has the formula $Na_2UO_6 \cdot 8H_2O$. These compounds have been studied by Fairley (*Chem. Soc. Trans.* 1877, 31, 134) and Melikoff and Pissarjewsky (*Ber.* 1897, 30, 2092; *Zeitsch. anorg. Chem.* 1898, 18, 59; *J. Russ. Phys. Chem. Soc.* 1902, 24, 472).

A red potassium peruranate $K_2UO_6 \cdot 3H_2O$ is obtained when peruranic acid is added to hydrogen peroxide containing alcohol, and the solution treated with potassium hydroxide (Aloy, *Bull. Soc. chim.* 1903, [iii.] 29, 292). The formation of this substance may be employed as a delicate colorimetric test for the presence of uranium (Aloy, *ibid.* 1902, [iii.] 27, 734).

URANIUM COMPOUNDS.

Uranium tetrafluoride or *Uranous fluoride* UF_4 is the main product of the action of fluorine on uranium. It is prepared by adding hydrogen fluoride to a solution of uranous chloride, and forms a green powder, insoluble in water and dilute acids (Smithells, *Chem. Soc. Trans.* 1883, 43, 125; Bolton, *J.* 1886, 209). It leaves a residue of oxide when heated in air; and forms double fluorides with the alkali fluorides.

Uranium hexafluoride UF_6 is best obtained by the action of fluorine on the cooled pentachloride—



It forms colourless, monoclinic prisms, which sublime at ordinary temperatures under diminished pressure. It melts at 69.2° under a pressure of two atmospheres, and boils at 56.2° . The solid has a density of 4.68; the vapour gives a value 11.7 (air=1). It is very hygroscopic, and highly reactive (Ruff and Heinzelmann, *Zeitsch. anorg. Chem.* 1911, 72, 63; cf. *Ber.* 1909, 42, 492).

Uranium trichloride UCl_3 , is obtained by heating the tetrachloride in hydrogen (Péligot, *Ann. Chim.* 1842, 5, 20), and is a reddish-brown substance, which easily dissolves in water, forming a red solution that slowly evolves hydrogen and becomes green.

Uranium tetrachloride or *Uranous chloride*

UCl_4 is produced when uranium is heated in chlorine, and is prepared by passing chlorine over heated uranium carbide or a mixture of any oxide of uranium with carbon (Péligot, *Annalen*, 1842, 43, 258; Zimmermann, *ibid.* 1882, 213, 320; 1883, 216, 8; Roscoe, *Chem. Soc. Trans.* 1874, [ii.] 12, 933; Aloy, *Bull. Soc. chim.* 1899, [iii.] 21, 264; Roderburg, *Zeitsch. anorg. Chem.* 1913, 81, 122). It forms dark-green octahedra, is volatile at a red heat, and the vapour has a density (air=1) of 13.33 (Zimmermann). In molten bismuth chloride as solvent the molecular weight is 373 (theory=380.3) (Rüchheimer and Gonder, *Annalen*, 1908, 364, 45). It is extremely deliquescent, fumes in the air, and readily dissolves in water with evolution of heat; the solution is a powerful reducing agent. The solution reacts acid, and on evaporation, leaves an oxychloride. Boiling water completely hydrolyses the chloride.

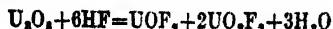
It forms double chlorides with the chlorides of the alkali and alkaline earth metals (Moissan, *Compt. rend.* 1896, 122, 1088; Aloy, *Bull. Soc. chim.* 1899, [ii.] 21, 264).

Uranium pentachloride UCl_5 is obtained by the direct union of the tetrachloride and chlorine. It exists in two forms: (i.) long, dark needles which are green by reflected, and ruby-red by transmitted, light, and (ii.) a light-brown, mobile powder. It is very hygroscopic, and is decomposed by water. It cannot be volatilised without decomposition; in an atmosphere of carbon dioxide, dissociation into the tetrachloride and chlorine is complete at 235° (Roscoe, *Chem. Soc. Trans.* 1874, 12, 933).

Uranium tetrabromide or *Uranous bromide* UBr_4 is obtained by heating the green oxide of uranium with excess of sugar charcoal, and passing bromine vapour over the heated mixture of uranous oxide and carbon thus produced (Zimmermann, *Annalen*, 1883, 216, 2; Alibegoff, *ibid.* 1886, 232, 132; Richards and Merigold, *Zeitsch. anorg. Chem.* 1902, 31, 250). It forms lustrous, dark-brown tablets of sp.gr. 4.838 at $21^\circ/4^\circ$. At a red heat it is volatile; the vapour density (air=1) is 19.46 (Zimmermann). It closely resembles the tetrachloride in properties.

Uranium tetraiodide or *Uranous iodide* UI_4 is prepared by passing the vapour of iodine over powdered uranium heated to 500° in the absence of air (Guichard, *Compt. rend.* 1907, 145, 921). It forms black, crystalline needles, which melt at about 500° , and have a sp.gr. of 5.6. The aqueous solution is dark green and closely resembles the chloride in properties.

Uranous oxyfluoride UOF_2 is obtained by the action of hydrofluoric acid on uranous uranic oxide—



It is a fine green powder, insoluble in water (Giollitti and Agamennone, *Atti R. Acad. Lincei*, 1905, 14, i. 114).

Uranyl fluoride UO_2F_2 is formed in the preceding reaction, and is a yellow soluble mass. It also exists, according to Smithells (*Chem. Soc. Trans.* 1883, 43, 125) in a white crystalline form, which can be sublimed; this modification is prepared by carefully heating the tetrafluoride in air. It is hygroscopic and forms a yellow solution in water. Both forms unite with

potassium fluoride forming a lemon-yellow crystalline double salt $\text{UO}_2\text{F}_2 \cdot 3\text{KF}$, which can also be obtained from uranyl acetate and an excess of potassium fluoride. This salt is trimorphous (Baker, *ibid.* 1879, 35, 763). The corresponding double salts of other metals are also known, and are converted into deep yellow-coloured peroxyfluorides by hydrogen peroxide (Lordkipanidzé, *J. Russ. Phys. Chem. Soc.* 1900, 32, 283).

Uranyl chloride UO_2Cl_2 is obtained by heating uranous oxide to redness in a stream of chlorine. It is a yellow crystalline mass, stable in dry air; it is reduced by hydrogen at a red heat to the dioxide. Uranous chloride is soluble in water, alcohol, and ether, and its aqueous solution yields the monohydrate $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ on evaporation. A solution of uranyl chloride may be prepared by oxidising uranous chloride with nitric acid or by dissolving uranium trioxide in concentrated hydrochloric acid (Mylus and Dietz, *Ber.* 1901, 34, 2774; de Coninck, *Compt. rend.* 1909, 148, 1769; *Bull. Acad. roy. Belg.* 1909, 836). For a table of specific gravities of its aqueous solutions, v. de Coninck, *Ann. Chim.* 1904, [viii.] 3, 500.

Uranyl bromide UO_2Br_2 may be obtained in an impure state by heating uranous oxide in bromine vapour. It is obtained in aqueous solution by acting on uranous oxide with bromine water, or by dissolving uranic oxide in hydrobromic acid. Yellow needles of the hydrated compound separate on concentrating the solution; they decompose when heated (de Coninck, *Bull. Acad. roy. Belg.* 1902, 12, 1025).

Uranyl iodide UO_2I_2 is obtained by adding barium iodide in slight excess to an ethereal solution of uranyl nitrate. It separates from ether in red deliquescent crystals, and is not very stable (Aloy, *Ann. Chim.* 1901, [vii.] 24, 412).

Uranium monosulphide US is a black, amorphous powder formed by heating the sesquisulphide in hydrogen (Alibegoff, *Annalen*, 1886, 233, 131, 135).

Uranium sesquisulphide U_2S_3 is a greyish-black substance formed by heating the tribromide of uranium in hydrogen sulphide (Alibegoff, *l.c.*).

Uranium disulphide US_2 is formed by the direct union of its elements at 500° (Moissan); at a higher temperature uranium burns vividly in sulphur vapour. The sulphide is best prepared by heating the double chloride of uranium and sodium in a current of hydrogen laden with the vapour of sulphur; or the double chloride may be fused with sulphide of sodium, aluminium, magnesium, antimony or tin (Colani, *Compt. rend.* 1903, 137, 382; *Ann. Chim.* 1907, [viii.] 12, 59). It forms large, slender, pearly crystals; the amorphous powder, obtained by heating uranous chloride in hydrogen sulphide, is greyish-black in colour. It oxidises in the air to uranyl sulphide, and with nitric acid is rapidly converted into uranyl sulphate.

A black, hydrated disulphide is obtained by precipitating a uranous salt with ammonium sulphide; it rapidly oxidises in the air to uranyl sulphide.

Uranyl sulphide UO_2S is obtained by adding ammonium sulphide to an alcoholic solution of uranyl nitrate, washing the precipitate with alcohol and drying *in vacuo*. By precipitating in aqueous solution a brown hydrated form is obtained (Remelé, Compt. rend. 1864, 58, 716). It rapidly decomposes by heating to 180° ; warm water converts it into hydrated uranous oxide and sulphur. It dissolves in dilute acids and in ammonium carbonate. When digested for 48 hours with cold ammonium sulphide exposed to air, a deep-red solid is obtained, soluble in acids with the evolution of hydrogen sulphide and deposition of sulphur. This substance is called *uranium-red* (Patera, J. pr. Chem. 1850, [i.] 51, 122; Remelé, Pogg. Ann. 1865, 124, 158; Hermann, J. 1861, 14; Zimmermann, Annalen, 1880, 204, 204). A complicated substance of the formula $5\text{UO}_2 \cdot 2\text{K}_2\text{O} \cdot \text{KHSO}_4 \cdot 2\text{H}_2\text{O}$ is obtained by precipitating uranyl nitrate with potassium sulphide and treating the precipitate with potassium carbonate (Kohlschütter, Annalen, 1900, 314, 311). This is also called *uranium-red*; acids decompose it, liberating sulphur and hydrogen sulphide.

Uranyl sulphide is formed in black, tetragonal needles by heating uranosouranic oxide with sulphur and potassium thiocyanate (Milbauer, Zeitsch. anorg. Chem. 1904, 42, 448).

The *oxysulphide* $2\text{UO}_2 \cdot \text{UO}_3$ has been described by Hermann (J. 1861, 260).

Uranium selenides USe_2 and U_2Se_3 are obtained in the crystalline state by heating the double chloride of uranium and sodium in a current of hydrogen containing the vapour of selenium (Colani, Compt. rend. 1903, 137, 382; Ann. Chim. 1907, [viii.] 12, 59).

Uranyl selenide is produced by heating uranosouranic oxide with selenium and potassium cyanide (Milbauer, Zeitsch. anorg. Chem. 1904, 42, 450).

Uranium telluride U_2Te_3 is prepared by fusing the double chloride of sodium and uranium with sodium telluride in an atmosphere of hydrogen (Colani, l.c.).

Uranium nitride U_3N_4 is a stable, greyish-black powder, prepared by heating uranous chloride in ammonia, and igniting the product mixed with ammonium chloride, once more in a stream of ammonia (Kohlschütter, Annalen, 1901, 317, 158). Uranium unites directly with nitrogen at 1000° , a yellow nitride being produced, the composition of which is not known (Moissan, Compt. rend. 1896, 122, 274).

Uranium phosphide U_3P_4 is obtained by fusing sodium uranous chloride with aluminium phosphide in a stream of hydrogen (Colani, l.c.). The *arsenide* U_3As_4 and *antimonide* U_3Sb_4 are similarly prepared. All three compounds are obtained as black crystalline powders; they are easily oxidised by nitric acid.

Uranium boride UB_2 is obtained by submitting a mixture of the finely powdered constituents to hydraulic pressure and using the mass as an electrode in the vacuum electrical furnace.

Uranium carbide U_2C_3 is prepared by strongly heating a mixture of 500 parts of uranosouranic oxide and 60 parts of carbon in the electric furnace. It is a lustrous, crystalline solid of

sp. gr. 11.28 at 18° , and is harder than quartz, although not so hard as corundum. It is decomposed by fluorine when gently warmed; chlorine readily attacks it at 350° , whilst it reacts with oxygen at 370° . Uranium carbide is decomposed by water, a very complex change occurring. About one-third of the carbon is evolved in combination with hydrogen, mainly as methane, propane, butane, but mixed with a little ethylene and traces of acetylene; the gaseous mixture contains about 15 p.c. of free hydrogen. The remainder of the carbon is converted into a mixture of solid and liquid hydrocarbons (Moissan, Compt. rend. 1896, 122, 274; Lebeau and Damiens, Compt. rend. 1913, 156, 1987). A shower of brilliant sparks is produced when two pieces of the carbide are rubbed together.

Uranium silicide USi_2 is obtained from a mixture of silica and uranosouranic oxide by the aluminothermic process (v. THERMIT PROCESS). It crystallises in the cubic system, and has a density of 8.0. At 500° it reacts with chlorine giving a mixture of uranous and silicon chlorides (Defacqz, *ibid.* 1908, 147, 1050).

SALTS OF URANIUM.

Saturated aqueous solutions of uranyl formate, acetate, benzoate, and citrate are unstable even in the dark. The propionate, butyrate, oxalate, tartrate, and salicylate are stable in the dark. The benzoate and salicylate are not reduced even in sunlight (Courtois, Bull. Soc. chim. 1923, 33 [iv.] 1773; Chem. Soc. Abstr. 1924, 126, i. 285).

Uranyl formate $\text{UO}_2(\text{HCO}_2)_2 \cdot 2\text{H}_2\text{O}$, greenish-yellow crystals, readily soluble in methyl alcohol or water. Formed by adding hydrogen peroxide to a slightly acid solution of uranyl nitrate and treating the washed precipitate with excess of formic acid and evaporating the solution *in vacuo*.

Uranyl acetate $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ is prepared by dissolving in warm acetic acid the yellowish-red mass produced by heating uranyl nitrate until evolution of oxygen commences. It crystallises in yellow, monoclinic needles, and is used in photography and also for the volumetric estimation of phosphates.

For other uranium salts of the monocarboxylic acids of the fatty series, see Courtois, Compt. rend. 1914, 158, 1511, 1688.

Uranous arsenate $\text{UH}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613; Rammelsberg, Pogg. Ann. 1842, 55, 318; 56, 125).

Uranyl arsenate $\text{UO}_2(\text{H}_2\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$, a yellow powder, insoluble in water and acetic acid, is obtained by double decomposition (Werther, Annalen, 1848, 68, 313). Several arsenates occur as minerals, e.g. *trögerite* $(\text{UO}_2)_2(\text{AsO}_4)_3 \cdot 12\text{H}_2\text{O}$; *valpurgite*, a basic bismuth uranyl arsenate; and *uranospinite*, a calcium uranium arsenate.

Uranyl benzoate $\text{UO}_2(\text{C}_6\text{H}_5\text{O}_2)_2$ (Courtois, Bull. Soc. chim. 1923, 33 [iv.] 1761; Chem. Soc. Abstr. 1924, i. 285).

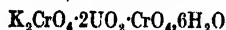
Uranyl bromate $\text{UO}_2(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, v. Rammelsberg, Pogg. Ann. 1842, 55, 77.

Uranous carbonate and uranyl carbonate are not known (Parkman, Amer. J. Sci. 1863, [ii.] 34,

326). Numerous double carbonates exist. *Potassium uranyl carbonate* $\text{UO}_2(\text{CO}_3)_2 \cdot 2\text{K}_2\text{CO}_3$ is obtained by dissolving potassium uranate in potassium bicarbonate and evaporating the solution at a moderate temperature; the corresponding ammonium and sodium salts are prepared in a similar manner (Ebelmen, Ann. Chim. 1842, [iii.] 5, 189; Anthon, J. 1860, 698; de Coninck, Bull. Acad. roy. Belg. 1904, 363, 448). They form yellow, rhombic prisms, which are not very soluble in water, but much more soluble in alkali carbonate solutions. The ammonium salt loses ammonia on keeping. Another ammonium compound $2\text{UO}_2 \cdot \text{CO}_3 \cdot 3(\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ has been obtained by mixing uranyl nitrate and ammonium carbonate (Giulitti and Vecchiarelli, Gazz. chim. ital. 1905, 35, ii. 170). *Uranyl calcium carbonate* $\text{UO}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 10\text{H}_2\text{O}$ occurs as the mineral *liebigite* in apple-green warty masses.

Uranyl chlorate $\text{UO}_2(\text{ClO}_3)_2 \cdot x\text{H}_2\text{O}$ is a very soluble substance, which readily decomposes when heated (Rammelsberg, l.c.).

Uranyl chromate $\text{UO}_2 \cdot \text{CrO}_4$ is obtained by adding uranic oxide to boiling chromic acid solution; it crystallises, on cooling the solution, in yellow needles, containing $5\frac{1}{2}\text{H}_2\text{O}$ (Formánek, Annalen, 1890, 257, 108), or $3\text{H}_2\text{O}$ (Orloff, Chem. Zeit. 1907, 31, 375). The double salt



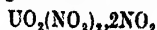
is obtained as yellow monoclinic crystals by treating potassium uranate with chromic acid. The ammonium salt is isomorphous with the preceding salt; the sodium salt contains $10\text{H}_2\text{O}$ (Formánek, l.c.).

Uranyl cyanate $\text{UO}_2(\text{CNO})_2$, a golden-yellow precipitate obtained by mixing dilute solutions of potassium uranyl cyanate and uranyl nitrate (Pascal, Bull. Soc. chim. 1914, [iv.] 15, 11).

Uranyl iodate $\text{UO}_2(\text{IO}_3)_2$ is precipitated on mixing boiling solutions of uranyl nitrate and sodium iodate in dilute nitric acid; it forms yellow prisms, slightly soluble in water. A hydrate $\text{UO}_2(\text{IO}_3)_2 \cdot 5\text{H}_2\text{O}$ is also known (Ditte, Thèse de doctorat es Sc. Paris, 1870).

Uranous nitrate has not yet been prepared in the solid form (Isambert, Compt. rend. 1875, 80, 1087).

Uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ is a yellow amorphous compound obtained by heating the tri- and tetra-hydrates in a current of nitric anhydride at a temperature of 170° – 180° . It reacts violently with ether and dissolves readily in water with development of heat. It combines with nitrogen dioxide to form



The trihydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ crystallises in yellow, monoclinic forms, and melts at 121.5° ; the dihydrate is rhombic and melts at 179.3° (Vasilieff, J. Russ. Phys. Chem. Soc. 1910, 42, 570). The commercial salt is the hexahydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It is formed when any of the oxides of uranium are dissolved in nitric acid, and is prepared commercially by heating ammonium uranate and dissolving the residue in nitric acid (Janda, Oester. Zeit. Berg-Hütt., 1901, 49, 325). For methods of preparation from pitchblende, v. Péligot, Ann. Chim. 1844,

[iii.] 12, 557; Ebelmen, *ibid.* 1842, [iii.] 5, 186. The hexahydrate forms lemon-yellow, fluorescent, rhombic prisms, which melt at 80.2° and deliquesce in the air (Vasilieff, l.c.; de Coninck, Compt. rend. 1900, 131, 1219, 1303; 1901, 133, 90, 204; Bull. Acad. roy. Belg. 1901, 222; 1909, 743). Water at 18° dissolves twice its weight of the salt. It is very soluble in alcohol and ether, and is best purified by crystallisation from the latter solvent. The aqueous solution is slightly hydrolysed, and has an acid reaction. An *icositetrahydrate* $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ forms spontaneously at -35° and exists only below -20° (Germann, J. Amer. Chem. Soc. 1922, 44, 1466; Ley, Zeitsch. physikal. Chem. 1899, 30, 193; Ber. 1900, 33, 2658; Dittrich, Zeitsch. physikal. Chem. 1899, 29, 440).

Uranium nitrate is triboluminescent, the crystals occasionally exploding with a bright flash in contact with water (Iwanow; Andrews, Chem. Zeit. 1912, 1463; Eichhorn, *ibid.* 1914, 38, 139). According to Müller (Chem. Zeit. 1916, 40, 38) this is not a property of the salt itself, but is due to the formation of an unstable compound of a lower oxide of nitrogen with a uranium-ether addition compound (Lebeau). The phenomenon only appears when the original aqueous solution contained free nitric acid.

Double nitrates of the type $\text{RUO}_2(\text{NO}_3)_2$, where R may be potassium, ammonium, thallium, rubidium, or caesium, but not sodium or lithium, are obtained by crystallising solutions of the mixed salts in nitric acid. Water decomposes them into their components (Meyer and Wendel, Ber. 1903, 36, 4055; Rimbach, *ibid.* 1904, 37, 461). For other double nitrates, see Lancein, Chem. Zentr. 1912, i. 208.

Uranyl nitrate is used in photography, and also for the volumetric estimation of phosphates and arsenates.

Uranous phosphate $\text{UH}_2(\text{PO}_4)_3 \cdot 5\text{H}_2\text{O}$ (Aloy, Bull. Soc. chim. 1899, [iii.] 21, 613).

Uranyl phosphate $\text{UO}_2 \cdot \text{HPO}_4$. This is precipitated in an amorphous form by adding a soluble phosphate to uranyl nitrate solution. When this precipitate is continuously boiled with dilute hydrochloric acid for a long time, it is converted into $\text{UO}_2 \cdot \text{HPO}_4 \cdot 4\text{H}_2\text{O}$, which crystallises in tetragonal plates (Bourgeois, *ibid.* 1897, [iii.] 19, 733). The *dihydrogen phosphate* $\text{UO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ is obtained by heating uranic oxide with dilute phosphoric acid, and concentrating the solution. It separates in small yellow crystals (Werther, J. pr. Chem. 1848, [i.] 43, 321). *Uranyl ammonium phosphate* $\text{UO}_2(\text{NH}_4)_2\text{PO}_4 \cdot x\text{H}_2\text{O}$ is a greenish-yellow precipitate formed by the addition of a soluble phosphate to a mixture of a uranyl and an ammonium salt. It is obtained in the volumetric estimation of phosphates. The precipitate is insoluble in acetic acid. Upon ignition it leaves a yellow residue of *uranyl pyrophosphate* ($\text{UO}_2)_2\text{P}_2\text{O}_7$.

Various phosphates occur in nature, e.g. *chalcophite* or *torberite* ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$) and *autunite* or *uranite* ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$).

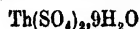
Complex uranyl hypophosphites have been described by Rosenheim and Trowendt (Ber. 1922, 55, [B] 1957). *Uranyl hypophosphite*



is a microcrystalline yellow powder, prepared by agitating solutions of one molecular proportion of uranyl nitrate with four molecular proportions of sodium hypophosphite; almost insoluble in water, but readily soluble in an excess of sodium hypophosphite or uranyl nitrate solution.

Uranyl salicylate $\text{UO}_2(\text{C}_6\text{H}_5\text{O}_2)_2$ forms orange-yellow crystals (Courtois, Bull. Soc. chim. 1923, 33, [iv.] 1761).

Uranous sulphate $\text{U}(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is prepared by dissolving the green oxide in dilute sulphuric acid, adding alcohol and allowing the solution to crystallise. The mother liquor contains uranyl sulphate; on exposure to light it is reduced to uranous sulphate, and another crop of crystals is obtained. A large number of other hydrates are known, e.g. di-, tri-, tetra-, penta-, hexa-, hepta-, and nonohydrates (Orloff, J. Russ. Phys. Chem. Soc. 1902, 34, 381; de Coninck, Bull. Acad. roy. Belg. 1901, 483; Kohlschütter, Ber. 1901, 34, 3628; Giolitti and Bucci, Gazz. chim. ital. 1905, 35, ii. 151, 162; Giolitti and Liberi, *ibid.* 1906, 36, ii. 443). The tetrahydrate is a stable substance, and the nonohydrate $\text{U}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ crystallises from aqueous solution in green monoclinic prisms that frequently exhibit twinning and are isomorphous with thorium sulphate



(Rammelsberg, Zeitsch. Krystall. 1889, 15, 640). Uranous sulphate forms double salts with sulphates of the alkali metals, e.g.



(Kohlschütter, Ber. 1901, 34, 3619). Aqueous solutions of uranous sulphate are readily hydrolysed, basic sulphates being precipitated.

A sulphate of the composition $\text{UH}(\text{SO}_4)_2$, which is supposed to contain trivalent uranium, has been described (Rosenheim and Loebel, Zeitsch. anorg. Chem. 1908, 57, 234).

Uranyl sulphate UO_2SO_4 is obtained by dissolving the hydroxide of uranium trioxide in concentrated sulphuric acid and crystallising the solution (Schultz-Sellack, Ber. 1871, 4, 13); or by drying either of its hydrates at 300° . It forms yellow fluorescent crystals. The hydrate $\text{UO}_2\text{SO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ is obtained by concentrating a solution of uranic hydroxide in dilute sulphuric acid; the solution does not crystallise readily. Another method is to dissolve uranosouranic oxide in concentrated sulphuric acid, dilute, and boil with nitric acid to oxidise the uranous sulphate present. The hydrate forms citron yellow prisms, which effloresce in air, losing water and leaving the trihydrate $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. This dissolves in twenty times its weight of water at ordinary temperatures (de Coninck, Bull. Acad. roy. Belg. 1901, 222, 349; 1902, 94, 161). Dried *in vacuo* or at 100° it retains 1 molecule of water. When dissolved in moderately concentrated sulphuric acid, a beautiful yellow, fluorescent, crystalline acid sulphate



crystallises out. The pyrosulphate $(\text{UO}_2)_2\text{S}_2\text{O}_7$ crystallises from a solution of the anhydrous sulphate in pyrosulphuric acid (Schultz-Sellack, Ber. 1871, 4, 13).

Uranyl sulphate forms a double sulphate with

hydroxylamine sulphate (Rimbach, Ber. 1904, 37, 461); a salt $\text{Ti}_2\text{SO}_4 \cdot \text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ with thalious sulphate (Kohn, Zeitsch. anorg. Chem. 1908, 59, 111); and combines with equimolecular quantities of the sulphates of ammonium, potassium, lithium, caesium, and magnesium, forming double salts which crystallise with from 2 to 5 molecules of water (de Coninck, Bull. Acad. roy. Belg. 1904, 1171; 1905, 50, 94, 151, 182; de Coninck and Chauvenet, *ibid.* 1908, 50).

A number of *basic sulphates* occur naturally, e.g. *zippite* $(\text{UO}_2\text{SO}_4 \cdot \text{UO}_2)_2$ and *uracomite* $(\text{UO}_2\text{SO}_4 \cdot 2\text{UO}_2 \cdot 14\text{H}_2\text{O})$, which are alteration-products of pitchblende.

Uranyl sulphite. The crystalline precipitate obtained by evaporating a solution of uranic oxide in aqueous sulphurous acid, or by passing sulphur dioxide into an aqueous solution of uranyl acetate, has the empirical composition $\text{UO}_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ (Girard, Compt. rend. 1852, 34, 22). According to Kohlschütter (Annalen, 1901, 314, 311) it is really uranyl sulphurous acid $\text{SO}_3\text{H} \cdot \text{UO}_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}$ (cf. Ley, Ber. 1900, 33, 2659).

Uranyl thiocyanate $\text{UO}_2(\text{CNS})_2 \cdot 8\text{H}_2\text{O}$, orange-yellow needles obtained by the action of barium thiocyanate on uranyl sulphate. Highly deliquescent and very soluble in water, alcohol, acetone, ether or amyl alcohol. Forms double salts with the alkali and alkaline earth metals (Pascal, Compt. rend. 1914, 158, 1672).

Tungstates. v. Rammelsberg, Pogg. Ann. 1843, 59, 31; Lefort, Compt. rend. 1878, 87, 748.

Detection and estimation.—In qualitative analysis uranium is obtained together with iron. All the uranyl salts of weak acids, e.g. carbonate, sulphide, phosphate, &c., are soluble in ammonium carbonate and the other alkali carbonates. The ferrocyanide, a brown precipitate, insoluble in dilute acids, is characteristic; alkalis turn it yellow. Uranium is usually weighed as uranosouranic oxide, or else as uranyl pyrophosphate; uranous salts may be titrated with permanganate. **V. ANALYSIS;** and Finn, J. Amer. Chem. Soc. 1906, 28, 1443; McCoy and Bunzel, *ibid.* 1909, 31, 367; Giolitti, Gazz. chim. ital. 1904, 34, ii. 166; Mazzucchelli, Atti R. Accad. Lincei, 1906, [v.] 15, ii. 429, 494; Campbell and Griffin, J. Ind. Engin. Chem. 1909, 1, 661; Ibbotson and Clark, Chem. News, 1911, 103, 146; Schwarz, Helv. chim. Acta, 1920, 3, 330; Auger, Compt. rend. 1920, 170, 995; Holladay and Cunningham, Trans. Amer. Electrochem. Soc. 1923, 43, 329; Jander and Reeh, Zeitsch. anorg. Chem. 1923, 129, 293; Moser, Monatsh. 1923, 44, 90.

URANIUM DISINTEGRATION PRODUCTS.

The disintegration of uranium proceeds in all probability in the following manner: Uranium I, of atomic weight 238, expels an α -particle and changes into uranium X_1 , an isotope of thorium. The half-period of this first change is 5000 million years. Uranium X_1 is short-lived, and changes with a half-period of 24.6 days into uranium X_2 or brevium, in the Vth family, expelling a very soft β -radiation. Uranium X_2 has a half-period of only 1.15 minutes, and expels a penetrating β -radiation. It produces uranium II, which after two further α -ray changes gives, first, ionium, and then radium. Uranium II is an isotope of uranium I,

with atomic weight four units less. Its half-period is estimated to be about two million years. All uranium must thus consist of a mixture of two isotopes differing by four units in atomic weight, the proportion between the heavier and the lighter being 2500 to 1. No separation, or even partial separation, has as yet been effected. Independent evidence of the existence of uranium II is afforded by the fact that uranium gives two α -particles of different ranges per atom disintegrating.

See also A. S. Russell (Phil. Mag. 1923, 46, 642); Soddy and Hitchens (Phil. Mag. 1924, 47, 1148).

Uranium X. Estimated at.wt. 234. A radioactive element produced by the disintegration of uranium. It emits two kinds of β -rays, and also γ -rays, and its presence in ordinary uranium salts is responsible for the penetrative rays they emit. Uranium salts, when freed from uranium X, only emit α -rays. In course of a few months the β -radiation is regenerated, whilst that of uranium X decays.

Uranium X may be separated in a number of ways. When a concentrated solution of uranyl nitrate (sp.gr. of solution 2.05) is allowed to cool, the mother liquor left after removing the crystals formed contains about 85 p.c. of the uranium X present (Soddy and Russell, Phil. Mag. 1909, [vi.] 18, 620). If crystals of hydrated uranyl nitrate are shaken with ether, two layers are formed; the aqueous (lower) layer retains the uranium X. In the purification of a uranyl solution from iron, aluminium, &c., by pouring into excess of ammonium carbonate, the precipitated impurities contain all the uranium X. If this precipitate is dissolved in concentrated hydrochloric acid, and the solution extracted with ether, saturated with hydrogen chloride, the ferric chloride is removed, but not the uranium X, which remains in the aqueous layer (Lloyd, J. Phys. Chem. 1910, 14, 509; Soddy, Phil. Mag. 1909, [vi.] 18, 861). It has been recommended to add a thorium salt to a uranyl salt, and then precipitate the thorium in acid solution as fluoride; the precipitate contains the uranium X (Keetman, Jahr. Radioaktivität, 1909, 6, 269; Ritzel, Zeitsch. physikal. Chem. 1909, 67, 725). Thorium fluoride is, however, quite soluble in uranium solutions when these are concentrated. By using a lanthanum salt containing a very little thorium, converting the precipitated fluorides into sulphates and then precipitating by boiling with sodium thiosulphate, a precipitate is obtained, consisting mainly of sulphur, which on ignition leaves a very slight residue containing all the uranium X originally present (cf. Antonoff, Phil. Mag. 1911, [v.] 22, 431).

The most practical way of obtaining a continuous supply of uranium X as required is to keep a strong ethereal solution of uranyl nitrate and to shake this with a few drops of water, pour the aqueous extract into excess of N/2 ammonium carbonate and filter off the insoluble precipitate which contains the uranium X.

Chemically, uranium X is an isotope of thorium; for its radioactive properties, v. RADIOLOGY.

On the influence of substances on the adsorp-

tion of uranium X, v. Ritzel (Zeitsch. physikal. Chem. 1909, 67, 724); Freundlich and Neumann (Zeitsch. physikal. Chem. 1914, 15, 537); Brown (Chem. Soc. Trans. 1922, 1736).

On the γ -radiation from uranium X, v. Richardson (Phil. Mag. 1914, [vi.] 27, 252).

On the electro-chemical separation of uranium X and uranium, v. Rossi (Nuovo Cim. 1913, [vi.] 5, i. 5).

On the magnetic spectrum of the β -rays of uranium X, v. von Baeyer, Hahn and Meitner (Zeitsch. physikal. Chem. 1914, 15, 649).

Uranium X₂, v. Fajans and Göhring (Zeitsch. physikal. Chem. 1913, 14, 877); Fleck (Phil. Mag. 1913, [vi.] 26, 528); Hahn and Meitner (Zeitsch. physikal. Chem. 1913, 14, 758).

On the γ -rays of Uranium X and their relations to Uranium X₁ and Uranium X₂, see Otto Hahn and Lise Meitner (Zeitsch. Phys. 1923, 7, 157-167; J. Chem. Soc. Abstr. 1923, 124, ii. 676).

Uranium X₁ is completely adsorbed by charcoal from a solution of uranium salt, but if a small quantity of a thorium salt is added the uranium X₁ is not adsorbed at all. If the thorium nitrate used is previously shaken with charcoal, it loses to a great extent its power of preventing the adsorption of uranium X₁. This is shown to be due to the fact that thorium nitrate contains colloidal particles, and these are responsible for the displacement of the equilibrium in the adsorption of uranium X₁ (H. Freundlich and M. Wreschner, Zeitsch. physikal. Chem. 1923, 106, 366-377; J. Soc. Chem. Ind. 1923, 42, 1220 A).

Uranium Y, v. Soddy (Phil. Mag. 1914, 215).

Uranium V, v. O. Hahn (Zeitsch. physikal. Chem. 1923, 103, 461); cf. also A. Piccard and E. Stahel (Physikal. Z. 1922, 23, 1; 24, 80).

Uranium Z (symbol U-Z), the existence of which has been announced by Hahn (Ber. 1921, 54 (B), 1131), has been further investigated by Guy and Russel (Chem. Soc. Trans. 1923, 123, 2618) (*q.v.*).

URANIUM MICA v. AUTUNITE; TORBERNITE; URANITE.

URANIUM YELLOW v. URANIUM.

URAO. A native form of sodium sesquicarbonate $\text{Na}_2\text{H}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, found in South America, Africa, and other places. According to Chatard (Bulletin No. 60, U.S. Geol. Surv. 1887-1880), the formula of urao is



URAPURGOL (*helmitol*). Trade name for hexamethylenetetramineanhydromethylene citrate.

URARI v. CURARA.

p-URAZINE v. HYDRAZINES.

UREABROMIN. A molecular combination of carbamide and calcium bromide



prepared by mixing the two components in solution. It is readily soluble in alcohol or water, insoluble in ether, light petroleum or benzene, and melts at 180°. It gives all the ordinary reactions of its components when

dissolved in water. Used in medicine as a substitute for alkali bromides (Biltz, Pharm. Zentr. 1912, 53, 245).

UREA, carbamide, aminoformamide, $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$

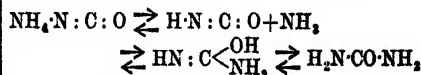
occurs in human urine to the extent of 1.5 p.c. to 2 p.c.; in the urine of other mammalia, especially the carnivora; in small quantities in the blood, bile, milk, perspiration, the aqueous humour of the eye, and other animal fluids (Wurtz, Compt. rend. 1859, 49, 52; Popp, Annalen, 1869, 151, 88; Argutinsky, Pflüger's Archiv. 1891, 46, 594; North, Proc. Roy. Soc. 1886, 39, 443; Pautz, Zeitsch. biol. 1894, 31, 212); in the liver, muscle and blood of the dog-fish, the blood containing 2.78 p.c. (v. Shroeder, Zeitsch. physiol. Chem. 1890, 14, 576; Baglioni, Beitr. chem. Physiol. Path. 1906, 9, 50); in the bile and blood of other fish (Hammarsten, Zeitsch. physiol. Chem. 1898, 24, 322; Baglioni, *l.c.*). According to Marshall and Davis (J. Biol. Chem. 1914, 18, 53) urea is present in all tissues and organs of normal animals; v. also Karr and Lewis (J. Amer. Chem. Soc. 1916, 38, 1615), and v. Cullen and Ellis (J. Biol. Chem. 915, 20, 571). In the vegetable kingdom urea has been found in *Lycoperdon bovista*, *Poelliotia campestris* and other higher fungi to the extent of 4.3 p.c. of the dry weight, and is present in minute quantities in the juice from the washed leaves of a number of plants and also in seedlings of wheat, barley, maize, peas, clover, and beans (Bamberger and Landseidl, Monatsh. 1903, 24, 218; Gaze, Arch. Pharm. 1905, 243, 78; Goris and Mascré, Compt. rend. 1908, 147, 1488; Fosse, *ibid.* 1912, 155, 851; 1913, 156, 567, and 1938; Ann. Chim. 1916, 6, 13; Compt. rend. 1919, 168, 1164).

As much as 13 p.c. of urea has been found in dried mushrooms that have been cultivated in manure (Ivanov, Biochem. Zeitsch. 1923, 143, 62; Chem. Soc. Abstr. 1924, 126, i, 353).

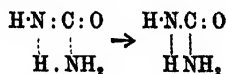
A. niger and *P. glaucum* both produce urea in the presence of ammonia and carbohydrates (Fosse, Compt. rend. 1912, 156, 263). For the formation of urea by higher plants, see Fosse (Ann. Chim. Phys. [ix.] 1916, 6, 567). A number of plants hydrolyse urea in presence of chloroform (Fosse, Ann. Inst. Pasteur, 1916, 30, 642).

Urea was first obtained synthetically by Wöhler in 1828 from ammonium cyanate, which undergoes a spontaneous transformation into its isomeric urea when an aqueous solution is

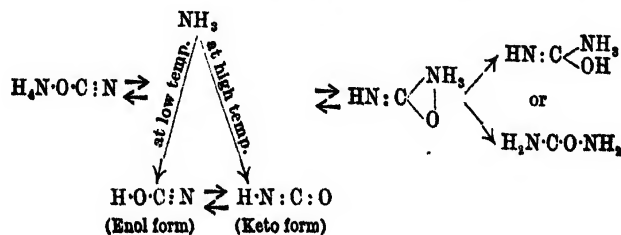
evaporated at the temperature of boiling water. The mechanism of the reaction has been studied by Walker and others (Chem. Soc. Trans. 1895, 67, 746; 1896, 79, 193; 1897, 71, 489; 1900, 77, 30), who have shown: (1) that the reaction is a reversible one, equilibrium being reached in a decinormal solution when there is about 95 p.c. of urea and 5 p.c. of ammonium cyanate present (*cf.* Lewis and Burrows, J. Amer. Chem. Soc. 1912, 34, 1515); (2) that the reaction is a bimolecular one; (3) that the velocity of the reaction is thirty times as great in 90 p.c. ethyl alcoholic as in aqueous solutions; and (4) that pure dry ammonium cyanate passes rapidly into urea when heated at about 80°. Those authors suggest that the active molecules in the reaction are ammonium ions and cyanic acid ions, $\text{NH}_4^+ + \text{CNO}^- = \text{CO}(\text{NH}_2)_2$; and that the increased velocity of the reaction in alcoholic solution is due to the effect of the alcohol in increasing the rate at which the dissociated ions interact, and this more than counterbalances the diminution in the velocity due to the diminished degree of electrolytic dissociation of the cyanate (*cf.* Burrows and Fawcitt, Chem. Soc. Trans. 1914, 105, 609). Another explanation of the reaction offered by Chattaway (Chem. Soc. Trans. 1912, 101, 170) is that ammonium cyanate dissociates into ammonia and cyanic acid, that these interact to form isourea, which rapidly undergoes molecular rearrangement



Wheeler and others (J. Amer. Chem. Soc. 1912, 34, 1269) offer a somewhat simpler explanation of the interaction between the cyanic acid and ammonia by introducing the idea of partial valency



Werner has shown that cyanic acid is capable of existing in equilibrium in the two forms, *normal* and *iso*-, or, as he prefers to call them, *enol* and *keto*, the relative proportions being a function of the temperature. Being a weak acid in the enolic form, cyanic acid would naturally yield a very unstable ammonium salt, easily dissociated by heat, both in the dry state and in solution, and transformable into urea according to the following scheme:



(Chem. Soc. Trans. 1913, 103), see also Werner and Fearon (*ibid.* 1920, 1356).

Urea can be obtained from lead cyanate by direct hydrolysis with boiling water (Cumming,

Chem. Soc. Trans. 1903, 83, 1391); by heating ammonium sesquicarbonate or ammonium carbamate at 130°-135° under pressure (Bourgeois, Bull. Soc. chim. 1897, [iii.] 17, 474; Fichter and

Becker, Ber. 1911, 44, 3473; J. Soc. Chem. Ind. 1915, 34, 924; Eng. Pat. 23939, 24117, 24042, 1914; Matignon and Fréjaques, Compt. rend. 1920, 171, 1003; Badische Anilin und Soda-Fabrik, D. R. PP. 332679, 301279; Eng. Pat. 145060; Krase and Gaddy, J. Ind. Eng. Chem. 1922, 14, 611; by the electrolysis of a solution of ammonium carbonate (Fichter, Steiger and Stanisch, Verh. Schweiz. Nat. ges. 1916, 28, ii, 66; Fichter, Zeitsch. Elektrochem. 1918, 24, 41); by passing a mixture of ammonia and carbon dioxide through a red hot tube (Mixer, Amer. Chem. J. 1882, 4, 34). For the explanation of the mechanism of these reactions, see Werner (Chem. Soc. Trans. 1920, 1040). Bailey (Compt. rend. 1922, 175, 279). Urea is also formed by the action of carbonyl chloride on ammonia (Natanson, Annalen, 1856, 98, 287; Bouchardat, Compt. rend. 1869, 69, 961; Fenton, Chem. Soc. Trans. 1879, 35, 793; Hantzsch and Stuer, Ber. 1905, 38, 1041; Werner, Chem. Soc. Trans. 1918, 694); by passing a stream of air charged with ammonia and benzene vapour or acetylene over a heated platinum spiral (Herroun, Chem. Soc. Trans. 1881, 39, 471); by heating a solution of carbon monoxide in ammonium cuprous chloride at 105° under pressure (Jouve, Compt. rend. 1899, 128, 114); by the decomposition of copper or ammonium fulminate with sulphuretted hydrogen (Gladstone, Quart. J. Chem. Soc. 1849, 1, 228); by the decomposition of an aqueous solution of prussic acid (Campani, Gazz. chim. ital. 1871, 1, 472), or by the oxidation of potassium cyanide with potassium permanganate or sodium hypochlorite (Volhard, Annalen, 1890, 259, 377; Reychler, Bull. Soc. chim. 1893, [iii.] 9, 327). (For industrial conversion of ammonia into urea, see Matignon and Fréjaques, Chem. Ind. 1922, 7, 1057. In abstract, J. Soc. Chem. Ind. Aug. 31, 1922, p. 646 A. See also under Patents, p. 647 A., Bad. Anil. u. Soda Fabrik, Eng. Pat. 182331). Urea is also obtained by the hydrolysis of guanidine (Flemming, Chem. Zeit. 1900, 24, 56), arginine (Schulze and Likiernik, Ber. 1891, 24, 2701) or lysatine (Drechsel, *ibid.* 1890, 23, 3096) with barium hydroxide solution; and is a constant product of oxidation with acid potassium permanganate of a large number of organic compounds containing nitrogen: for example, acid amides and amino acids (Hofmeister, Chem. Zentr. 1896, ii, 389; Jolles, Ber. 1900, 33, 2834; J. pr. Chem. 1901, [ii.] 63, 516), and proteins (Ritter, Compt. rend. 1872, 73, 1219; Hofmeister, *l.c.*; Hugounenq, Compt. rend. 1901, 132, 1240; Jolles, Ber. 1901, 34, 1447; Fosse, Compt. rend. 1912, 154, 1187, 1819; 1919, 168, 320). Urea is found abundantly when *d*-glucose, levulose, sucrose, dextrin or cellulose is oxidised in presence of ammonia; and much higher yields of urea are obtained by oxidising under the same experimental conditions formaldehyde or urotropine (Fosse, Ann. Inst. Pasteur, 1916, 30, 642; Compt. rend. 1919, 168, 1164; 1921, 172, 684, 1240; 173, 318).

Cyanamide is slowly converted into urea by the action of water (Schmidt, Arch. Pharm. 1917, 255, 351), by the action of dilute mineral acids in the presence of ferrousferrous oxide (Farbwerke vorm. Meister, Lucius and Brüning,

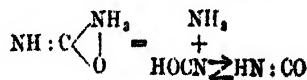
D.R.P. 301278, from Chem. Zentr. 1922, ii, 1135).

Urea is usually obtained from urine by treating the concentrated filtered liquid with a hot saturated solution of oxalic acid and decomposing the sparingly soluble urea oxalate thus obtained with powdered chalk; the filtrate is decolorised with animal charcoal and evaporated until the urea crystallises out on cooling. Another method consists in extracting the urea with alcohol from the syrup obtained by evaporating the urine, precipitating the urea as the sparingly soluble nitrate by the addition of concentrated nitric acid, and decomposing the salt by boiling with barium carbonate and alcohol; the urea is obtained by crystallisation from the filtrate. It can be purified and decolorised by boiling it in aqueous solution with hydrogen peroxide (Kunz-Krause, Kolloid Zeitsch. 1919, 25, 240).

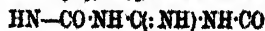
Urea can be prepared on a large scale by passing dry ammonia into fused phenyl carbonate until the odour of ammonia is persistent. The product is poured into hot water, when it separates into two layers consisting respectively of phenol and a solution of urea; 5 kilos. of phenyl carbonate yield 1 kilo. of urea and the whole of the phenol is recovered. The phenyl carbonate is obtained in an almost theoretical yield by passing dry carbonyl chloride into a solution of phenol in its equivalent quantity of dilute caustic soda (Hentschel, Ber. 1884, 17, 1286). By a similar reaction, guaiacol carbonate is rapidly converted into urea and guaiacol when an alcoholic solution is saturated with ammonia (Cazeneuve, Compt. rend. 1896, 122, 999).

Urea crystallises in needles, or in four-sided rhombic anhydrous prisms; it is readily soluble in water, 1 gm. of water dissolving 0.779 gm. of urea at 5.5°, 1.00 gm. at 17.1°, and 1.094 gm. at 20.92° (Krummacker, Zeitsch. biol. 1905, 46, 302). It dissolves in five parts of cold alcohol, is soluble in methyl and in amyl alcohol, and is insoluble in ether, ethyl acetate or chloroform. The heat of combustion is 2.532 cal., and the heat of solution 3.57 cal. (Krummacker, *l.c.*). For the entropy changes at low temperature, see Gibson, Latimer and Parks (J. Amer. Chem. Soc. 1920, 42, 1533).

Urea melts at 130°–132°, and sublimes readily when heated under reduced pressure at 120°–130° (Bourgeois, Bull. Soc. chim. 1892, [iii.] 7, 45). When pure dry urea is heated slightly above its melting-point it undergoes rapid dissociation into ammonia and cyanic acid



Cyanuric acid is produced as a result of the polymerisation of a portion of the cyanic acid originally present in the keto-form, whilst biuret is simultaneously formed by the action of cyanic acid on unchanged urea. Biuret $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, when heated at 185° decomposes into ammonia and cyanic acid, cyanuric acid $\text{C}_3\text{N}_3(\text{OH})_3$, and ammeline



(Werner, Chem. Soc. Trans. 1913, 103, 2275; Chem. Soc. Proc. 1914, 262). When urea is sublimed in a vacuum at 160°–190°, the sublimate consists of ammonium cyanate (Escalas, Chem. Zeit. 1911, 35, 595). When an aqueous solution of urea is boiled, it is partially converted into ammonium cyanate. The reaction is a reversible one, equilibrium being reached in a N/10 solution, when there is about 5 p.c. ammonium cyanate present (Walker and Hambly, Chem. Soc. Trans. 1895, 67, 746; Fawcitt, Zeitsch. physikal. Chem. 1902, 41, 602). When heated with water in a sealed tube at 180°, urea undergoes complete hydrolysis, forming ammonium carbonate. For the decomposition of urea by acids and alkalis, see Werner (Chem. Soc. Trans. 1918, 84; 1920, 1078). Urea is decomposed by the action of nitrous acid, yielding nitrogen and carbon dioxide (Claus, Ber. 1871, 4, 140); compare, however, Werner (Chem. Soc. Trans. 1914, 863). Urea is decomposed when heated with dilute hydrochloric, sulphuric, or nitric acid, yielding carbon dioxide and the ammonium salt of the acid (Fawcitt, Zeitsch. physikal. Chem. 1902, 41, 601; Werner, Chem. Soc. Trans. 1918, 113, 84; Price, *ibid.* 1919, 115, 1354; Burrows, J. Roy. Soc., New South Wales, 1919, 53, 125). It is oxidised by a hot acid solution of potassium permanganate, yielding two vols. CO₂ and 1 vol. N (Wanklyn and Gamgee, Chem. Soc. Trans. 1868, 21, 25). By the action of sodium hypochlorite or hypobromite, urea is converted into carbon dioxide, nitrogen, and water; together with a small quantity of carbon monoxide (Hurtley, Bio-Chem. J. 1921, 15, 11). For an explanation of the course of this reaction, compare Schestakow (J. Russ. Phys. Chem. Soc. 1905, 37, 1); Dehn (J. Amer. Chem. Soc. 1910, 31, 1220); Werner (Chem. Soc. Trans. 1922, 2318). Urea is decomposed by bromine, yielding cyanuric acid, ammonium bromide, and nitrogen: chlorine has a similar reaction on fused urea (Smolka, Monath. 1887, 8, 64). Urea is converted into cyanamide NC-NH₂ by the action of sodium (Fenton, Chem. Soc. Trans. 1882, 41, 262) or of sulphuryl chloride (Moureu, Bull. Soc. chim. 1894, [iii.] 11, 1068). Compare Werner (Chem. Soc. Trans. 1915, 107, 715) for the relationship of cyanamide to urea, and (*ibid.* 1913, 105, 923) for the constitution of carbamides and isocarbamides.

Urea readily undergoes bacterial fermentation with production of ammonium carbonate (Miguel, Compt. rend. 1890, 111, 397; Frankland, Chem. Soc. Trans. 1885, 47, 175; Hatton, *ibid.* 1881, 39, 256; Jacoby, Biochem. Zeitsch. 1916, 74, 109); a ferment present in urine is particularly active in causing this decomposition, and if this ferment is collected on paper by filtration, washed and dried at 35°–40°, its activity revives when brought into contact with water; and such papers, when previously coloured with turmeric, form a convenient test for urea, becoming deep brown when dipped into a solution containing even *rupp* part of urea (Musculus, Compt. rend. 1874, 78, 132). For the decomposition of urea by moulds, v. Kossowicz (Amer. Chem. Abs. 1913, 807).

Detection.—Urea can be detected by the formation of its sparingly soluble nitrate or oxalate. In the case of the latter salt, the

precipitation is facilitated by using an amyl alcoholic solution of the urea and of the oxalic acid (Brücke, Monath. 1881, 3, 195). The *biuret* test is the commonest test for urea. It consists in heating gently the urea until it ceases to evolve ammonia freely, dissolving the residue in a little water and adding a few drops of very dilute copper sulphate solution, on the subsequent addition of a drop of concentrated potassium hydroxide, a beautiful violet colour is developed. If the urea is in solution, it may be detected by evaporating to dryness with hydrochloric acid, heating the residue until it ceases to evolve thick white fumes and then dissolving in ammonia; on adding barium chloride solution and stirring, crystals of barium cyanurate separate on the lines of friction made by the rod; or copper sulphate may be added to the ammoniacal solution of the residue, when violet crystals of cuprammonium cyanurate separate out (Bloxam, Chem. News, 1883, 47, 285; v. Werner, Chem. Soc. Proc. 1914, 30, 262, for proof that biuret is formed by the interaction of urea and its dissociation product cyanic acid). Other colour reactions that can be used for the detection of urea are (1) the formation of a fine purple violet colour, when a solution of urea is treated with a concentrated solution of furfural and a few drops of concentrated hydrochloric acid (Schiff, Ber. 1877, 10, 773; Ganassini, Arch. Farm. sperim. sci. app. 1918, 26, 238; from Chem. Zentr. 1919, ii, 473); (2) the development of an intense blue colour when minute quantities of urea (or other compounds containing the $\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ group) and methylfural ($\text{C}_6\text{H}_5\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_3$) are mixed on a filter paper and treated with a drop of fuming hydrochloric acid (Fenton, Chem. Soc. Trans. 1903, 83, 187; Proc. Camb. Phil. Soc. 1911, 16, 64); (3) the development of the characteristic red colour of the sodium violurate when the urea (or its mono- or sym. di-substituted derivatives) is condensed with malonic acid by cautiously heating the mixture moistened with phosphoryl chloride, the resulting barbituric acid dissolved in water, neutralised with solid sodium carbonate, and then treated with a crystal of sodium nitrite and a drop of acetic acid (Whiteley, *private communication*); (4) urea condenses with o-nitrobenzaldehyde when heated in alcoholic solution, the o-nitrobenzodiureide $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ thus obtained melts at 200°, and if present in very small amount may be readily detected by decomposing it with dilute hydrochloric acid and testing for o-nitrobenzaldehyde by the red colour it gives with phenylhydrazine (Lüdy, Monath. 1889, 10, 295); see also Arreguine and Garcia (Anal. Assoc. Quim. Argentina, 1921, 9, 183). According to Fosse (Compt. rend. 1913, 157, 948) it is possible to precipitate urea by means of its xanthhydrol derivative at a dilution of 1 in 1,000,000, to identify it by analysis at a dilution of 5 parts in 100,000, and to identify it microscopically at a dilution of 1 in 100,000; see also Werner and Fearon (Chem. Soc. Trans. 1920, 1360); and Bonnet and Haushalten (Compt. rend. Soc. Biol. 1922, 86, 395); Stübel (Anat. Anz. 1921, 54, 236).

Estimation.—The determination of the amount of urea present in urine, blood serum or other animal liquids, is a problem of great

physiological importance. Of the large number of methods that have been described for the estimation of urea, only those are now in use that involve the conversion of urea into ammonia, under such conditions that other nitrogenous substances that may be present in the specimen are not simultaneously hydrolysed. The most important methods are those of Folin and of Benedict, Mörner and Sjöquist, and of Pfüger and Bleibtreu. For estimation by the hypobromite method, see Philibert (J. Pharm. Chim. 1919 [vii.] 19, 335, 386, 434); Golse (*ibid.* 1919, [vii.] 19, 20). For estimation by the xanthhydrol method, v. Fosse (Compt. rend. 1914, 158, 1076, 1588; 1914, 150, 253, 367); Maestri (Chem. Zentr. 1915, 11, 984, from Arch. Pharmacol. Suppl. 19, 572); Frenkel (Ann. Chim. anal. 1920, [ii.] 2, 234); Carra (Biochem. therapia. sper. 1921, 8, 225), who has examined the various methods for the estimation of urea, states that this method is very accurate. For a microchemical method based on this reaction, see Nicloux and Welter (Compt. rend. 1921, 173, 1490).

I. Folin's method is based on the fact that urea is quantitatively converted into ammonia and carbon dioxide when heated with fused magnesium chloride $MgCl_2 \cdot 6H_2O$. In using this method for the estimation of urea in urine, 3 c.c. of the sample are boiled for half an hour with 20 grms. of hydrated magnesium chloride (phosphoric acid or potassium acetate, v. Folin, J. Biol. Chem. 1912, 11, 507) and 2 c.c. concentrated hydrochloric acid in a small reflux apparatus supplied with a special 3-bulb safety tube. After careful dilution, 7 c.c. of 20 p.c. sodium hydroxide are added to liberate magnesium hydroxide and the ammonia distilled over into a known volume of N/10 acid, the distillation being prolonged until the contents of the flask are almost dry. Allowance must be made for the ammonia present in the magnesium chloride (Folin, Zeitsch. physiol. Chem. 1901, 32, 504; 1902, 36, 333; Folin and Farmer, J. Biol. Chem. 1912, 11, 493, 507, 523; cf. Bock, *ibid.* 1913, 14, 295). In this method creatinine yields traces of ammonia and allantoin yields all its nitrogen as ammonia. Benedict (J. Biol. Chem. 1910, 8, 405) modifies the method by adding to the urine potassium hydrogen sulphate, zinc sulphate, a little powdered pumice, and a piece of paraffin to prevent frothing; the mixture is boiled to dryness, the residue heated at 162°–165° for an hour, then mixed with sodium hydroxide and the liberated ammonia distilled into standard acid. For the conversion of urea to ammonia by means of urease, which does not decompose allantoin, v. Marshall, J. Biol. Chem. 1913, 14, 283; Van Slyke and Cullen, *ibid.* 1914, 19, 211; 1916, 24, 117; Plimauex and Skelton, Bio-Chem. J. 1914, 8, 70; 1916, 24, 117; Fiske, J. Biol. Chem. 1915, 23, 455; Halen, Chem. Zentr. 1916, 1, 997, from Deut. med. Woch. 1916, 42, 414; Yamazaki, J. Tokyo Chem. Soc. 1918, 39, 125. This method, according to Carra (*l.c.*), gives excellent results. Folin and Denis (*ibid.* 1916, 26, 501) give directions for the estimation of the nitrogen by direct Nesslerisation after hydrolysing the urea by urease and removing the latter with phosphoric acid.

When crude soya-bean meal is used for the estimation of urea, the addition of sodium

carbonate in sufficient amount to liberate the ammonia formed in the free state is without deleterious effect upon the activity of the urease. This observation is made use of in the following method: Three large test tubes are constricted by drawing them out in a blowpipe flame in such a manner that the capacity below the constriction is about three times that of the liquid to be contained. These tubes are fitted with corks and connecting tubes as wash-bottles, the upper end of the first inlet tube being provided with a three-way piece and stop-cock. Into the first tube 20 c.c. of water, 5 c.c. of urine, and 3 to 5 grms. of soya-bean meal are placed, and the central narrow tube is inserted and surrounded by a few glass beads above the constriction. The remaining tubes contain known volumes of 0.1 N sulphuric acid for absorption of the ammonia liberated. The tube containing the mixture is immersed in a water-bath at 40°C., and a current of ammonia-free air is drawn through the apparatus at a rate exceeding $5\frac{1}{2}$ litres per minute. Two c.c. of saturated sodium carbonate solution are introduced by means of the stopcock into the tube containing the mixture, and aeration is continued for 40 minutes, after which the urea is calculated from the titration of the standard acid. Results obtained with known amounts of urea show a maximum error of 0.88 p.c. (G. M. Wishart, Bio-Chem. J. 1923, 17, 403–405; Analyst, 1923, 48, 501).

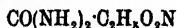
Urea in urine or in milk may be estimated by means of urease obtained from the seeds of *Canavalia ensiformis* by extracting the powder with glycerol and water, then, after about 3 hours, acidifying with hydrochloric acid and filtering. In the case of urine, the estimation is carried out by diluting about 5 c.c. with 50 c.c. of water and adding 3 c.c. of the solution of urease and 1 c.c. of 3 p.c. solution of calcium caseinate to serve as indicator; after about 3 hours, 40 c.c. of 0.1 N hydrochloric acid are added, and the excess of acid titrated back with sodium hydroxide solution, the precipitation of the casein indicating the end-point. In the case of milk, 10 c.c. are diluted with 40 c.c. of water, 3 c.c. of urease solution are added, and the estimation continued as above. Cow's milk usually contains 0.25 to 0.30 gm. of urea per litre, and, for the first few weeks after calving, 0.75 gm. per litre. Goat's milk is richer in urea than that of the cow, the average being 0.80 gm. per litre (G. Morimoto, Bio-Chem. J. Japan, 1922, 69; Ann. Chim. anal. 1923, 5, 153; Analyst, 1923, 48, 394).

II. In the Mörner-Sjöquist method of estimating urea in urine, uric acid, purine bases, tyrosine, allantoin, &c., are removed by precipitation with barium chloride and hydroxide in a mixture of alcohol and ether. The filtrate and washings are evaporated at 55° to about 25 c.c., a little water and magnesia added and the distillation continued until the steam has no longer an alkaline reaction. The volume is then concentrated to 10–15 c.c. and the nitrogen present estimated by the Kjeldahl method (Chem. Soc. Abstr. 1891, 758; compare Braunstein, Zeitsch. physiol. Chem. 1900, 31, 381).

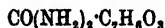
III. In the Pfüger-Bleibtreu method for the estimation of urea in urine, the nitrogenous compounds other than urea are precipitated by

means of a mixture of hydrochloric and phosphotungstic acids; the urea decomposed in the neutralised filtrate by heating it with phosphoric acid, and the ammonia estimated. For working details of this and the other methods, see Abderhalden's *Handbuch der Biochemischen Arbeitsmethoden*, vol. iii. part 2, 776-782.

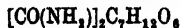
Derivatives. Salts.—Urea forms salts with metals; *silver urea* $\text{CO}(\text{NH}_2)_2$ (Mulder, Ber. 1873, 6, 1019); *monopotassium urea* $\text{CON}_2\text{H}_4\text{K}$, colourless needles; *dipotassium urea* $\text{CON}_2\text{H}_4\text{K}_2$, gelatinous mass (Franklin and Stafford, Amer. Chem. J. 1902, 28, 83). It also forms salts with acids, some of which combine with metallic salts to form stable crystalline double salts. The *nitrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$ forms sparingly soluble monoclinic crystals that decompose at 140° (Gaubert, Compt. rend. 1907, 145, 378; v. Barker, Min. Mag. 16, 207, for crystallographic constants); it is precipitated quantitatively when concentrated solutions of cyanamide and nitric acid are mixed at below 20° (D. R. P. 285259, from J. Soc. Chem. Ind. 1915, 34, 1166); the *hydrochloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}$ dissociates in aqueous solution (Datta, Chem. Soc. Trans. 1912, 101, 166); see also du Toit (Proc. K. Akad. Wetensch. Amsterdam, 1913, 16, 555); the *phosphate* $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, large rhombic crystals, readily soluble in alcohol or water; the *phosphotungstate* crystallises in rhombic prisms (Drummond, Bio-Chem. J. 1918, 12, 5); *acetate* $\text{CO}(\text{NH}_2)_2 \cdot \text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, large deliquescent crystals (Matignon, Compt. rend. 1891, 112, 1367); *glycine urea*



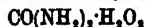
large crystals (Matignon, Bull. Soc. chim. 1894, [iii.] 11, 575); the *salicylate (ursal)*



has m.p. 122° ; the *acid salt* $\text{CO}(\text{NH}_2)_2 \cdot 2\text{C}_7\text{H}_5\text{O}_2$ has m.p. 115° ; the *quinate (urocol)*



m.p. 107° ; the *picrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_2$ decomposes at 142° (Smolka, Monatsh. 1885, 6, 916); the *oxalate* $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ forms rhombic plates or prisms, sparingly soluble in water (1:23), less so in alcohol (1:62), amyl alcohol, and insoluble in ether. With hydrogen peroxide urea forms the compound

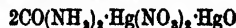


crystallising in large transparent crystals (Tanatar, J. Russ. Phys. Chem. Soc. 1908, 40, 376). Urea forms crystalline compounds with *sodium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{NaCl} \cdot \text{H}_2\text{O}$ rhombic plates or prisms, m.p. 60° - 70° ; with *ammonium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$ quadratic plates or needles that readily dissociate; with *calcium nitrate* $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, the compound is crystalline, readily soluble in water and not deliquescent (Bosch, U.S. Pat. 1369383); with *calcium chloride* $\text{CaCl}_2 \cdot 4\text{CO}(\text{NH}_2)_2$, m.p. 158° - 160° , stable in air, said to be useful for subcutaneous injection in hay fever and asthma (Knoll & Co., D.R.P. 306804, from Chem. Zentr. 1918, ii. 420; Okuda and Fujiwaka, J. Tokyo Chem. Soc. 1919, 40, 404); with *calcium bromide (ureabromin)* $4\text{CO}(\text{NH}_2)_2 \cdot \text{CaBr}_2$, m.p. 186° , which has therapeutic properties resembling those of the alkali bromides (Blitz, Pharm.

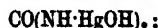
Zentr. 1912, 53, 245); $\text{CaBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$, hexagonal plates, m.p. 146° (Okuda and Fujiwaka, l.c.); with *calcium iodide* $\text{CaI}_2 \cdot 8\text{CO}(\text{NH}_2)_2$, hexagonal plates, m.p. 168° - 169° (Okuda and Fujiwaka, l.c.); $\text{CaI}_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, large transparent plates, m.p. 167.5° (Sptz, D. R. P. 318343, from Chem. Zentr. 1920, ii. 601); with *mercuric chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{HgCl}_2$; with *zinc chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{ZnCl}_2$; with *cadmium chloride* $\text{CO}(\text{NH}_2)_2 \cdot \text{CdCl}_2$; with *silver nitrate* $\text{CO}(\text{NH}_2)_2 \cdot \text{AgNO}_3$; with *palladium chloride* $\text{PdCl}_2 \cdot 2\text{CO}(\text{NH}_2)_2$; and with *magnesium bromide* $\text{MgBr}_2 \cdot 6\text{CO}(\text{NH}_2)_2$, m.p. 167° - 170° , with decomposition, and $\text{MgBr}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ decomposes at 165° - 170° (Menschutkin, Petersburger polytechn. Inst. 1906, 6, 101). Among the double salts formed by urea are the *platini-chlorides* $[\text{CO}(\text{NH}_2)_2 \cdot \text{HCl}]_2 \cdot \text{PtCl}_2 \cdot 2\text{H}_2\text{O}$, hygroscopic yellow prisms (Heintz, Annalen, 1879, 198, 91) and $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{PtCl}_6$, m.p. 119° - 120° , red prismatic crystals (Pickard and Kenyon, Chem. Soc. Trans. 1907, 91, 902); the *aurichlorides* $2\text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot \text{AuCl}_3$ and $\text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot \text{AuCl}_3 \cdot \text{H}_2\text{O}$; the *guanine hydrochloride* $\text{C}_6\text{H}_4\text{N}_4\text{O}_2 \cdot \text{HCl} \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{HCl} \cdot 5\text{H}_2\text{O}$, and similar compounds containing quinidine and cinchonidine (Drygin, Chem. Zentr. 1881, 245); the double hydrobromide



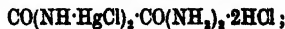
m.p. 70° - 75° , decomposes at 130° - 140° ; the corresponding double hydrochloride is employed as a local anæsthetic (Golubev, J. Russ. Phys. Chem. Soc. 1914, 46, 189); *cotarnine carbamide*, m.p. 180° , possesses therapeutic properties (Knoll & Co., D. R. P. 232785). The compounds with *mercuric nitrate* $2\text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $2\text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO}$ and



are obtained by precipitation between urea and mercuric nitrate under different conditions of concentration. Urea also combines with mercuric salts to form salts of the divalent radicle $\text{CO}(\text{NHHg})_2$, 'mercurocarbamide'; the *hydroxide*



the *chloride* $\text{CO}(\text{NH} \cdot \text{HgCl})_2$, and



the *nitrate*



and the *acetate* $\text{CO}(\text{NH} \cdot \text{HgOAc})_2$ (Ruspaggiari, Gazz. chim. ital. 1897, 27, I, 1). Salts containing chromium complexes and urea have been described by Sell (Proc. Roy. Soc. 1882, 33, 267; 1889, 45, 321).

Acyl derivatives of urea, v. UREIMES.

Chloro and nitro derivatives.—*Chlorourea*



decomposes at 71° , dissolves in five parts of water at ordinary temperature, giving a neutral solution that loses nitrogen and forms biuret. It reacts slowly in aqueous solution with aliphatic ketones, yielding the monochloroketone (Béhal and Detoeuf, Compt. rend. 1911, 153, 681 1229); and with ethylenic hydrocarbons, giving the corresponding chlorohydrin (Detoeuf, Bull. Soc. chim. 1922, [iv.] 31, 102). *Dichlorourea* $\text{CO}(\text{NHCl})_2$, prepared by passing a rapid stream of chlorine into a well-cooled solution

of urea in water, forms colourless plates that melt with decomposition at 82° when cautiously heated and detonate when rapidly heated, forming nitrogen chloride; on decomposition with ammonia in strong aqueous solution *p*-urazine $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{CO}$ is formed (Chattaway, Proc. Roy. Soc. 1908, A. 81, 381; Chem. Soc. Trans. 1909, 95, 236; compare Datta, *ibid.* 1912, 101, 166; Dowell, J. Amer. Chem. Soc. 1919, 41, 124).

Nitrourea $\text{NO}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, prepared by the action of concentrated sulphuric acid on urea nitrate, forms sparingly soluble crystals that decompose on melting; it is a strong acid, liberating acetic acid from its salts. The potassium, sodium and mercury salts have been prepared. On reduction with zinc dust and sodium hydroxide, it forms *nitrosourea* $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NO}$, and this develops a purple colour with ferrous sulphate (Thiele and Lachmann, Annalen, 1895, 288, 281). On further reduction it yields semicarbazide



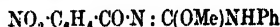
See Backer (Rec. trav. chim. 1912, 31, 1) for the electrolytic reduction of nitrourea. *Carbaminoazoisimide* $\text{NH}_2 \cdot \text{CO} \cdot \text{N}$, from sodium nitrite and semicarbazide has m.p. 92°–93° (Thiele and Stange, Annalen, 1894, 283, 1); *cyanocarbamide* $\text{CN} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ (Mauguin and Simon, Compt. rend. 1920, 170, 998).

The *alkyl* and *aryl* derivatives of urea are prepared by Wöhler's method from the corresponding mono- or di-substituted ammonium cyanate; by the action of ammonia on the isocyanic ester, and by the action of carbonyl chloride on the amine. For a description of these derivatives, see Michler, Ber. 1875, 8, 1664; Schiff, Annalen, 1877, 189, 157; Michler and Escherich, Ber. 1879, 12, 1162; Hemmelmayr, Monatsh. 1891, 12, 89; Chancel, Compt. rend. 1892, 115, 242; Schneegans, Arch. Pharm. 1894, 231, 675; A. E. Dixon, Chem. Soc. Trans. 1895, 47, 559; Diels and Golimann, Ber. 1911, 44, 3158; Cannizzaro, Gazz. chim. ital. 1871, 1, 41; Letts, Chem. Soc. Trans. 1872, 25, 448; Paternó and Spica, Gazz. chim. ital. 1875, 5, 388; Michler, Ber. 1876, 9, 396, 710; Claus, *ibid.* 693; Weith, *ibid.* 821; Pagliani, Gazz. chim. ital. 1879, 9, 28; Cosack, Ber. 1879, 12, 1449; 1880, 13, 1088; Michler and Zimmermann, *ibid.* 1881, 14, 2177; Michler and Keller, *ibid.* 2181; Traube, *ibid.* 1882, 15, 2122; Kym, *ibid.* 1890, 23, 424; Kühn and Landau, *ibid.* 811; Manuelli and Comanducci, Gazz. chim. ital. 1899, 29, ii, 136; Davis, Roberts, Brewster, J. Amer. Chem. Soc. 1916, 38, 731. For a summary of the alkyl substituted ureas, see Abderhalden's Biochemisches Handlexikon, 1911, vol. i. part 2, pp. 772, 773. For ureas of the naphthalene series, v. Bayer & Co., D. R. PP. 278122, 284938, 289107, 289163, and for the di-aryl-urea chlorides v. D. R. P. 285134.

Urea forms condensation derivatives with *formaldehyde* (Goldschmidt, Ber. 1896, 29, 2438; Chem. Zeit. 1897, 21, 460; Di Palma, Boll. Chim. Farm. 1912, 51, 78; Einforn and Hamburger, Ber. 1908, 41, 24; Dixon, Chem. Soc. Trans. 1918, 113, 238; Van Laer, Bull. Soc. chim. Belg. 1919, 28, 381); with β -diketones (Evans, J. pr. Chem. 1892, [ii.] 45, 499); with

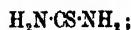
maleic anhydride (Dunlap and Phelps, Amer. Chem. J. 1897, 19, 492); with *acetone* (Weinschenk, Ber. 1901, 34, 2185); with *ethyl acetoacetate* (Müller, J. pr. Chem. 1897, [ii.] 55, 505); with *hydrazine* (Curtius and Heidenreich, Ber. 1894, 27, 55) with *phenylhydrazine* (Edeleanu, Chem. Zentr. 1892, i. 628); with *chloral hydrate* (Coppin and Titherley, Chem. Soc. Trans. 1914, 105, 32); and with *allozan* (Biltz, Annalen, 1921, 423, 282). For the condensation derivatives of ureas with acid esters, v. Roeder, Ber. 1913, 46, 2560.

*iso*Ureas, ψ -carbamides. The tautomeric form of urea $\text{HN}:\text{C}(\text{OH})\text{NH}_2$ is not known in the free state, but certain of its ethers have been prepared by the action of hydrogen chloride on cyanamide and the corresponding alcohol at 60°–70°. *Methyl-isourea* $\text{HN}:\text{C}(\text{OMe})\text{NH}_2$ has m.p. 44°–45°, b.p. 82°/0 mm.; the *hydrochloride* melts at 130°; *ethyl-isourea* $\text{HN}:\text{C}(\text{OEt})\text{NH}_2$ has m.p. 42°, b.p. 95°–96°/15 mm.; asym. *phenylmethyl-ethyl-isourea* $\text{HN}:\text{C}(\text{OEt})\text{NMePh}$ has b.p. 137°/21 mm., the isomeric asym. *phenylethylmethyl-isourea* $\text{HN}:\text{C}(\text{OMe})\text{NEtPh}$ has b.p. 126°/15 mm. (Stieglitz and McKee, Ber. 1900, 33, 807); *propyl-isourea* *hydrochloride* melts at 64° and decomposes at 121° (Stieglitz and Noble, *ibid.* 1905, 38, 2243); sym. *n*-nitrobenzoylphenyl-iso-urea *methyl ether*



has m.p. 124° (Bruce, J. Amer. Chem. Soc. 1904, 26, 419).

Thiourea. Isomerism amongst the derivatives of the sulphur analogue of urea is much more general than is the case with the derivatives of urea, and the convention has been adopted of limiting the term *thiocarbamides* to derivatives of the true thiocarbamide



derivatives of the isomeric form $\text{HN}:\text{C}(\text{SH})\text{NH}_2$, being called *thioureas*¹ (Reynolds, Chem. Soc. Trans. 1891, 59, 395).

Thiourea is prepared by heating ammonium thiocyanate at 160°–170°, the reaction is a balanced one; equilibrium is reached in about an hour, when the mixture contains about 25 p.c. of thiourea (Reynolds, Annalen, 1869, 150, 224; Reynolds and Werner, Chem. Soc. Trans. 1903, 83, 1; Findlay, *ibid.* 1904, 85, 403). Thiourea can also be obtained by the action of hydrogen sulphide on cyanamide



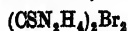
(Baumann, Ber. 1875, 8, 26).

Thiourea crystallises in needles that melt at about 172° if rapidly heated; the true melting-point cannot be determined, owing to tautomeric change; it is probably above 177° (Findlay, l.c.).

Derivatives. The *nitrate* $\text{CSN}_2\text{H}_4 \cdot \text{HNO}_3$, the *hydrochloride* $\text{CSN}_2\text{H}_4 \cdot \text{HCl}$, and the *silver*

¹ To distinguish between the three isomeric forms of substituted derivatives of thiourea, Dixon (Chem. Soc. Trans. 1896, 67, 564) proposes to designate the NH and NH_2 attachments as α and γ , whilst if the sulphur attachment is occupied by the substituent the compound is designated a *pseudothiourea*. Thus, for example, the systematic names of $\text{EtN}:\text{C}(\text{SH})\text{NMe}$, $\text{NH}:\text{C}(\text{SH})\text{NEt}$, and $\text{EtN}:\text{C}(\text{SH})\text{NEt}$ would be, respectively, α -ethyl- γ -dimethylthiourea, methyl- γ -thiourea, and methyl- α - γ -diethylthiourea.

nitrate derivative $\text{OSN}_2\text{H}_4\cdot\text{AgNO}_3$ are crystalline (Stevens, Chem. Soc. Proc. 1902, 17, 210; Kurnakow, Ber. 1891, 24, 3956). Dithiocarbamide dichloride $(\text{CSN}_2\text{H}_4)_2\text{Cl}_2$ can be crystallised from concentrated hydrochloric acid, and forms the dinitrate $(\text{CSN}_2\text{H}_4)_2(\text{NO}_3)_2$ by the action of dilute nitric acid; the dibromide



and di-iodide $(\text{CSN}_2\text{H}_4)_2\text{I}_2$ are colourless and decompose on warming or by the action of solvents (Claus, Annalen, 1875, 179, 135; McGowan, Chem. Soc. Trans. 1886, 49, 190). The potassium compound $\text{CSN}_2\text{H}_4\cdot\text{K}(\text{CSN}_2\text{H}_4)_2$ forms needles, m.p. 145° (Werner, Chem. Soc. Trans. 1916, 109, 1120); acetylthiocarbamide, m.p. 165° ; diacetylthiocarbamide, m.p. 151° – 152° (Hohmann, J. Amer. Chem. Soc. 1915, 37, 2130; Werner, l.c.).

For the alkyl and aryl substituted derivatives of thiourea and thiocarbamide, see Arzruni, Ber. 1871, 4, 406; Miguel, Bull. Soc. chim. 1877, [ii.] 28, 104; de Clermont, Compt. rend. 1876, 82, 512; Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358; A. E. Dixon, Chem. Soc. Trans. 1891, 59, 562; 1892, 61, 536; 1893, 63, 318, 538; 1895, 67, 556; 1899, 75, 373; 1906, 89, 892; 1907, 91, 912; 1908, 93, 18; Werner, Chem. Soc. Trans. 1919, 115, 1168. M. W. A.

UREASE v. FERMENTATION.

Urease is produced more profusely by pure cultures of *Bacterium radicola* than by the nodules, particularly by viciae, trifolii, and pisiforms. Urease is also, in certain cases, a product of normal papilionaceous plants (M. W. Beijerinck, Chem. Soc. Abstr. 1923, 124, i. 1157).

From dried cultures of *Bacillus proteus* a soluble urease has been extracted by the use of various phosphate solutions (Tetsugoro Takahata, Chem. Soc. Abstr. 1923, 124, i. 1157).

The presence of two constituents in urease has been confirmed by N. Katô (Biochem. Zeitsch. 1923, 139, 352–365). The urease system consists of a thermo-labile constituent which possesses fermentative properties, and a thermo-stable constituent with no fermentative action which N. Katô calls 'stable component X'. This last, at urea concentrations above the 'equivalent urea concentration' (l.c.), increases the activity of the urease, but has no influence at substrate concentrations below this value; its action resembles that of glycine. The action of 'stable component X' is not due to alteration of the hydrogen ion concentration nor to the presence of mineral salts (J. Chem. Soc. Ind. 1923, 42, 993 A).

Urease effects complete conversions of urea into ammonium carbonate. The sample of urea, in aqueous solution, is brought to exact neutrality, a neutral urease solution (freshly extracted from jack-bean flower by means of water, the mixture being exactly neutralised with hydrochloric acid) added, and the mixture kept at room temperature for one hour. A known excess of N/10 hydrochloric acid is then added and the carbon dioxide removed by aeration. The excess of acid is titrated with N/10 sodium hydroxide; each c.c. of N/10 acid consumed is equivalent to 3 mg. of urea originally present. The results are accurate to within a few hundredths of 1 p.c. The method can be used for determining urea in cyanamide and in

phosphate mixtures (after precipitating the phosphate with baryta), and appears to be of quite general application. Most salts have a depressant effect on the action of urease, and barium and calcium chlorides must be removed prior to its addition (E. J. Fox and W. J. Geldard, Ind. Eng. Chem. 1923, 15, 743–745; J. Soc. Chem. Ind. 1923, 42, 901 A).

UREIDES or acyl derivatives of urea are formed by condensation between urea and the acid with the elimination of water; in the case of a monocarboxylic acid the product may be a monoureide $\text{RCONH}\cdot\text{CO}\cdot\text{NH}_2$ or a diureide $\text{CO}(\text{NH}\cdot\text{COR})_2$, according as one or two molecules of the acid condense with one molecule of urea. Similar products may be obtained in the cases of the hydroxy acids and the di-carboxylic acids, but usually condensation occurs between one molecule of the acid and one of urea with the elimination of two molecules of a water and the formation of a cyclic ureide. The more important cyclic ureides have already been de-

scribed; they include glycolylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$

v. HYDANTOIN. β -Lactylurea, hydracrylurea, hydroureacil $\text{CO}\begin{matrix} \text{NH}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CH}_2$ v. PYRIMIDINES.

Oxalylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$ v. PARABANIC ACID. Malonylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CH}_2$ v. Barbituric acid, art.

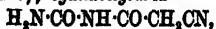
PYRIMIDINES. Hydrozomalonylurea, tartronylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CH}\cdot\text{OH}$ v. DIALURIC ACID. Mesoxalylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CO}\cdot\text{H}_2\text{O}$ v. ALLOXAN. Nitromalonylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CH}\cdot\text{NO}_2$ v. DILUTURIC

ACID. isoNitrosomalonylurea $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{C}\cdot\text{NOH}$ v. Violuric acid, art. PYRIMIDINES. Aminomalonylurea, aminobarbituric acid $\text{CO}\begin{matrix} \text{NH}\cdot\text{CO} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CH}\cdot\text{NH}_2$

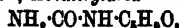
v. Uramil, art. PYRIMIDINES. For the action of ureides on ethyldiazoacetate, v. Calcagni (Atti R. Accad. Lincei, 1916, [v.] 25, 1, 643).

Of the open chain mono- and di-ureides, the following have been described: formylurea $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHO}$, m.p. 168° – 169° (Geuther, Marsh and Scheitz, Zeitsch. Chem. 1868, 300; Gorski, Ber. 1896, 29, 2046), forms a mercury salt (Matignon, Bull. Soc. chim. 1880, [ii.] 34, 207); acetylurea $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{COCH}_3$, m.p. 218° (Behrend, Annalen, 1885, 229, 30; Ber. 1896, 28, Ref. 63; cf. Kohman, J. Amer. Chem. Soc. 1915, 37, 2133; Werner, Chem. Soc. Trans. 1916, 109, 1120), forms mercury, silver and cuprous salts (Matignon, l.c.; v. also Pieroni, Gazz. chim. ital. 1911, 41, 11, 754, for mercuri-methylurethane hydroxide); ab-diacetylurea $\text{CO}(\text{NH}\cdot\text{COCH}_3)_2$, m.p. 152° – 153° (Schmidt, J. pr. Chem. 1872, [ii.] 5, 63; Werner, l.c.); chloroacetylurea $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ decomposes at 160° (Tommasi, Bull. Soc. chim. 1873, [ii.] 19); trichloroacetylurea, m.p. 150° with decomp. (Meldola and Tommasi, Chem. Soc. Trans. 1874, 404); bromoacetylurea $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$;

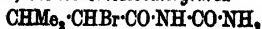
tribromacetylurea, m.p. 158° (Baeyer, Annalen, 1864, 130, 149); *cyanacetylurea*



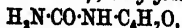
m.p. 200°–210°; *isovalerylurea*



m.p. 191°; *monobromoisovalerylurea*

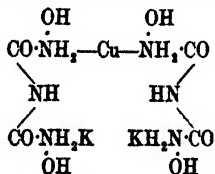


(*bromoura*l), m.p. 149°, is a narcotic (van der Eeckhout, Arch. exp. Path. Pharm. 1907, 57, 338); it yields two *colarnine* derivatives, m.p. 125°–127° and 105°–110° respectively, and these have therapeutic values (Knoll & Co., D. R. P. 232785); *butyrylurea*



m.p. 176°; *succinylurea* $\text{C}_4\text{H}_7\text{O}_2(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$; *benzoylurea* $\text{NH}_2\cdot\text{CO}\cdot\text{NHCOPh}$, m.p. 200°; *ab-dibenzoylurea* $\text{CO}(\text{NH}\cdot\text{COPh})_2$, m.p. 210°; *aa-dibenzoylurea* $\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{COPh})_2$, m.p. 197°; *p-nitrobenzoylurea*, m.p. 243°–245° (evolution of gas); *o-chloroacetylaminobenzoylurea*, m.p. 222°–223° (effervesces); the *meta*-derivative melts at 252°–253° (decomp.) (Jacobs and Heidelberger, J. Amer. Chem. Soc. 1917, 39, 2418).

Carbonyldiurea $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, decomposes on heating (Schmidt, J. pr. Chem. 1872, [ii.] 5, 39); *carboxylurea*, *allophanic acid* $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{COOH}$ does not exist in the free state; the *esters* can be obtained by the action of phosphoric oxide on the corresponding urethane (Billmann and Bjerrum, Ber. 1917, 50, 503); the *methyl ester* has m.p. 208° (Ephraim, Ber. 1893, 26, 2172); the *ethyl ester*, m.p. 191° (Liebig and Wöhler, Annalen, 20, 396; 59, 291); the *amide* $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CONH}_2\cdot\text{H}_2\text{O}$ is *biuret*, m.p. 190°; it gives a purplish-violet colour with copper sulphate and potassium hydroxide, due to the formation of the double salt



A similar reaction is given by proteids which contain two amino groups in the molecule, these groups being joined directly together or through a single atom of nitrogen or carbon. The amino groups must be either two $\cdot\text{CONH}_2$ groups or one $\cdot\text{CONH}_2$ group and one $\cdot\text{CSNH}_2$, $\text{C}(\text{NH})\text{NH}_2$, or $\cdot\text{CH}_2\text{NH}_2$ group. Substances that are non-proteid in character but which contain the necessary groups will also give the biuret reaction, for example, *oxamide* and *malonamide*.

The *ureides* of substituted *aminonaphthol sulphonic acids* form dyes when coupled with diazotised aniline or similar compounds, and may be employed as therapeutic agents for destroying blood parasites. They form metallic salts, which also possess therapeutic properties (Heymann, Dressel, Kothe, Ossenbeck, U.S. Pat. 1308071).

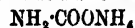
Carbonyldiurethane, m.p. 108°, is produced by the action of urethane on carbonyl chloride; for the action of ammonia and amines on this compound, see Daina, Greder and Kidwell (J. Amer. Chem. Soc. 1919, 41, 1004); Dains and Wertheim (*ibid.* 1920, 42, 2303).

Ureides of sugar. The term *ureide* is also

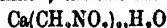
applied to certain condensation products of urea with aldehydes; these are of the type $\text{RCH:N}\cdot\text{CO}\cdot\text{NH}_2$ and the most important are those derived from the aldoses. *Glucoseureide* $\text{CH}_2\text{OH}[\text{CH}\cdot\text{OH}]_4\text{CH:N}\cdot\text{CO}\cdot\text{NH}_2$, thick rhombic crystals, m.p. 207° (decomp.), $[\alpha]_D^{15} -23.5^\circ$ in 10 p.c. aqueous solution; the *penta-acetyl derivative* $\text{C}_7\text{H}_9\text{O}_5\text{N}_2(\text{CH}_3\text{CO})_5$ has m.p. 200°, and the *tetrabenzoyl* m.p. 117°. *Galactoseureide* is a white amorphous powder $[\alpha]_D +15^\circ$; *mannoseureide*, m.p. 188°, $[\alpha]_D^{20} -45.8^\circ$; *lactoseureide* $(\text{C}_{12}\text{H}_{21}\text{O}_{11}\text{N})_2\text{N}\cdot\text{CO}\cdot\text{NH}_2$ decomposes at 240°, $[\alpha]_D^{20} +2.1^\circ$ (Schoorl, Rec. trav. chim. 1903, 22, 31; Mayer, Biochem. Zeitsch. 1909, 17, 1345).

URETHANE v. SYNTHETIC DRUGS.

URETHANES are the esters of *carbamic acid* (*aminoformic acid*) $\text{H}_2\text{N}\cdot\text{COOH}$; the free acid is not known, but it is said to occur in blood serum (Drechsel, J. pr. Chem. 1875, [ii.] 12, 417; cp. Hofmeister, Archiv. Physiol. 1876, 12, 337), and in urine (Abel and Drechsel, Chem. Zentr. 1891, ii. 713; Hahn and Nencki, Arch. Sc. biol. Petersb. 1892, 1, 467; Abel and Muirhead, Arch. exp. Path. Pharm. 1893, 31, 15; 32, 467). The ammonium salt

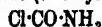


is produced by the direct action of carbon dioxide on ammonia in cooled absolute alcohol. It is a white crystalline powder. The *sodium* $\text{NaCH}_2\text{NO}_2\cdot\text{H}_2\text{O}$ and *potassium* KCH_2NO_2 salts are also crystalline; the *calcium* salt



is insoluble in alcohol and crystallises from concentrated ammonia solution in four-sided prisms.

Carbamyl chloride (chloroformamide)



prepared by passing hydrogen chloride over heated metallic cyanates, or carbonyl chloride over heated ammonium chloride, forms long, broad needles, m.p. 50°, b.p. 61°–62° (Gattermann and Schmidt, Ber. 1887, 20, 858).

Urethane, *ethyl carbamate* $\text{NH}_2\cdot\text{COOEt}$, prepared by the action of ammonia on ethyl carbonate or ethyl chlorocarbonate; by heating urea nitrate with alcohol; or by the action of alcohol on carbamyl chloride, crystallises in large pliable plates or prisms that break with a fibrous fracture, sublime readily, melt at 50° and boil at 184°. The system urethane-benzene forms a eutectic containing 97 mols. p.c. at 4.2°, and solid solutions in the interval from 97 to 100 mols. p.c. of benzene (Puschin and Masarvitch, J. Russ. Phys. Chem. Soc. 1914, 46, 1366). For the use of urethane as a cryoscopic solvent, see Bruni (Atti R. Accad. Lincei, 1918, [v.] 27, i. 321). When heated with water or ammonia, urethane yields a small quantity of urea; for the explanation of this reaction, see Werner (Chem. Soc. Trans. 1918, 113, 622).

Urethane has therapeutic properties, being employed as a hypnotic. Certain of its substituted derivatives have similar properties; for example, *phenylurethane* or *euphorine*



methylpropylcarbinal urethane or *ledonal*



and *o*-carbonyl-urethane, m.p. 110° (Knoll & Co., D. R. P. 232785).

Urethanes when heated with calcium or strontium bromide yield double compounds of the urethane and the metallic bromide;



is a powerful hypnotic (v. J. Soc. Chem. Ind. 1915, 34, 1166; and Gebe & Co., D. R. P. 284734).

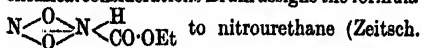
p-Benzylphenyl carbamate, m.p. 144°, *p*-iso-amyphenyl carbamate, m.p. 73°–74°, *p*-butylphenyl carbamate, m.p. 123°–124°, *p*-isopropylphenyl carbamate, m.p. 93°–95°, *p*-butylphenyl *N*-dimethylcarbamate, m.p. 92°, *o*-allylphenyl carbamate, m.p. 122°–123°, are white powders, sparingly soluble in water, and possess anthelmintic properties (Synthetic Patents Co., U.S. Pat. 1252452, and Farbenfabriken vorm. Friedr. Bayer & Co., D. R. P. 296889, from Chem. Zentr. 1917, i. 714).

4-Hydroxy-3-urethano-phenylarsine



is a white powder, (Farbwerke vorm. Meister, Lucius and Brüning, D. R. P. 275216, addition to D. R. P. 268220).

Nitrourethane $\text{NO}_2 \cdot \text{NH} \cdot \text{COOEt}$ melts at 64°, is readily soluble in water and alcohol and forms metallic salts, the *potassium*, *mercury*, and *silver* salts having been prepared (Thiele and Lachmann, Annalen, 1895, 288, 304). From spectrochemical considerations Brühl assigns the formula



physikal. Chem. 1898, 26, 47; 25, 577). Nitroso-urethane $\text{NO} \cdot \text{NH} \cdot \text{COOEt}$ melts and decomposes at 51°–52° and does not develop a purple colour with ferrous sulphate and potassium hydroxide: the *silver*, *potassium* and *ammonium* derivatives are yellow (Thiele and Lachmann, l.c.). From index of refraction values, Brühl regards nitro-

sourethane as diazourethane $\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{NH} \cdot \text{COOEt}$

(Ber. 1902, 35, 1148), whilst Hantzsch formulates it as an *antidiazohydrate* $\text{HO} \cdot \text{N} \cdot \text{N} \cdot \text{COOEt}$ (*ibid.* 1899, 32, 575). *Dibromourethane* $\text{NBr}_2 \cdot \text{COOEt}$ has b.p. 100°–104°/10–11 mm. (Diels and Ochs, Ber. 1907, 40, 4571). *Ethylchlorocarbamate* $\text{NHCl} \cdot \text{CO}_2\text{Et}$ is obtained by the action of chlorine on ethyl carbamate if the solution is kept well cooled; it is a pale yellow viscous oil, b.p. near 99° (decomp.) (Datta and Gupta, J. Amer. Chem. Soc. 1914, 36, 386); it is slowly hydrolysed by water, yielding ethyl 4-chloromethylcyclohexylmethylenhydrazineimide 1:3-dicarboxylate $\text{CH}_2\text{Cl} \cdot \text{CH} \begin{array}{c} \diagup \text{N}(\text{CO}_2\text{Et}) \diagdown \\ \diagdown \text{N}(\text{CO}_2\text{Et}) \diagup \end{array} \text{NH}$, colourless needles, m.p. 143°, which forms a crystalline *acetyl* derivative, m.p. 117°–118°, and *imide chloride*, m.p. 75°–76° (Datta and Chatterjee, *ibid.* 1922, 44, 1538).

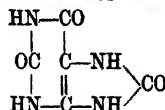
Urethane forms condensation products with aldehydes and keto acids. *Chloralurethane* $\text{CCl}_2 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{COOEt}$ has m.p. 103°; *bromalurethane* $\text{CBr}_2 \cdot \text{CH}(\text{OH}) \cdot \text{NH} \cdot \text{COOEt}$ has m.p. 132° (Birchhoff, Ber. 1874, 7, 628, 1078; Conrad and Hook, *ibid.* 1903, 36, 2206; Simon, Compt. rend. 1901, 133, 535; Simon and Chavanne, *ibid.* 1906, 143, 51).

Thiourethane, a mixture of the isomeric thiourethanes, is obtained by acting on an alcoholic solution of potassium thiocyanate with concentrated hydrochloric acid; these correspond with two of the isomeric forms of the hypothetical thiocarbamic acid, *ethyl xanthamide* $\text{NH}_2 \cdot \text{CS} \cdot \text{OEt}$, m.p. 38°, and *carbonylthioethylamine* $\text{NH}_2 \cdot \text{CO} \cdot \text{SEt}$ (Blankenhorn, J. pr. Chem. 1877, [ii.] 16, 358).

M. A. W.

URGINEA. v. SQUILL.

URIC ACID, 2:6:8-trioxypurine



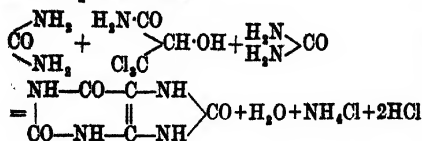
was discovered in human urine by Scheele in 1776 (Opuscula, 1776, 2, 73), independently by Bergmann in urinary calculi (*ibid.* 1776, 4, 232), and in 'chalk-stones' by Pearson in 1798 (Trans. Roy. Soc. 1798, 15).

Uric acid occurs in the urine of all animals, though only to a small extent in the case of herbivorous animals; the average daily excretion in normal man being 0.597 grm. (Hanzlik and Hawk, J. Biol. Chem. 1908, 5, 355). It occurs in the excrement of birds, reptiles, scaly amphibians, snails and insects; the wing scales of the group of butterflies known as the white *Pieridae* contain uric acid, those of the yellow *Pieridae* contain, as their pigment, a yellow derivative of uric acid, which can be obtained synthetically by heating uric acid with water in sealed tubes at a high temperature (Hopkins, Proc. Roy. Soc. 1894, 57, 5). Uric acid is a normal constituent of the organs and blood of birds, but only occurs in human blood under certain pathological conditions. For its occurrence in blood, v. Bass (Amer. Chem. Abs. 1914, 1602).

Preparation.—Uric acid can be isolated from serpent's excrement, bird's excrement or guano by boiling the material with dilute alkali hydroxide or milk of lime, filtering the hot liquid and precipitating the uric acid by adding excess of hydrochloric acid to the filtrate. Uric acid can also be obtained from the yellow acid urates deposited from urine; this is boiled with sodium hydroxide until it ceases to evolve ammonia, the liquid is filtered and the acid sodium urate precipitated from the filtrate by means of carbon dioxide; this is redissolved in sodium hydroxide and the solution decomposed by acetic acid, or the hot solution of the alkali salt may be purified by boiling with a little potassium permanganate or dichromate and the filtrate decomposed by hydrochloric acid.

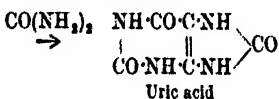
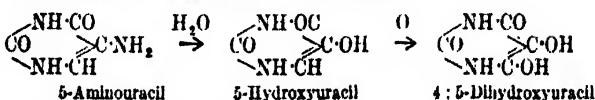
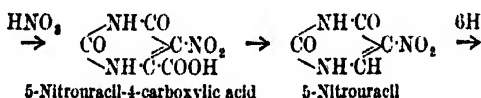
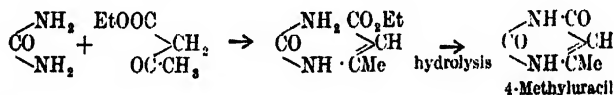
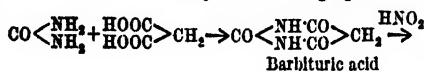
Synthesis.—Uric acid was first synthesised by Horbaczewski by carefully fusing glycine with 10 to 15 times its weight of urea in small quantities at a time, until a considerable quantity of precipitate had formed in the molten mass; the uric acid was precipitated in the form of its sparingly soluble silver magnesium salt, which on treatment firstly with potassium sulphide and subsequently with hydrochloric acid, yielded pure uric acid (Monatsh. 1882, 3, 796; 1885, 6, 366). Compare, however, Behrend (Annalen, 1925, 441, 2159; Chem. Soc. Abstr. 1925, i. 441). Further syntheses were effected by Horbaczewski

(*ibid.* 1887, 8, 201) by fusing trichlorolactamide with 10 parts of urea



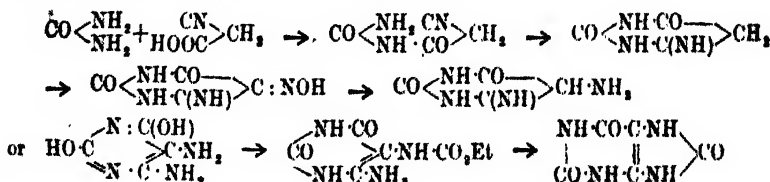
and by fusing trichlorolactic acid with urea (*ibid.* 1887, 8, 584).

In 1863, Baeyer (Annalen, 1863, 127, 3, 234) synthesised *pseudouric acid*, starting with malonic acid and urea; but it was not until 1895 that Fischer and Ach (Ber. 1895, 28, 2473) showed that uric acid could be readily obtained from pseudouric acid by fusion with oxalic acid, or by boiling with hot dilute mineral acids (Fischer, *ibid.* 1897, 30, 559); a complete synthesis of uric acid from malonic acid and urea is therefore represented by the following equations:



Traube's synthesis of uric acid, starting with cyanacetic acid and urea, is also important, and by substituting alkyl ureas for urea, the method can be extended to the preparation of substituted uric acids. Cyanacetylurea, prepared by the condensation of urea with cyanacetic acid, is converted by the action of alkali into 4-amino-

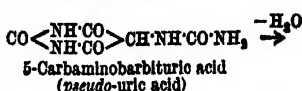
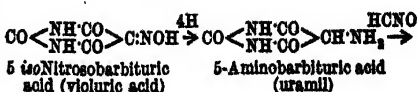
2:6-dioxypyrimidine, from which 4:5-diamino-2:6-dioxypyrimidine is obtained by reducing its isonitroso derivative; this diamine condenses with ethyl chloroformate to form a urethane derivative, from the sodium derivative of which uric acid is produced by heating at 180°-190° (Ber. 1900, 33, 1375, 3035).



Properties. Pure uric acid forms a colourless microcrystalline powder consisting of rhombic transparent plates or prisms; as precipitated from urine or guano extracts, the crystals are yellowish red or brown. These exhibit, under the microscope, characteristic irregularities in form, due to the rounding of the obtuse angles of the rhombic prisms, and the interpenetration of the crystals, and present the form of dumb-bells, whetstones, rosettes of

prismatic crystals, six-sided irregular plates or rectangular plates with partly jagged sides.

Uric acid is odourless and tasteless; it is sparingly soluble in water, one part dissolving in 39,480 parts at 18° (His and Paul, *Zeitsch. physiol. Chem.* 1900, 31, 41), or 15,505 parts at 37° (Gudzent, *ibid.* 1909, 60, 27). When shaken with water, uric acid decomposes so that the solubility tends to increase with the time; the increase is only noticeable at the end of 24 hours

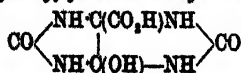


This is the most important synthetic method of preparing uric acid, and by replacing urea by its alkyl or aryl substituted derivatives, it is possible to prepare the corresponding alkyl or aryl substituted uric acids.

The synthesis of uric acid effected by Behrend and Roosen (Annalen, 1888, 251, 235), starting with ethyl acetoacetate and urea, is represented in the following series of equations:

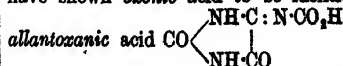
and then rises rapidly until at the end of 10 days the solubility is 11 times as great as at the end of a few hours, and in the same time the electrical conductivity has increased 55 times (Gudzent, *l.c.*; cf. Biltz and Herrmann, *Annalen*, 1923, 104). The supersaturation which occurs when a warm aqueous solution of uric acid is allowed to cool to a room temperature in contact with solid uric acid is probably the cause of the high values for the solubility found by Bensch (*Annalen*, 1845, 54, 190); Behrend and Roosen (*Annalen*, 1889, 251, 250). The molecular electrical conductivity of a saturated solution of uric acid is 32.24 at 18° (His and Paul, *l.c.*) or 33.92 at 37° (Gudzent, *l.c.*); the dissociation constant $k=0.000151$ at 18° or 0.000233 at 37°. See also Kanitz (Zeitsch. physiol. Chem. 1921, 116, 96). Uric acid has the power of adsorbing precipitated colloids from their solutions. If a trace of dye is added to a hot saturated solution of uric acid, coloured crystals of the latter are deposited from the cold solution (Benoit, *Compt. rend. soc. biol.* 1919, 82, 1051, 1052). Uric acid is fairly readily soluble in lactic acid, acetic acid (see Rossi, *Biochem. Zeitsch.* 1913, 54, 297) or warm concentrated sulphuric acid. For the influence of hydrogen-ion concentration on its solubility, see Jung (Helv. Chim. Acta, 1922, 5, 688). It dissolves in glycerol, but is insoluble in alcohol or ether; it dissolves readily in aqueous solutions of alkali hydroxides, of lithium carbonate, and of certain bases such as ethylamine, propylamine, piperazine, but is only sparingly soluble in solutions of urotropine (hexamethylenetetramine), *lycetol* (piperazine tartrate) or ammonia (Stevens and May, *J. Amer. Chem. Soc.* 1911, 33, 434; v. also Hanzlik, *Amer. Chem. Abs.* 1916, 1226). The solubility of uric acid in a 1 p.c. solution of sodium salicylate is twice as great, and in a 0.1 p.c. solution of sodium 2-phenylquinoline 4-carboxylate three times as great as in water (Stern, *Biochem. Zeitsch.* 1924, 151, 268; 1925, 159, 192).

Uric acid is not volatile: on being strongly heated it breaks up into urea, hydrocyanic acid, cyanuric acid and ammonia (Wöhler, *Pogg. Ann.* 1839, 15, 529, 619). When oxidised by strong nitric acid or potassium chlorate and hydrochloric acid, or by chlorine or bromine water in the cold, uric acid is broken down into alloxan (mesoxalylurea) (*q.v.*) and urea. For cyanuric acid as oxidation product of uric acid, v. Venable and Moore (*J. Amer. Chem. Soc.* 1917, 39, 7750). Warm dilute nitric acid produces parabanic acid (oxalylurea) (*q.v.*). By the action of such oxidising agents as potassium permanganate, or ferricyanide, lead peroxide, mercuric oxide or ozone in neutral or alkaline media, uric acid yields carbon dioxide and allantoin (glyoxyldiureide) (*q.v.*). According to Behrend (*Annalen*, 1904, 333, 141) and Behrend and Schultz (*ibid.* 1909, 365, 21), the first product of oxidation of uric acid in alkaline media is *hydroxyglycoluril carboxylic acid*



which on treating (a) with an excess of alkali hydroxide takes up the elements of water, forming *ureanic acid* (dicarbaminomalonic acid)

(COOH), $\text{C}(\text{NH} \cdot \text{CO} \cdot \text{NH})_2$ (*q.v.*; see also Behrend and Zieger, *Annalen*, 1915, 410, 337; Biltz and Max, *Ber.* 1920, 53, 1964; Biltz and Robl, *ibid.* 1967); (b) with acetic acid yields potassium hydrogen *oxonate* (Strecker, *Chem. Soc. Trans.* 1875, 555); Biltz and Robl (*Ber.* 1920, 53, 1967), have shown *ozonic acid* to be identical with



When oxidised by hydrogen peroxide in alkaline solution, uric acid yields *tetracarboximide* $\text{CO} < \begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \cdot \text{NH} \end{array} > \text{CO}$ (Scholtz, *Ber.* 1901, 34, 4130), *carbonyldiurea* $\text{CO}(\text{NH} \cdot \text{CO} \cdot \text{NH})_2$, and *urea* (Schittenhelm and Wiener, *Zeitsch. physiol. Chem.* 1909, 62, 100; cf. Venable and Moore, *l.c.*; Venable, *ibid.* 1918, 40, 1099; Moore and Thomas, *ibid.* 1120; see also Ohta, *Biochem. Zeitsch.* 1913, 54, 439).

Uric acid is decomposed when fused with potassium hydroxide, yielding the potassium salts of prussic, cyanic, carbonic and oxalic acids. When heated under pressure at 160°–170° with concentrated hydrochloric or hydriodic acid, it yields carbon dioxide, ammonia and glycocholl; it is oxidised by a solution of copper oxide in ammonia (Schweizer's reagent) in the presence of potassium hydroxide to urea and oxalic acid, and a similar oxidation is effected by boiling with ferric chloride. It is decomposed by certain moulds (Kossowicz, *Bied. Zentr.* 1912, 41, 791; *Chem. Zentr.* 1912, ii, 1300, 1482; 1913, i, 640).

For the physiological properties of uric acid, its origin, and the rôle it plays in the animal economy, see *Article URINE*; also *Biochemisches Handlexikon von Abderhalden*, vol. iv. 1095–1106; and *Oxidations and Reductions in the Animal Body*, by H. D. Dakin, 92. For the influence of drugs on the elimination of uric acid from the blood, v. Abl (*Arch. Expt. Path. Pharm.* 1913, 74, 119); Denis (*J. Pharmacol.* 1915, 7, 255, 601); Folin and Lyman (*J. Pharmacol. Expt. Ther.* 1913, 4, 539); Impens (*Chem. Zentr.* 1914, 563).

Detection.—Uric acid is readily identified by the appearance of the crystals under the microscope. The most characteristic and delicate test for uric acid is the 'murexide test,' which is applied as follows: a few drops of strong nitric acid is added to the uric acid or urate and the solution evaporated to dryness on the water bath, preferably in a porcelain basin; a yellowish-red residue of alloxantin is obtained which acquires the rich purple colour of ammonium purpurate (*murexide*, *q.v.*) on moistening with ammonia, the colour changing to blue on the addition of sodium hydroxide. The nitric acid employed in the test may be replaced by chlorine or bromine water, or by a few drops of concentrated hydrochloric acid and a small crystal of potassium chlorate. Other colour reactions of uric acid are described by (1) Denigès (*J. Pharm. Chim.* 1888, [v.] 18, 161), the uric acid is oxidised to alloxan by evaporating a solution in dilute nitric acid; on adding successively to the residue a few drops of concentrated sulphuric acid and of benzene containing thiophen, a bluish coloration is obtained; (2) Genassini (*Boll. chim. farm.* 1908, 47, 715), the uric acid or urate is suspended in water and

dissolved in 10 p.c. sodium hydroxide; subsequent saturation of the solution with potassium persulphate and the gradual addition of 10 p.c. zinc sulphate solution, until the precipitate formed no longer redissolves, causes the precipitate to assume a bluish-green colour. This test is not disturbed by the presence of proteins, other purines or pyrimidines, and may be applied for the detection of uric acid in urine or in blood. According to Vitali (*ibid.* 1911, 50, 799), sodium peroxide is the only oxidising agent that can replace the potassium persulphate in the above test, and no other metallic salt can be used instead of the zinc salt. (3) Folin and Denis (J. Biol. Chem. 1912, 12, 239), a blue coloration is developed when a solution containing 1 mg. of uric acid is mixed with 2 c.c. of a solution prepared by boiling for two hours a mixture of 100 grms. sodium tungstate, 80 c.c. of 85 p.c. phosphoric acid, and 750 grms. of water, cooling and diluting to a litre (compare Leturc, Ann. Chim. anal. 1907, 12, 194; Bass and Wiechowski, Chem. Zentr. 1913, i. 331; Obermayer, Popper and Zak, *ibid.* 658). Tests based upon the reducing properties of uric acid are the formation of a yellow, brown, or black stain of silver, when filter paper previously moistened with silver carbonate is treated with a drop of a solution of uric acid in sodium carbonate; and the reduction of Fehling solution on boiling an alkaline solution of uric acid with excess of the reagent. For the detection of uric acid in blood, Weber (Pharm. Zeit. 1912, 57, 252) recommends the following method: the blood is treated with sodium chloride and potassium phosphate to remove the proteins, the filtrate evaporated to a small bulk and saturated with ammonium chloride, the uric acid is thus precipitated as ammonium urate, which is collected and treated with a few drops of hydrochloric acid and the crystals of uric acid identified under the microscope or by the murexide test.

Estimation.—The methods of estimating uric acid in urine are based upon the precipitation of the uric acid in the form of the sparingly soluble ammonium or the double silver magnesium salt, and the subsequent determination of the uric acid in the carefully washed precipitate. Hopkins' method (Proc. Roy. Soc. 1892, 62, 93; J. Path. and Bacteriology, 1893, 1, 451), 30 grms. of ammonium chloride are added to 150 c.c. of the filtered urine previously warmed to 40° to 45°, after about an hour the precipitate of ammonium urate is collected on a small filter, washed with a 10 p.c. solution of ammonium sulphate until free from chlorine, and transferred to a beaker by means of a jet of hot water, the solution cooled and diluted with water to 100 c.c., 20 c.c. of pure concentrated sulphuric acid are added, and N/20 potassium permanganate run into the acid liquid at 60° until it acquires a pink tint permanent for some seconds and not changed by stirring. Each c.c. of N/20 permanganate solution decolorised represents 0.00375 gm. of uric acid. See Herles (Eighth Inter. Cong. App. Chem. 1912, 19, 141); Telle (Bull. Sci. Pharmacol. 1918, 25, 208).

Wärner (Zeitsch. physiol. Chem. 1900, 29, 70) recommends decomposing the washed ammonium urate with 1-2 p.c. sodium hydroxide solution, heating the solution on the water-bath

until it ceases to evolve ammonia and then determining the nitrogen in the residue by the Kjeldahl method: 1 c.c. N/10 sulphuric acid corresponds with 0.0042 gm. uric acid; Kowarsky (Berlin, Klin. Woch. 1917, 54, 987) recommends the estimation of the ammonia in the ammonium urate by the formalin method.

Folin and Shaffer's modification of Hopkins' method (Zeitsch. physiol. Chem. 1901, 32, 552) is as follows: A solution containing 500 grms. of ammonium sulphate, 5 grms. uranium acetate, and 10 p.c. acetic acid, 60 c.c. per litre is prepared, and 75 c.c. of this solution are mixed with 300 c.c. of the urine, kept for five minutes, passed through a double filter and two quantities of 125 c.c. each collected. Five c.c. of concentrated ammonia are added to each and after about 12 hours the precipitates of ammonium urate are collected and washed and the uric acid in each estimated by the permanganate method. The addition of uranium acetate is made in order to precipitate a small quantity of protein material which is otherwise thrown down on the addition of the ammonia, and which reduces permanganate. Ganasini (Boll. Chim. Farm. 1914, 53, 257) uses a modification of this method for precipitating the uric acid, which is then estimated by means of standard iodine solution, the uric acid being oxidised to alloxan, see Curtman and Lehmann (J. Biol. Chem. 1918, 26, 187).

Salkowski's method modified by Ludwig (Chem. Zentr. 1891, 390) consists in precipitating the uric acid in the urine (100 to 200 c.c.) with a mixture of ammoniacal silver solution and magnesium mixture (*cf.* Salkowski, Zeitsch. physiol. Chem. 1913, 83, 152); the precipitate containing all the uric and phosphoric acids is filtered and washed with very dilute ammonia. It is then decomposed by a warm dilute solution of potassium sulphide forming potassium urate which passes into solution, the filtrate is acidified with hydrochloric acid, evaporated to a small bulk, and the uric acid that separates on cooling is collected on a tared filter, washed with water, alcohol, ether, carbon disulphide, and again with ether, dried at 110° and weighed, see Salkowski (Zeitsch. physiol. Chem. 1913, 83, 152); Kretschmer (Biochem. Zeitsch. 1913, 50, 223); Graves and Kober (J. Biol. Chem. 1915, 20, xx.); (v. Bernard (Chem. Zentr. 1913, 1, 1364; from Bull. Sci. Pharmacol. 1913, 20, 66, for a comparative investigation of different methods; he maintains Salkowski's method gives the best results).

Folin and Shaffer (Zeitsch. physiol. Chem. 1901, 32, 552) recommend the following modification of the method in order to facilitate the removal of the silver from the silver magnesium urate; the double salt is decomposed by sulphuretted hydrogen in an acid solution containing 5 to 10 c.c. of 1 p.c. copper sulphate solution and the liquid boiled for a few minutes before filtering (*cf.* Schneller, Chem. Zentr. 1913, i. 1234).

Folin and Macallum recommend a colorimetric method for estimating uric acid in dilute solution based upon the blue colour produced when phosphotungstic acid and an alkali are added to uric acid (J. Biol. Chem. 1912, 11, 365; Folin and Denis, *ibid.* 1912, 14, 95; Brugsch and Kristeller, Chem. Zentr. 1915, i. 1090;

Benedict and Hitchcock, J. Biol. Chem. 1915, 20, 619, 629). The replacement of phosphotungstic by arsenotungstic or arseno-phosphotungstic acid gives a greater depth of colour (Morris and Macleod, J. Biol. Chem. 1922, 50, 55; Benedict, *ibid.* 1922, 51, 187; 52, 387). It is claimed that the method as modified by Benedict and Hitchcock (*ibid.* 1915, 20, 624) gives as accurate results as the titration method of Folin and Shaffer (v. Morris, *ibid.* 1916, 25, 205; Proc. Amer. Soc. Biol. 1916, xiii.; 1917, 29), who recommends precipitating the uric acid with zinc acetate in alkaline solution as a preliminary to the application of Benedict's method. See Salkowski (Zeitsch. physiol. Chem. 1913, 85, 346); Kaschiwabara, (*ibid.* 1913, 84, 223); Hüst (Zeitsch. physiol. Chem. 1915, 95, 88); Bogert (J. Biol. Chem. 1917, 31, 165); Morris (Proc. Amer. Soc. Biol. Chem. 1917, xxi.; J. Biol. Chem. 1918, 33; 1919, 37, 231); Cohen Tervaert (Arch. Néerland. physiol. 1918, 2, 337); Zaleski and Sachnowska (Russ. Physiol. J. 1919, 2, 14); Folin and Wu (J. Biol. Chem. 1919, 38, 81, 459); cf. Brown and Raiziss (J. Lab. Clin. Med. 1922, 8, 129); and Rogers (J. Biol. Chem. 1923, 55, 325); Guillaumin (J. Pharm. Chim. 1922, [vii.] 25, 5); Thiéry (*ibid.* 87); Jackson and Palmer (J. Biol. Chem. 1922, 50, 89; 53, 373).

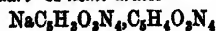
For the rapid estimation of uric acid in urine, Vaillant (Ann. Chim. Anal. 1922, [ii.] 4, 178) titrates the liquid with a standard iodine solution made by dissolving 3.78 grms. of iodine and 15 grms. of potassium iodide in 1 litre of water. Two c.c. of this solution oxidise 0.005 grm. of uric acid to alloxan and urea. The analysis is carried out by measuring into a small tube 2 c.c. of iodine solution and 1 c.c. of carbon disulphide, and allowing the urine to fall a drop at a time from a burette, shaking the tube after each addition, until the carbon disulphide becomes first pale rose and then colourless. The uric acid content per litre of urine is calculated by dividing the number of c.c. used into 5. Sugar and small amounts of albumin do not interfere; larger amounts should be removed by heating to coagulate and then filtering. If the urine is alkaline a few drops of acetic acid are added (Chem. Soc. Abstr. 1922, ii. 668).

For the separation of and estimation of uric acid and xanthine bases by means of potassium-zinc ferrocyanide, see Thiéry (J. Pharm. Chim. 1921, 23, 494).

A colorimetric method, based on the action of uric acid on iodic acid, whereby iodine is liberated, is recommended by Autenrieth and Funk (Chem. Zentr. 1915, 1, 1918 from Münch. med. Wchschr. 1914, 61, 457); Maase and Zondek (Chem. Zentr. 1915, ii. 858). For a critical review of methods for estimating uric acid and xantho-uric substances, v. Sauzéat (J. Pharm. Chem. 5, 164, 445, 485).

Derivatives. Salts.—All four hydrogen atoms of uric acid are acidic and can be replaced by metals, as is shown by the formation of salts from each of the four trimethyl uric acids; the hydrogen atom 3 is the most acidic, then hydrogen 9, the hydrogen atoms 1 and 7 are much weaker in their acidity; hence uric acid behaves as a feeble dibasic acid (Biltz and Herrmann, Ber. 1921, 54, 1676), and forms three

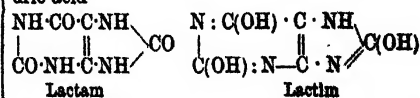
series of salts, the normal urates of the type $\text{Na}_2\text{C}_5\text{H}_3\text{O}_7\text{N}_4$ are readily soluble in water and are never found in the animal system; the acid or diurates $\text{NaC}_5\text{H}_2\text{O}_7\text{N}_4$ are sparingly soluble and occur pathologically in gouty concretions; and the quadri- or hemi-urates



are more readily soluble than the diurates and are the common form in which uric acid occurs physiologically.

Normal urates may be obtained by dissolving uric acid in the theoretical quantity of alkali. They are alkaline in reaction and are decomposed by carbon dioxide, forming the acid salt. The potassium salt $\text{K}_2\text{C}_5\text{H}_3\text{O}_7\text{N}_4$ is crystalline; it dissolves with partial decomposition into the acid salt in about 36 parts of cold water; the sodium salt $\text{Na}_2\text{C}_5\text{H}_3\text{O}_7\text{N}_4\cdot\text{H}_2\text{O}$ is less soluble than the potassium salt, and is stated to be rendered more soluble by radium D (Gudzent, Zeitsch. f. klin. Med. 71, 3-6), and to be decomposed by the α -rays from radium emanation (Mesernitzky, Compt. rend. 1912, 154, 770); according to Knaff-Lenz and Wiechowski (Zeitsch. physiol. Chem. 1912, 77, 303), and to Kerb and Lazarus (Biochem. Zeitsch. 1912, 42, 82), radium has no action on the salt under sterile conditions, but accelerates the degradation of the compound in the presence of enzymes or moulds; the calcium $\text{CaC}_5\text{H}_3\text{O}_7\text{N}_4$, strontium $\text{SrC}_5\text{H}_3\text{O}_7\text{N}_4\cdot 2\text{H}_2\text{O}$, barium $\text{BaC}_5\text{H}_3\text{O}_7\text{N}_4\cdot\text{H}_2\text{O}$, and lead $\text{PbC}_5\text{H}_3\text{O}_7\text{N}_4$ salts are sparingly soluble. The mercury salt $\text{HgC}_5\text{H}_3\text{O}_7\text{N}_4$ is a white amorphous precipitate; it does not give mercuric oxide with sodium hydroxide solution and is therefore probably a lactam salt (Auld, Chem. Soc. Trans. 1907, 1046). Zinc, nickel, and copper salts are described by Curtman and Hart (J. Biol. Chem. 1921, 46, 599).

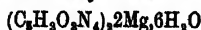
Acid or di-urates.—According to Gudzent (Zeitsch. physiol. Chem. 1909, 60, 38), uric acid forms two series of primary metallic salts (mono-sodium, potassium and ammonium urates), which differ as regards solubility. The salts of the α -series cannot be obtained pure, as at the moment of formation in water they tend to pass into the salts of the β -series. The probable cause of the change is an intramolecular rearrangement, so that the two series correspond with the two tautomeric forms of uric acid



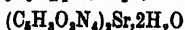
The unstable α -salts are probably the lactam urates, and the stable β -salts the lactim urates. The α -salts have solubilities and specific conductivities that at 18° are some 33-4 p.c., or at 37° some 33-9 p.c. greater than the corresponding values for the more stable β -salts.

The sodium salt $\text{NaC}_5\text{H}_2\text{O}_7\text{N}_4\cdot 11\text{H}_2\text{O}$ forms a crystalline powder soluble in 1200 parts of cold or 120 parts of boiling water, forming a neutral solution. The solubility of freshly percolated sodium urate at 18° is 2.03 grms. or 9.8×10^{-3} grms. molecules per litre. On keeping, or more particularly on stirring in contact with the solution, the solubility decreases and approaches that of the crystalline form. The potassium salt $\text{KC}_5\text{H}_2\text{O}_7\text{N}_4$ is amorphous

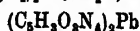
and dissolves in 800 parts of cold or 70-80 parts of boiling water; lithium salt $\text{LiC}_5\text{H}_3\text{O}_3\text{N}_4$ forms crystalline grains and is soluble in 370 parts of cold or 39 parts of boiling water; the ammonium salt $\text{NH}_4\text{C}_5\text{H}_3\text{O}_3\text{N}_4$ is soluble in 1500 parts of cold water and quite insoluble in saturated solutions of ammonium chloride or sulphate; and the magnesium



calcium $(\text{C}_5\text{H}_3\text{O}_3\text{N}_4)_2 \cdot \text{Ca} \cdot 2\text{H}_2\text{O}$, strontium



barium $(\text{C}_5\text{H}_3\text{O}_3\text{N}_4)_2 \cdot \text{Ba} \cdot 3\text{H}_2\text{O}$, and lead

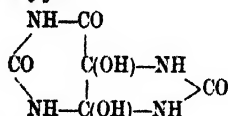


salts are described. For the formation of colloidal uric acid in the presence of alkalis, see Schade and Boden (Zeitsch. physiol. Chem. 1913, 83, 347); compare, however, Lichtwitz (*ibid.* 1913, 84, 416); Schade and Boden (*ibid.* 1913, 86, 238); Gudzent (*ibid.* 1914, 89, 352); Haskins (J. Biol. Chem. 1916, 26, 205); Kohler (Z. Klin. Med. 1919, 88, 14); Schade (*ibid.* 1922, 23, 1).

The quadri-urates are difficult to obtain pure as they readily break down into diurates and uric acid; according to Rosenheim (Lancet, 1900; Zeitsch. physiol. Chem. 1911, 71, 272) and Kohler (*ibid.* 70, 360) the quadri-urates are only mixtures, in molecular proportions, of primary urates and uric acid; they are stated to exist normally in the urine and constitute the whole of the urinary excretion of birds and reptiles (v. URINE).

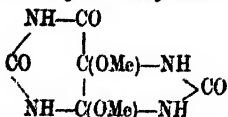
Adrenaline urate $\text{C}_5\text{H}_3\text{O}_3\text{N}_4 \cdot \text{N} \cdot \text{C}_8\text{H}_9\text{O}_3\text{N}_3$ forms small pointed plates (Pauly, Ber. 1904, 37, 1388). Piperazine urate $\text{C}_5\text{H}_3\text{O}_3\text{N}_4 \cdot \text{C}_4\text{H}_8\text{N}_2$ is soluble in 50 parts of water at 17°. The phosphotungstate of uric acid forms reddish-brown cubical plates (Drummond, Bio-Chem. J. 1918, 12, 5).

Uric acid glycol



crystallises with half a molecule of water of crystallisation; it reddens at 150° and melts 165°-168° (effervesces) (Biltz and Heyn, Ber. 1912, 45, 1877; *ibid.* 1914, 47, 459; Ann. 1916, 413, 7).

4:5-Di-methoxy-4:5-dihydrouric acid



crystallizes in slender needles, m.p. 202°-203° (decomp.); it is reduced by sodium amalgam to uric acid and by hydriodic acid (D 1-96) on the water bath to ψ -uric acid (Biltz, Annalen 1916, 413, 1; Ber. 1921, 54, 2477).

p-Nitrobenzyl urate $\text{C}_5\text{H}_3\text{O}_3\text{N}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ melts above 350° (Lyons and Reid, J. Amer. Chem. Soc. 1917, 39, 1727).

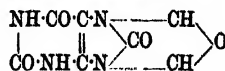
Uric acid forms the following condensation products with formaldehyde:—

Diformaldehyde-uric acid $\text{C}_7\text{H}_5\text{O}_3\text{N}_4 \cdot 2\text{CH}_2\text{O}$ is a crystalline, sparingly soluble compound,

monobasic towards N/3 sodium hydroxide and forms a barium and a calcium salt (Weber, Pott and Pollens, Ber. 1897, 30, 2514; Annalen, 1898, 299, 340). Formaldehyde uric acid



crystallises in needles or prisms, decomposes at 37°, and forms crystalline alkali salts; and anhydroformaldehyde-uric acid



formed by dissolving diformaldehyde-uric acid in concentrated sulphuric acid and pouring the solution into ice water (Nicolai, Chem. Zentr. 1907, i, 949). For other derivatives of uric acid, v. Biltz (*l.c.*). M. A. W.

ψ -URIC ACID v. PYRIMIDINES.

URIDINE v. PYRIMIDINES.

URINE. The kidneys are compound tubular glands, and possess the power of excreting from the blood certain waste products which in aqueous solution constitute the urine. Its most important constituents are the result of the breakdown of nitrogenous materials in the body, but these substances, urea, uric acid, &c., are not actually formed in the kidneys themselves. The liver is the most important organ for their actual formation; the kidney is merely the situation where they find an exit from the body.

The characters of the urine differ greatly in different parts of the animal kingdom, according to the character of the food ingested, and the different metabolic habits of animals. The most striking difference is seen when one compares the liquid urine of mammals (in which urea is the main substance in solution) and the semi-solid urine of birds and snakes, in which urates form the preponderant constituents. In the following account attention will be in the main directed to the urine which is most familiar, namely that of man and other mammals.

A man of average weight and height, taking a normal mixed diet, passes from 1400 to 1600 c.c. (about 50 oz.) daily, and this contains about 50 grms. (1½ oz.) of solids. Its yellow colour varies considerably with the concentration of the urine, and is due to the presence of a number of pigments, of which urochrome (an amorphous nitrogenous substance of doubtful composition, originally so named by Thudichum) is the most abundant. Another named urobilin, a derivative of the bile pigment, is present in health in small quantities, but may be considerably increased in certain diseases.

The reaction of urine is acid; this is partly due to free acid, but mainly to acid salts, of which acid sodium phosphate is the most abundant. During digestion, however, there is a formation of free hydrochloric acid in the stomach, and a corresponding liberation of bases in the blood causes the urine to be less acid, or even alkaline. Alkaline urine is also seen in herbivorous animals and vegetarians; here the food contains excess of alkaline salts of acids such as tartaric, citric, malic, &c. These acids in the body are oxidised into carbonates which, passing into the urine, give it an alkaline reaction.

The specific gravity varies inversely as the quantity of urine passed; the quantity depends on the amount of water ingested, and also on

the amount of water that leaves the body by other channels, such as the skin. It varies normally from 1.015 to 1.025. A sp.gr. below 1.010 should excite suspicion of hydruria; one over 1.030 of a febrile condition, or of diabetes, in which disease it may rise to 1.050. The sp.gr. has, however, been known to sink as low as 1.002 (after large potations, *urina potus*), or to rise as high as 1.035 (after great sweating) in perfectly healthy people.

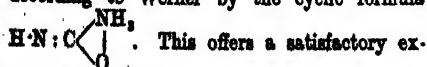
When a normal urine is distilled, an unknown, or imperfectly known, substance begins to volatilise at 60°-70°C., but does not completely leave the urine until the boiling-point is reached. The distillation is carried out on the urine which has been acidified with phosphoric acid: at least one-quarter of the urine should distil over. This distillate is a limpid colourless liquid of intense urinous odour, and is neutral to all reagents. It is not precipitated by alkalis or acids, nor with the bicarbonate and sublimate mixture; it does not react with Fehling's solution, nor give the diazo reaction in neutral or acid media; no apparent change takes place with salts of silver, cadmium, iron, lead, mercury, or zinc. With Nessler's reagent it gives a greenish-yellow precipitate similar to that given with many other substances, such as alkaloids, amides, all amines, organic ammonias, aldehyde and methylene derivatives. It is concluded that there is a volatile body in normal urine resembling ketone, but different from ordinary acetone, precipitated by Nessler's reagent, and that it is to this substance that the characteristic odour of the urine is due (E. Pittarelli, *La Riforma Med.* May 14th, 1923, through *Lancet*, June 9th, 1923, 1172).

The following table gives the average amounts of the urinary constituents passed by a man taking an ordinary diet containing about 100 grms. of protein in the 24 hours—

Total quantity of urine	1500	grms.
Water	1400	"
Solids	80	"
Urea	35	"
Creatinine	0.9	"
Uric acid	0.75	"
Hippuric acid	1.0	"
Ammonia	0.65	"
Sodium chloride	16.5	"
Phosphoric acid	3.5	"
Sulphuric acid	2.0	"
Chlorine	11.0	"
Potassium	2.5	"
Sodium	5.5	"
Calcium	0.26	"
Magnesium	0.21	"

The most abundant constituents are, therefore, water, urea, and sodium chloride. We will take the most important individual constituents one by one.

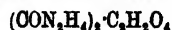
Urea. The time-honoured formula of urea as carbamide $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$ must be replaced according to Werner by the cyclic formula



This offers a satisfactory explanation for the behaviour of urea during hydrolysis. It was first prepared synthetically

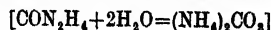
by Wöhler (1828) from its isomeride ammonium cyanate.

It crystallises in the dimetric system, and is readily soluble in water and in alcohol; it has a faint saltish taste, and is neutral to litmus. When treated with nitric acid, octahedra, or lozenge-shaped tablets are formed of urea nitrate ($\text{CON}_2\text{H}_4 \cdot \text{HNO}_3$); when treated with oxalic acid prismatic crystals of urea oxalate



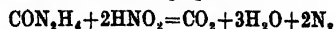
are formed.

Under the influence of certain micro-organisms which grow readily in stale urine, it is converted into ammonium carbonate



Hence the ammoniacal odour of putrid urine. In the soil the urinary ammonia is converted into nitrates by nitrifying organisms (*see SOILS*).

By means of nitrous acid, urea is broken up, as shown in the following equation:



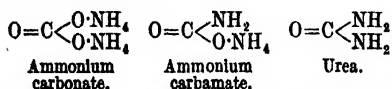
Sodium hypobromite decomposes urea as follows:



A critical examination of this reaction shows that there is always a deficit in the quantity of urea found, whether it is calculated from the volume of the nitrogen liberated, the carbon dioxide formed, or the hypobromite used. Side reactions of a complex nature also occur under usual conditions, giving rise to a small amount of CO. Moreover, other urinary constituents (uric acid, creatinine, &c.) also yield nitrogen under the conditions of the experiment. Hence the method which was formerly much used for the estimation of urea is now abandoned when accuracy is required. The methods at present in use are those in which the urea is decomposed into ammonia and carbon dioxide; the ammonia formed is estimated, but as the urine contains a small amount of preformed ammonia this has to be previously estimated and deducted from the total. The methods of Mörner and Sjöquist, Folin and others (*v. UREA*) are examples of this type of estimation, but the enzymatic method depending on the action of the enzyme urease contained in soy-beans promises to replace all other methods. It was introduced by Marshall. Urease is a specific enzyme, which rapidly and quantitatively decomposes urea at 35°-40°C. into ammonia and carbon dioxide. The ammonia formed is driven off in a suitable apparatus by a current of air, absorbed with standard acid, and estimated by titration, alizarin-red or methyl-orange being used as indicator.

The quantity of urea is practically uninfluenced by muscular work, but depends mainly on the amount of protein ingested. The amino acid fragments formed by the digestion of protein are utilised in two ways. A small portion is used by the tissue cells to repair their waste. In time this will be catabolised and the waste products discharged as urea, ammonia, creatinine, &c. The amount of such *endogenous* metabolism is constant. The other and larger part of the cleavage products of the food proteins are deaminised and converted into urea by the liver, the non-nitrogenous fatty residue being

burnt, and so utilised as a source of heat and other forms of energy. This part of metabolism is termed *exogenous*. Urea excretion is usually at a maximum about 3 hours after a meal. The conversion of amino acids into urea is, in part at any rate, due to enzymic action; e.g. arginase is an enzyme which converts arginine (one of the more complex amino acids resulting from protein disintegration) quantitatively into urea and ornithine (di-amino-valeric acid). There is also no doubt that ammonia is an important intermediate between such amino acids as glycine (amino-acetic acid), leucine (amino-caproic acid), &c., and the final product urea. Ammonia so liberated unites with the carbon dioxide of the blood, and ammonium carbonate and carbamate are thus formed. The close relationship of these two salts to urea is apparent from their formulae—



This view, though simple, must be modified if Werner's conception of the structure of urea is accepted.

A small quantity of ammonia always slips through into the urine, because a small quantity of the ammonia-containing blood passes through the kidney before reaching the organ (the liver), which is capable of converting it into urea. Acids are very toxic to the body, and the defence of the body against acids (administered as such, or produced in pathological metabolism, e.g. fatty acids in diabetes) is an increase of ammonia formation, or to put it more correctly, less of the ammonia formed is converted into urea.

Creatine and creatinine.—Creatine is an abundant constituent of muscular tissue; *in vitro* by boiling it with baryta it takes up water and splits up into urea and methyl-glycine, as shown in the following equation—

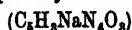
$\text{C}_4\text{H}_7\text{N}_3\text{O}_2 + \text{H}_2\text{O} = \text{CON}_2\text{H}_2 + \text{CH}(\text{CH}_3)\text{NH}_2 \cdot \text{COOH}$
Creatine, however, is absent from normal urine, and only occurs in starvation and in other conditions, in which there is a rapid loss of muscular tissue. Its normal fate in the body is unknown, since creatine injected into the circulation leaves the body in the urine unchanged, and leads to no increase of urea.

It also is not converted into creatinine, which was formerly held to be its fate. Here, again, we have an instance of reactions, which occur *in vitro*, but not *in vivo*. Creatinine is a crystalline, strongly basic substance, which chemically is creatine *minus* a molecule of water. It is always present in the urine, and next to urea, is its most abundant nitrogenous constituent. Mellanby believes that certain products of protein catabolism, the nature of which is uncertain, are carried to the liver, and from these the liver forms creatinine; this is transported to the muscles, and there stored as creatine, excess being then eliminated in the urine. The small amount of creatinine excreted in liver disease favours the view that the liver is the great agent in its production, as it is in that of urea and uric acid. In health the amount of creatinine is very constant, and is not influenced by diet or muscular exercise.

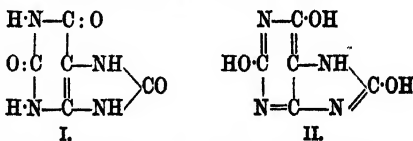
Uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_6$) is excreted as urates in mammals in small quantities only, but in birds and serpents is the principal nitrogenous constituent of their urine. It can be readily prepared from the latter urine, in which it is mainly present as the acid ammonium urate, by dissolving it in sodium hydroxide and precipitating with hydrochloric acid. It crystallises in rectangular plates and prisms. Uric acid dissolves in pure water in the proportion 1 : 15,000 (Gudzent), and at 18° in the proportion 1 : 39,500 (His and Paul). On oxidation it yields urea and oxalic acid, alloxan ($\text{C}_8\text{H}_2\text{N}_4\text{O}_4$) or allantoin ($\text{C}_4\text{H}_6\text{N}_4\text{O}_3$), being intermediate products, according to the oxidising agent employed. It can be best identified by the *murexide* reaction, which consists in evaporating to dryness with nitric acid; the yellowish-red residue gives, on the addition of ammonia, the violet ammonium purpurate.

Uric acid does not contain the COOH group which is typical of organic acids, and in aqueous solution its reaction is neutral. Nevertheless one of its hydrogen atoms is replaceable by a metallic radicle, and it acts therefore as a monobasic acid, and forms *primary* salts (mono- or acid urates). In the presence of strong bases it forms *secondary* salts (di-urates); these only exist in the solid condition or in the presence of strong alkali. By water they are at once decomposed forming primary salt and alkali. A third series of salts (quadri-urates) was formerly assumed to exist, but these are merely mixtures of uric acid and primary urate.

In water, urine and blood, we have therefore only to deal with primary urates. It has been shown that the primary sodium urate



occurs in two modifications, the α - and the β -forms. The unstable α salt is gradually transformed in aqueous solution into the stable β salt, owing to an intramolecular change. These two salts correspond to two tautomeric modifications of uric acid, the lactam form (formula I) giving rise to the unstable, and the lactim form (formula II) to the stable salt.



These facts have a bearing on gouty conditions; normally the small amount of urate in the blood is held in solution. In gout the amount is increased, and the excess is probably in the unstable α -form. The conversion of this into the β -form gives rise to the deposition of urates in the tissues which occurs during the course of the attack.

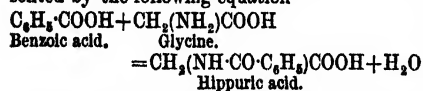
The quantity of uric acid excreted by an adult varies from 0.5 to 0.75 gm. daily. The method used for estimation is based on Hopkins' discovery, that when the urine is saturated with an ammonium salt (chloride or sulphate), all the uric acid is precipitated as ammonium urate; this is collected and the uric acid in it determined. The Folin-Shaffer method is founded on this reaction. Folin has also introduced a colorimetric method, which depends on the

blue colour uric acid strikes with phosphotungstic acid (*v. URIC ACID*).

In birds uric acid originates from the combination of ammonia and lactic acid. In mammals it mainly arises from the purine bases of the food, which are cleavage products of nucleic acid, the main constituent of the nuclei of the body cells. In this process several tissue enzymes come into play; first nuclease liberates adenine (amino-purine $C_5H_4N_4 \cdot NH_2$) and guanine (amino-oxypurine $C_5H_4N_4O \cdot NH_2$) from nucleic acid; then 'deaminising' enzymes convert adenine into hypoxanthine (monoxypurine $C_5H_4N_4O$) and guanine into xanthine (dioxypurine $C_5H_4N_4O_2$); oxidases step in next and convert hypoxanthine into xanthine, and xanthine into uric acid (trioxypurine $C_5H_4N_4O_3$). The liver is the principal seat of these transformations, and in some animals some of the uric acid so formed is destroyed in the same organ, and appears as allantoin and urea. So far as tissue extracts can give a true picture of metabolism *in vivo* the human tissues are destitute of the uricolytic (uric acid destroying) enzyme)

Small quantities of purine bases are found in the urine in addition to uric acid.

Hippuric acid ($C_9H_9NO_3$) in the form of hippurates is present in small quantities in the urine of man, but is specially characteristic of herbivorous urine. This is due to the food of herbivora containing substances of the benzoic acid group. The condensation of benzoic acid with glycine to form hippuric acid appears to occur in the kidney itself, and may be represented by the following equation—



For the estimation of hippuric acid in urine, see Snapper and Laquer, Archives Néerlandaises de Physiologie, 1921, 6, 48, which contains further references to the literature of the subject.

Kynurenic and urocanic acids are present in small quantities in dog's urine. Kynurenic acid $C_{12}H_9NO_3$ is hydroxyquinoline carboxylic acid ($HO \cdot C_6H_4 \cdot N \cdot COOH$) and originates from one of the decomposition products of protein called tryptophan (indole-amino-propionic acid). Urocanic acid ($C_{10}H_7N_2O_4$) is a rarer constituent, and its origin in the body is not clear.

Inorganic constituents of urine. The principal salt is *sodium chloride*, and its amount varies with that in the food. The *sulphates* present are principally those of sodium and potassium. They are derived from the metabolism of protein, and their excretion, although it occurs earlier than that of urea, runs parallel with it. About one-tenth of the total sulphates are ethereal sulphates, such as potassium phenyl sulphate and potassium indoxyl sulphate (urinary indican); the organic radicles originate from protein putrefaction in the alimentary canal, and abnormally great putrefactive processes there lead to an increase in the excretion of such sulphates. Sulphur is also present in the form of less highly oxidised organic compounds, usually spoken of as 'neutral sulphur,' a term which includes thiooxyanic acid and its salts, taurine, cystine, methyl mercaptan.

Carbonates are only present in alkaline urine. Alkaline and earthy *phosphates* are also present and small quantities of organic phosphates, for instance, glycerophosphates. They arise partly from the food, but chiefly from the metabolism of organic phosphorised constituents of the body, such as nucleic acid, lecithin, and other phosphorised fats (phosphatides).

According to Amberg and Mayer (Amer. J. Physiol. 1922, 60, 564) minute quantities of citric acid occur in normal human urine.

Abnormal constituents of urine. The most commonly occurring of these are albumin (in Bright's disease) and other proteins, dextrose, acetone, aceto-acetic acid, and β -hydroxybutyric acid in diabetes, lactose in nursing mothers, bile in jaundice, blood when hæmorrhage occurs in any part of the urinary tract, hæmoglobin, and certain derivatives of hæmoglobin in black water fever and other pathological states, and pus as the result of suppuration in any part of the urinary tract.

Urinary deposits. Normal urine is clear except for a faint cloud of mucus. Formed or anatomical elements such as blood corpuscles, pus corpuscles, bacteria, entozoa, &c., may be present in various pathological conditions, and are identified by microscopic examination. A special chemical interest attaches, however, to crystalline deposits, and without entering into any discussion of the medical reasons that lead to their appearance, these may be briefly enumerated as follows:—

A. In acid urine may be found—

1. Uric acid, as whetstone, dumb-bell, or sheaf-like aggregations of crystals deeply tinged with urinary pigment, looking like cayenne pepper.

2. Urates. These are generally amorphous. The acid urate of sodium and ammonium may sometimes occur in star-shaped clusters of needles or spheroidal clumps with projecting spines. The deposit has the appearance of brick-dust, as it is coloured by one of the urinary pigments (uroerythrin). This deposit dissolves on warming the urine.

3. Calcium oxalate in the form of octahedral crystals insoluble in acid.

4. Cystine (diamino-dithio-lactic acid $C_6H_{12}N_2S_2O_4$)

in colourless hexagons; a rare condition often hereditary.

5. Calcium phosphate $CaHPO_4 \cdot 2H_2O$, rare.

6. Leucine (amino-caproic acid) and tyrosine β -p-hydroxyphenyl- α -aminopropionic acid, rare.

B. In alkaline urine we may find—

1. Phosphates; calcium phosphate



which is amorphous; triple phosphate



in 'coffin lid' crystals or feathery stars; calcium hydrogen phosphate $CaHPO_4$ in rosettes, spherules, or dumb-bells; magnesium phosphate $Mg_3(PO_4)_2$ in long plates. All are soluble in acetic acid without effervescence.

2. Calcium carbonate $CaCO_3$, biscuit-shaped crystals, common in herbivorous urine, soluble in acetic acid with effervescence.

3. Ammonium urate $C_5H_4(NH_4)_2N_4O_3$, 'thorn apple' spherules.

4. Leucine and tyrosine, very rare.

Of these deposits, urates in acid urine, and phosphates in alkaline urine are the commonest; these are not necessarily pathological; thus urates may form in the urine when it cools, especially if that secretion is concentrated, e.g. after sweating profusely. Urine, when it becomes alkaline, always deposits phosphates, and the alkaline urine of herbivora is always thick for that reason.

Urinary calculi. Concretions called sand, gravel, and stones, according to their size, may form in the kidney, the ureter, or in the bladder. They result from the conglomeration of urinary deposits, the deposition occurring in concentric layers. The substances deposited in acid urine are most frequently uric acid, urates or calcium oxalate, or a mixture of these materials; in alkaline urine, phosphates. If the reaction of the urine changes during the formation of the calculus alternate layers of these two sets of materials will be found. The uric acid calculus is generally regarded as the commonest form of stone in the bladder, but in renal calculi, as B. Moore has shown, the most abundant constituent is calcium oxalate, frequently mixed with calcium phosphate, the second constituent in frequency and abundance. Calcium is practically the only base associated with oxalic acid, phosphoric acid, and in less amount with uric acid. All these acids form highly insoluble salts with calcium. Oxalic and uric acids are associated products in metabolism, and occur in cases of incomplete oxidation.

The physical properties of a calculus—colour, hardness, smoothness, or roughness, &c.—give little or no clue to its chemical nature. A chemical analysis is always necessary, and this gives valuable indications for after treatment; for instance, in renal calculi, consisting of calcium oxalate, the treatment should be designed to diminish alkalinity, to avoid calcium-rich foods, and to induce the taking of exercise to promote oxidation in the body.

There are, in addition to these common forms of stone, others of a rarer kind, and a list of the different varieties of calculus is as follows—

1. Those composed of uric acid or urates with little or no admixture with phosphates.

2. Mixed calculi, like the preceding, but containing often in alternate layers a large quantity of phosphate.

3. Calcium oxalate calculi, often containing small quantities of phosphates and urates.

4. Phosphate calculi: a stone composed of pure calcium phosphate is rare; a nucleus of uric acid is generally present.

5. Calcium carbonate calculi are those generally found in the prostate.

6. Cystine calculi are mostly small, smooth, and have a yellow tinge, turning to green on exposure to air. These are rare.

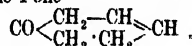
7. Xanthine calculi are still rarer.

8. Fibrinous calculi composed of fibrin or inspissated albumin, have a glassy appearance on fracture; blood calculi have been described in cases of renal hæmaturia; 'urosteolith' calculi have been described, and consist of fatty acid with more or less cholesterol. One case of 'is-ligo' calculus has been described.

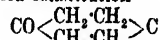
No attempt has been made in the foregoing outline sketch of the chemical properties of the

urine in health and disease to give complete bibliographical references. The literature of urine is enormous, and those interested in it should consult standard works on physiology, physiological chemistry, pathology, and medicine. One of the most trustworthy handbooks on the urine only, and containing abundant references to literature, is Neubauer and Vogel's *Analyse des Harns*, edited by Huppert, Wiesbaden, C. W. Kreidel. W. D. H.

URINOD C_8H_8O , a pale yellow oil, obtained from urine, slightly heavier than water, b.p. $108^\circ/23$ mm.; possessing a very penetrating, persistent and disagreeable odour and to which the characteristic smell of urine is due. Is readily volatile with steam, reduces potassium permanganate and ammoniacal silver nitrate in the cold, and reacts with Millon's reagent, but not with Barreswil's (Fehling's) solution, or solution of alkali picrate. The dinitro-derivative, m.p. 78° , forms golden needles. Urinod acts with semicarbazide with production of a compound, m.p. 254° , which crystallises in thin, hexagonal leaflets. When urinod is treated with bromine, two compounds are produced; one of these has m.p. about 110° , whilst the other is not melted at 250° . The compound probably has the structure of cyclohexene-4-one



or the quinonoid constitution



Urinod does not occur in the free state in urine, but exists in a conjugated form, and is liberated by fermentation, or by the action of dilute sulphuric acid. It is very toxic, and may have some connection with uræmia (Dehn and Hartman, J. Amer. Chem. Soc. 1914, 36, 2136).

URISOL. Syn. for hexamethylenetetramine.

URITONE (hexamine). Syn. for hexamethylenetetramine.

UROCITRAL, UROPHENIN, v. SYNTHETIC DRUGS.

URODONAL. Trade name for a preparation of hexamethylenetetramine, piperazine quinate and methylglyoxalidine.

UROGENIN. Trade name for an addition product of theobromine and lithium hippurate.

UROL. Trade name for urea quinate.

UROPHERIN v. SALICYLIC ACID.

UROPURGOL (helmitol, neurotpine, formamol). The hexamethylenetetramine salt of anhydromethylene-citric acid.

UROSIN. Trade name for lithium quinate.

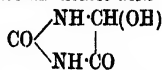
UROTROPIN. Hexamethylenetetramine, v. SYNTHETIC DRUGS.

UROXANIC ACID, dicarbaminomalonic acid $(CO_2H)_2C(NH \cdot CO \cdot NH_2)_2$, is prepared by the gradual oxidation of uric acid in alkaline solution by the oxygen of the air (Städeler, Annalen, 1851, 78, 286; Strecker, *ibid.* 1870, 155, 177; Biltz and Robl, Ber. 1920, 53, 1950); by oxidising an alkaline solution of uric acid with 5 p.c. potassium permanganate solution (1 atom of oxygen to 1 mol. of uric acid) (Behrend, *ibid.* 1904, 333, 152; Sundvik, Zeitsch. physiol. Chem. 1904, 41, 343; Behrend and Schultz, *ibid.* 1909, 365, 21; Biltz and Robl, *l.c.*).

For the mechanism of the formation of uroxanic acid from uric acid, see Biltz and

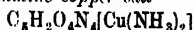
Max (Ber. 1920, 53, 1964). The two carbamido groups in uroxanic acid can be quantitatively eliminated by sodium nitrite with the formation of mesoxalic acid (Biltz and Robl, l.c.).

Uroxanic acid crystallises in indistinct tetrahedra (decomp. 162°); it is sparingly soluble in cold water and insoluble in alcohol; it is a strong dibasic acid and its normal alkali salts are neutral towards litmus and phenolphthalein. It readily loses CO₂ and yields allantoic acid when shaken for several days with cold 95 p.c. methyl alcohol. When heated with water it breaks down into allanturic acid



mesoxalic acid and urea. The aniline and hydroxylamine salts are sparingly soluble; the latter, melts at 155°; the normal phenylhydrazine salt, (C₆H₅O₂N₄·2(C₆H₅N₂)) crystallises in colourless plates, m.p. 130°–132° (decomp.), when boiled with water it is decomposed, yielding the phenylhydrazine salt of mesoxalic acid phenylhydrazone C₁₁H₁₀O₄N₄·1½H₂O, this forms yellow needles that melt at 154°–158° solidify at 160° and then decompose at 183°. The normal silver, sodium, barium, and calcium salts of uroxanic acid are crystalline.

The potassium salt forms colourless crystals, a : b : c = 0.88576 : 1 : 1.2044, and gives hydrates containing 3.5, 3, and probably 0.5, H₂O; the ammonium salt decomposes at 182°. The methyl ester decomposes at 213°, and is converted by boiling water into spirodihydantoin, which yields the di-silver salt C₈H₂O₄N₄Ag₂·2H₂O and the diammine copper salt



(Biltz and Robl, l.c.).

For the physiological action of uroxanic acid, see Saiki (J. Biol. Chem. 1910, 7, 263).

M. A. W.

URSAL. Ureasalicylate. A uric acid eliminant.

URSOL v. *p*-PHENYLENEDIAMINE.

URSOL P v. *p*-AMINOPHENOL.

URSONE. *Ursone*. A white crystalline optically active substance C₂₂H₄₀O₇·COOH·2H₂O, m.p. 273°, [α]_D²⁰ = +58°, found in holly, maté, and other species of *Ilex*, and in many ericaceous plants. With sulphuric acid it gives an orange-yellow colour with green fluorescence; an acetic anhydride solution gives with sulphuric acid a red coloration passing to violet, green, and blue; a chloroform solution shaken with an equal volume of sulphuric acid colours the latter

yellow. Soluble in ethyl and methyl alcohols, chloroform, carbon disulphide, ether, and ethylene bromide. Yields a readily crystallisable methyl ester (Dodge, J. Amer. Chem. Soc. 40, 12; Nooyen, Pharm. Weekblad. 1920, 57, 1128). According to van Der Harr (Rec. trav. chim. 1924, 43, 387) urson has the formula C₂₁H₃₈O₇, m.p. 279°–280°, and gives sesquiterpene and CO₂ on distillation with zinc dust. It forms an acetyl derivative, m.p. 201°, a methyl ester, m.p. 165°, and an acetyl derivative of the methyl ester, m.p. 245°. It thus appears to contain a hydroxyl and a carboxyl group.

URUSHIOL v. LACQUER; RESINS. Cf. Majima, Ber. 1922, 55 [B.] 172; Levin, J. Amer. Med. Assoc. 1924, 465; Pharm. J. 1924, 112, 236.

USNIC ACID C₁₁H₁₀O₇ (Stenhouse, Proc. Roy. Soc. 18, 222), C₁₁H₁₀O₈ (Paterno, Ber. 9, 345). An acid found in certain lichens (v. LICHENS).

UVANITE. Hydrated uranium vanadate 2UO₂·3V₂O₅·15H₂O, crystallised in the orthorhombic system. It occurs as a brownish-yellow powder disseminated in sandstone at Temple Rock in Emery Co., Utah. In appearance and mode of occurrence it thus resembles carnotite (*q.v.*), but it has not the clear yellow colour characteristic of carnotite. The mineral dissolves readily in a solution of ammonium carbonate. The name uvanite is a contraction of the words uranium and vanadium with the mineralogical termination *ite*. (F. L. Hess and W. T. Schaller, 1914.) L. J. S.

UVAROVITE v. GARNET.

UVITONIC ACID v. BONE OIL.

UZARA. The root of a species of *Gomphocarpus* (N.O. *Asclepiadaceae*) is used by medicine men in the region of the great African lakes against diarrhoea. The action of an extract was first described by Gürber (Muench. Med. Wochenschr. 1911, 58, 2100) and was found to be specific on the intestine, resembling that of opium, but without the undesirable after effects of the latter drug. A dried alcoholic extract has been placed on the market in Germany under the name uzaron. According to Hennig (Arch. Pharm. 1917, 255, 382) the active principle is the glucoside *uzarin* (5 p.c. of the root) C₂₈H₄₀O₁₀·9H₂O, relatively well soluble in water and hydrolysed by acids into one molecule of propyl alcohol, three of dextrose and three of *uzaridin* C₁₈H₂₂O₆, which is strongly bitter. The glucoside is only slightly bitter. Cf. Kofler, Arch. Pharm. 1917, 255, 550; and Holmes, Pharm. J. 1920, 507. G. B.

V

VALAMIN. Trade name for the isovaleric ester of tertiary amyl alcohol.

VAL D'ARNO SUPERIORE RESIN v. RESINS.

VALEARIN. Trade name for valeryl trimethylammonium chloride.

VALENTINITE. Antimony trioxide Sb₂O₃, crystallised in the orthorhombic system and dimorphous with senarmonite (*q.v.*). The small tabular or prismatic crystals are often arranged in fan-shaped groups. They have perfect cleavages in three plane directions (the unit prism and the brachypinacoid) parallel to the

vertical axis, and consequently broken surfaces present a fibrous aspect with pearly lustre. They are white or greyish, translucent, adamantine in lustre, very soft (H. 2), and readily distorted. Sp.gr. 5.76. The mineral occurs in the upper oxidised portions of lodes, having resulted by the alteration of stibnite and other antimony minerals. It is found at Bräunsdorf in Saxony, Příbram in Bohemia, Malaczka in Hungary, Algeria, Bolivia, &c. L. J. S.

VALERIAN. The root of *Valeriana officinalis* (Linn.) yields on distillation with water an essential oil of a pale yellow or greenish colour,

having a strong smell of valerian, an aromatic taste, and acid reaction; sp.gr. 0.90-0.93. Thickens at -15° , and begins to boil at about 200° . Consists of a mixture of valeric acid, a camphene, a stearoptene, and a resin (Pierlot, Ann. Chim. [iii.] 56, 291; Gerhardt, *ibid.* [iii.] 7, 275).

Valerian root contains two alkaloids: *chatinine* and *valerine*. One kilo of the fresh root yielded only 0.10 grm. of mixed alkaloids, chatinine predominating (Goris and Vischniac, Compt. rend. 1921, 172, 1059).

For the assay of Valerian Root, see Bullock, Pharm. J. 1924, 113, 109.

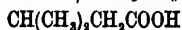
VALERIC or PENTOIC ACIDS C_5H_9COOH .

Four isomerides are known.

1. *n*-Valeric acid $CH_3(CH_2)_3COOH$, is found in pyroligneous acid, and occurs free and as esters in the animal and vegetable kingdoms, chiefly in the roots of *Valeriana officinalis* (Linn.) and of *Archangelica officinalis* (Hoffm.), from which it may be isolated by boiling with water or sodium hydroxide. It may be obtained by boiling *n*-butyl cyanide with potash (Lieben and Rossi, Annalen, 159, 58); by oxidation of α -hydroxycaproic acid (Erlenmeyer, Ber. 1876, 1840); by reduction of levulic acid (β -acetylpropionic acid) with phosphorus iodide or sodium amalgam (Kehrer and Tollens, Annalen, 206, 233; Fittig and Wolf, *ibid.* 208, 109); by heating propylmalonic acid (Juslin, Ber. 1885, 2504); by the fermentation of calcium lactate (Fitz, *ibid.* 1890, 1309); and by the action of CO_2 on magnesium *n*-butyl bromide (Gilman and Parker, J. Amer. Chem. Soc. 1924, 46, 2816; Chem. Soc. Abstr. 1925, 128, i, 228). A colourless oil having a disagreeable smell, b.p. 186° - 186.4° (Fürth, Monatsh. 9, 310); sp.gr. 0.9415 at $20^{\circ}/4^{\circ}$ (Lieben and Rossi); 1 vol. of acid dissolves in 27 vols. of water at 16° .

Methyl valerate boils at 127.3° , *ethyl valerate* at 144.6° (736.5 mm.), and *isobutyl valerate* at 167.0° - 168.5° ; sp.gr. 0.8544 $20^{\circ}/4^{\circ}$.

2. isoValeric acid, β -methylbutyric acid



Discovered in 1817 by Chevreul in dolphin oil from *Delphinus globiceps* and *D. phocaena*, and termed by him *phocenic acid* (cf. André, Compt. rend. 1924, 178, 1188; J. Soc. Chem. Ind. 1924, 43, 479). Found in other fish oils and in perspiration. In the roots of *Valeriana officinalis* (Linn.), *Archangelica officinalis* (Hoffm.), and in the berries of *Viburnum Opulus* (Linn.). Formed in the putrefaction of albuminoids; by the oxidation of glue, oleic acid, fats, and fusel oil (Lawkrow and Jazukowitsch, J. 1864, 337; Pierre and Pouchet, Ann. Chim. [iv.] 29, 229; Koizumi and Ichinose, Japan. Pat. 41910; Chem. Soc. Abstr. 1924, 126, i, 259). Prepared by the action of alcoholic potash on isopropyl cyanide, and by long boiling of amyl alcohol with sodium methoxide (Guerbet, Compt. rend. 128, 512). Colourless oily liquid, smelling like valerian root and putrid cheese; b.p. 173.7° (Kahlbaum, Ber. 1883, 2480), sp.gr. 0.931 at 20° . Soluble in 23.6 parts of water at 20° . The valeric acid of pharmacy is prepared from valerian root or from amyl alcohol. The ammonium and zinc valerates are also used in medicine.

For quantitative estimation of isovaleric acid

in the presence of acetic acid, v. Chapman, Annalen, 1899, 114.

Methyl isovalerate boils at 116.7° , and *Ethyl isovalerate* at 134.3° .

isoAmyl isovalerate $C_5H_{11}O(C_4H_9O)$; b.p. 194° ; dissolved in spirits of wine is used in confectionery as *essence of apples*.

3. α -Methylbutyric acid $CH_3\cdot CH(C_2H_5)COOH$ is found in the oil of *Archangelica officinalis* (Hoffm.) (Ciamician and Silber, Ber. 1896, 1815), and may be obtained by heating methyl-crotonic acid (tiglic acid) with hydriodic acid (Schmidt and Berendes, Annalen, 191, 117); by the action of sodium amalgam on bromomethyl-ethyl-acetic acid in a sulphuric acid solution (Fagenstecher, *ibid.* 195, 109); and by heating methyl-ethyl-malonic acid (Conrad and Bischoff, *ibid.* 204, 151). On oxidising optically active amyl alcohol, a mixture of isovaleric and α -methylbutyric acids is obtained which can be separated by converting them into their silver salts, silver isovalerate being six times less soluble in water than silver α -methylbutyrate (Erlenmeyer and Hell, Annalen, 180, 301; Conrad and Bischoff, *ibid.* 204, 157). A colourless somewhat mobile liquid; b.p. 173° - 174° , sp.gr. 0.938 at $20^{\circ}/20^{\circ}$ (Schütz and Marckwald, Ber. 1896, 26).

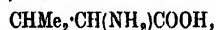
4. $\alpha\alpha$ -Dimethylpropionic acid $(CH_3)_2C\cdot COOH$. Obtained by heating trimethyl-acetonitrile with strong hydrochloric acid (Butlerow, Annalen, 170, 151; 173, 355); or by the oxidation of pinacolin (Butlerow, l.c.; Friedel and Silva, Ber. 6, 146, and 816). Crystallises in the regular system; m.p. 34° - 35° , b.p. 163° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 475), sp.gr. 0.905 at 50° ; soluble in 45 parts of water at 20° .

VALEROBROMINE $(CH_3)_2CH\cdot CHBr\cdot COONa$. Obtained by hydrolysing and neutralising the product formed by the action of bromine on valerianic acid. Used as a sedative.

VALEROPHEN. Methyl ester of phenolphthalein.

VALERYDIN, VALIDOL, VALISAN, VALYL, v. SYNTHETIC DRUGS.

VALINE, α -aminoisovaleric acid



was isolated first by Gornp-Besanez (Annalen, 1856, 98, 1) from the pancreas of the ox, and occurs in the young seedlings of *Lupinus luteus* (L.), *Lupinus albus* (L.), *Lupinus angustifolius* (L.), *Vicia sativa* (L.), the etiolated seedlings containing more than the green plants (Schulze and Barbieri, J. pr. Chem. 1883, [i.] 27, 33 7; Schulze and Winterstein, Zeitsch. physiol. Chem. 1902, 35, 308; Schulze, *ibid.* 1894, 20, 306; 1896, 22, 423; Schulze and Castoro, *ibid.* 1903, 38, 199; Wassilief, Landw. Versuchsstat. 1901, 55, 45; Schulze, Zeitsch. physiol. Chem. 1893, 17, 193; Menozzi, Ber. 1888, 21, 619); in zeln (Osborne and Clapp, Amer. J. Physiol. 1908, 20, 470); Dakin (J. Biol. Chem. 1924, 61, 137); in Emmenthaler cheese (Winterstein, Zeitsch. physiol. Chem. 1904, 41, 500). Valine is one of the products of hydrolysis of such proteins as horn, keratin, edestin, etc., and occurs together with leucine and proline in the fraction of esters, b.p. 60° - $90^{\circ}/10$ mm.; it is formed in the autolysis of the pancreas and liver, and in peptic and tryptic digestion (Fischer and Dörpinghaus, *ibid.* 1902, 36, 462; Abderhalden and Voitino-

vici, *ibid.* 1907, 52, 348; Levene and van Slyke, J. Biol. Chem. 1909, 6, 419; Levene, Zeitsch. physiol. Chem. 1904, 41, 393; Lawrow, *ibid.* 1901, 33, 312). The valine occurring naturally is the dextrorotatory form; the racemic form was prepared first synthetically by Fittig and Clark (Annalen, 1866, 139, 200) by the action of concentrated ammonia on α -bromoisovaleric acid at 100°; and later by Lipp (*ibid.* 1880, 205, 1) by hydrolysing the aminoisovaleronitrile obtained by the condensation of isobutyraldehyde with ammonia and hydrocyanic acid. It is prepared most conveniently, and the yield is 70 p.c. of the theoretical, by Slimmer's modification of Fittig and Clark's method (Ber. 1902, 35, 400); 500 grms. of α -bromoisovaleric acid with 1500 grms. of aqueous ammonia saturated at 15° and 500 grms. of powdered ammonium carbonate are heated in an autoclave at 100° for eight hours; the resulting brownish liquid is filtered and evaporated to one-third its bulk, when most of the amino acid crystallises out. The rest is obtained in the form of its hydrochloride by acidifying the mother liquor with hydrochloric acid, evaporating to dryness and extracting the residue with 80 p.c. alcohol.

Racemic valine can be resolved into its optically active isomerides by the fractional crystallisation of the brucine salt of the formyl derivative; the brucine salt of formyl-*l*-valine being less readily soluble in methyl alcohol than is the corresponding salt of formyl-*d*-valine: *d*-valine and *l*-valine are obtained by hydrolysing with hydrobromic acid the corresponding formyl derivatives (Fischer, Matsubara and Hilpert, Ber. 1906, 39, 2320).

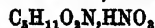
dl-Valine. In addition to the synthetic methods already described for the preparation of *dl*-valine, it can be obtained by racemising the active acids by heating them with baryta water at 180° (Fischer, Zeitsch. physiol. Chem. 1911, 33, 102).

dl-Valine crystallises in colourless plates from alcohol, has a sweet taste, and melts in a closed tube at 298° (corr.) with decomposition; it is readily soluble in water, 1 part dissolving in 11.7 parts of water at 15°, is almost insoluble in cold alcohol or ether, sparingly so in boiling alcohol (Slimmer, *l.c.*); when oxidised by hydrogen peroxide it yields isobutyraldehyde, isobutyric acid (part of which is further oxidised to acetone and carbon dioxide), ammonia and carbon dioxide; with lead peroxide or sodium hypochlorite as the oxidising agent, isobutyraldehyde is the product (Dakin, J. Biol. Chem. 1908, 4, 63; Langheld, Ber. 1909, 42, 2360). When *dl*-valine undergoes putrefactive decomposition it yields isovaleric acid and a small quantity of butylamine; the residual amino-valeric acid is levorotatory indicating an asymmetric attack by the bacteria (Neuberg and Karczag, Biochem. Zeitsch. 1908, 18, 435).

Salts and derivatives of dl-Valine.—The copper salt $(C_5H_{11}O_2N)_2Cu$, blue crystals soluble in 3644 parts of methyl alcohol at 20°, or in 9230 parts of 96 p.c. ethyl alcohol at 21°, and sparingly soluble in cold water (Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 399); the silver salt $C_5H_{11}NO_2Ag$ is crystalline and insoluble in cold water. The hydrochloride



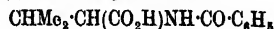
crystalline plates, readily soluble in water or in alcohol, insoluble in ether; the nitrate



is a readily soluble crystalline compound. The ethyl ester $CHMe_2.CH(NH_2)CO_2Et$ has b.p. 63.5°/8 mm. or 174° with decomposition under atmospheric pressure, sp.gr. 0.9617 at 15°/4°; it forms a sparingly soluble crystalline picrate, m.p. 139.5° (corr.), and a soluble hydrogen tartrate which on crystallisation suffers partial resolution into its optically active isomerides (Slimmer, *l.c.*). Of the acyl derivatives of *dl*-valine, the formyl derivative



obtained by heating *dl*-valine with 1½ times its weight of formic acid crystallises in large rhombic plates from water, sinters at 137° and melts at 140°–145° (corr.), is readily soluble in hot water, alcohol or acetone (Fischer, Ber. 1906, 39, 2322); the benzoyl derivative

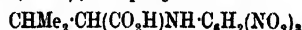


crystallises in plates, m.p. 132.5° (corr.), is readily soluble in alcohol or ether, sparingly so in water (Slimmer, *l.c.*); the phenylisocyanate derivative $CHMe_2.CH(CO_2H)NH\cdot CO\cdot NHPh$ forms colourless plates, soluble in 130 parts of hot water, m.p. 163.5° (corr.) with decomposition, is readily soluble in hot alcohol, sparingly so in ether, and is converted into phenylisopropylhydantoin

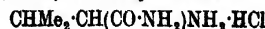
$$\begin{array}{c} NH\cdot CHPr^s \\ | \\ CO\cdot NPh\cdot CO \end{array}$$
 by boiling with hydrochloric acid; this compound crystallises from ether in long needles, m.p. 124°–125° (corr.), and is sparingly soluble in hot water, readily so in alcohol or ether (Slimmer, *l.c.*); the carbamino derivative



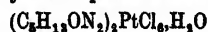
crystallises in needles, m.p. 176°, is soluble in 213 parts of water at 20°, and forms crystalline barium, mercury and silver salts (Lippich, Ber. 1908, 41, 2962); the picryl derivative



forms bright yellow needles, sparingly soluble in cold water, and has m.p. 171° (Hirayama, Zeitsch. physiol. Chem. 1909, 59, 290). *dl*-Valinamide $CHMe_2.CH(NH_2)CONH_2$, obtained by the action of liquid ammonia on the ester prolonged over a period of three months, crystallises from benzene in colourless prisms, m.p. 78°–80° (corr.), and yields a β -naphthalenesulphonic derivative $C_{10}H_7SO_3N_2$, m.p. 256°–257° (corr.), a carbothoxy derivative $C_5H_{11}O_2N_2$, m.p. 143–144° (corr.) (Königs and Mylo, Ber. 1908, 41, 4427), and a hydrochloride



crystallising in the monoclinic system, and forming a crystalline platinumchloride



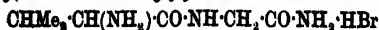
(Lipp, Annalen, 1880, 205, 1). *dl*-Valine anhydride $C_{10}H_{18}O_2N_2$, obtained by heating *dl*-valine, or by heating the ethyl ester under pressure at 180°–190°, forms long colourless needles, m.p. 303° (corr.) (Fischer and Schenkel, Annalen, 1907, 354, 1).

When α -bromoisovalerylglycinamide is

heated at 120° with alcoholic ammonia, it yields a mixture of *valylglycine anhydride* (diketoisopropylpiperazine)



needles from hot water, m.p. 245°, and the *hydrobromide of valylglycinamide*



microscopic needles from alcohol-ether, m.p. 235° (Bergell, *Zeitsch. physiol. Chem.* 1916, 97, 293). α -Amino- β -hydroxyisovaleric acid has been synthesised from ethyl β -dimethylacrylate, it melts with decomposition at 218°; the *methyl ester* $\text{OMe--CHMe}_2\text{--CH(NH}_2\text{)--CO}_2\text{H}$ forms colourless lustrous plates, m.p. 250°–260° (decomp.); the naphthalene β -sulphonyl derivative $\text{C}_{10}\text{H}_7\text{O}_2\text{NS}$ forms small colourless needles, m.p. 281° (Schrauth and Geller, *Ber.* 1922, 55, 2783).

Valinol $\text{CHMe}_2\text{--CH(NH}_2\text{)--CH}_2\text{--OH}$, prepared by reducing valine ethyl ester, is a colourless oil with a strong odour, b.p. 181°–186°/720 m.m.; the *hydrochloride*, m.p. 114°, is very hygroscopic.

Dimethylvalinol, prepared by reducing *ethyl α -dimethylaminoisovalerate* (b.p. 160°), gives with methyl iodide *valinecholine* in the form of its iodide, m.p. 195°; the *aureichloride*



forms yellow leaflets, m.p. 225°, the *platinichloride*, brownish-red prisms, m.p. 210°–211° (Karrer, Gisler, Horlacher, Locher, Mäder and Thomann, *Helv. chim. Acta*, 1922, 5, 469).

d-Valine is most conveniently obtained from the two to three weeks old etiolated seedlings of *Lupinus luteus* and *Lupinus albus*; contamination with leucine, which is very difficult to separate from valine, can be obviated by removing the cotyledons from the young plants before they are dried (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1902, 35, 312). *d*-Valine is prepared from the synthetic compound by the fractional crystallisation of the brucine salts of the formyl derivative (Fischer, Matsubara and Hilpert, *Ber.* 1906, 39, 2320).

d-Valine crystallises in colourless, shining six-sided plates. It melts in a closed capillary tube at 315° (corr.); when heated in an open tube it sublimes and decomposes partially with formation of the anhydride. It dissolves in 11 parts of water at 16.5°. The taste is first slightly sweet, then bitter (Fischer, Matsubara and Hilpert, *l.c.*). The natural compound obtained from *Lupinus luteus* has $[\alpha]_D^{16} + 28.2^\circ$ in 20 p.c. hydrochloric acid (0.5 gm. in 10 c.c.); from *Lupinus albus* $[\alpha]_D^{16} + 27.9^\circ$ in 20 p.c. hydrochloric acid (0.5012 gm. in 10 c.c.) (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1902, 35, 299). The synthetic compound prepared by hydrolysing the formyl derivative has $[\alpha]_D^{20} + 23.76^\circ$ in 20 p.c. hydrochloric acid, or $[\alpha]_D^{20} + 6.42^\circ$ in aqueous solution (Fischer, Matsubara and Hilpert, *l.c.*). For the practically quantitative separation of *d*-valine and *d*-alanine by the alternate crystallisation of valine as the free amino acid and of alanine as the phosphomolybdate, v. Levene and Slyke (*J. Biol. Chem.* 1912, 18, 193).

Salts and derivatives of d-valine.—The *copper salt* $(\text{C}_5\text{H}_{11}\text{O}_2\text{N})_2\text{Cu}$, blue crystalline plates, soluble in 52 parts of methyl alcohol at 18°. The *hydrochloride* $\text{C}_5\text{H}_{11}\text{O}_2\text{N--HCl}$, small prismatic crystals readily soluble in water or alcohol, the *platinichloride* is also readily soluble (Schulze and Barbieri, *J. pr. Chem.* 1883, 27, 337); the *picrolonate* has m.p. 170°–180°, and $[\alpha]_D^{20} + 23.4^\circ$ (Levene and van Slyke, *J. Biol. Chem.* 1912, 12, 127).

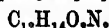
Formyl *d*-valine



obtained by the resolution of *dl*-formyl-valine through the brucine salt, forms small prisms, sinters at 150° and melts at 156° (corr.), and has $[\alpha]_D^{20} + 12.8^\circ$ to 13.27° in alcoholic solution; *d*-valine *phenylcarbimide*



forms small microscopic prisms, m.p. 147° (corr.) with decomposition (Fischer, Matsubara and Hilpert, *l.c.*), m.p. 154° (Schulze and Winterstein, *Zeitsch. physiol. Chem.* 1902, 35, 303), and yields the *d*-phenylisopropylhydantoin



on treatment with concentrated hydrochloric acid. This forms colourless thin prisms, m.p. 131°–133° (corr.), and has $[\alpha]_D^{20} - 97.5^\circ$ in alcoholic solution (Fischer, Matsubara and Hilpert, *l.c.*); m.p. 124° (Schulze and Winterstein, *l.c.*); *chloroacetyl-d*-valine



has m.p. 113°–115° (corr.) $[\alpha]_D^{20} + 15.8^\circ$; *glycyl-d*-valine $\text{NH}_2\text{--CH}_2\text{--CO--NH--CHPr}^s\text{--CO}_2\text{H}$ has m.p. 254° (corr.), $[\alpha]_D^{20} - 19.7^\circ$ in aqueous, -10.5° in hydrochloric acid or -6.9° in sodium hydroxide solution; it forms a crystalline *hydrochloride* and a *copper salt*. The *hydrochloride* of the *methyl ester* $\text{C}_5\text{H}_{11}\text{O}_2\text{N}_2\text{--HCl}$ is converted by methyl alcoholic ammonia into *glycyl-d*-valine-anhydride $\text{CH}_2\text{--}\begin{array}{c} \text{NH--CO} \\ \text{CO--NH} \end{array}\text{--CHPr}^s$, m.p. 266° (corr.), $[\alpha]_D^{20} + 20.8^\circ$ in glacial acetic, $+ 32.7^\circ$ in aqueous or $+ 41^\circ$ in alcoholic solution; *l*-valyl-*d*-valine $\text{C}_5\text{H}_{11}\text{O}_2\text{N}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ becomes anhydrous at 95°/12–15 mm. over phosphoric oxide; has m.p. 308° (corr.), and $[\alpha]_D^{20} - 70.6^\circ$ to -74° ; the *hydrochloride* of the *methyl ester* yields on treatment with methyl alcoholic ammonia the *trans*-valine-anhydride $\text{CHPr}^s\text{--}\begin{array}{c} \text{NH--CO} \\ \text{CO--NH} \end{array}\text{--CHPr}^s$ prisms, m.p. 316°–318° (corr.), which is optically inactive (Fischer and Scheibler, *Annalen*, 1906, 363, 136).

l-Valine is obtained by the resolution of the racemic formyl derivative through the brucine salt (Fischer, Matsubara and Hilpert, *l.c.*); by the action of ammonia on *d*- α -bromoisovaleric acid (Fischer and Scheibler, *Ber.* 1906, 41, 2891); and by the selective action of yeast on *dl*-valine (Ehrlich, *Biochem. Zeitsch.* 1906, 1, 8; 1906, 8, 438).

l-Valine is soluble in 17.1 parts of water at 25°, possesses a markedly sweet taste, and has $[\alpha]_D^{20} - 6.06^\circ$ in 0.24 p.c. aqueous solution.

—29.34° in 20 p.c. hydrochloric acid solution (Fischer, Matsubara and Hilpert, l.c.). A specimen obtained from yeast had $[\alpha]_D^{20}$ —27.62° in a 4.61 p.c. solution of 20 p.c. hydrochloric acid.

1-Formylvaline $\text{CHMe}_2\text{CH}(\text{CO}_2\text{H})\text{NH}\cdot\text{CHO}$ crystallises in small prisms, sinters at 150° and melts at 156° (corr.); it has $[\alpha]_D^{20}$ —12.93° to 13.07° in alcoholic solution, or +16.9° in aqueous solution; 1-valine phenylisocyanate $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ has m.p. 147° (corr.) decomp., and $[\alpha]_D^{20}$ —19.02° in absolute alcoholic solution, and yields 1-phenylisopropylhydantoin $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ on treatment with hydrochloric acid. It has m.p. 131°–133° (corr.) and $[\alpha]_D^{20}$ +97.22° in absolute alcoholic solution. For iso-valine, α -amino- α -methylbutyric acid, v. Gadamer and Rukop (J. pr. Chem. 1914, [ii.] 90, 405). M. A. W.

VALONIA (Valonée, Fr.; Valonea, Acker-doppen, Orientalische Knopfer, Ger.). An important tanning material. Is the acorn cup of certain species of oak, usually *Quercus Aegilops* (Linn.), and probably *Q. macrolepis*, *Q. graeca*, *Q. Ungeri*, and *Q. coccifera* (Linn.). The former is most prolific in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, whereas the *Q. macrolepis* forms great forests in Greece. These acorn cups have a diameter up to about 1½ ins., and in good condition possess a bright colour.

The fruit ripens in Asia Minor about July or August, and the trees are then shaken, and the material left on the ground to dry; this is subsequently collected into heaps, and allowed to ferment for some weeks, until the acorn contracts and falls from the cup. The acorn, which contains but little tannin, is employed for feeding purposes.

In Greece distinct qualities of valonia are known, the best (*chamada*) collected about April before the fruit is ripe, a second (*rhabdisto*) in September or October, and a third little used inferior variety (*charcola*).

Smyrna valonia may contain 40 p.c., Greek 19–30, and Candia valonia 41 p.c. of tannin matter, which consists of a mixture of a gallo-tannin and an ellagitannin. Valonia is, indeed, an excellent source for the preparation of ellagic acid, because it so readily yields a product easy to purify. Extract of valonia frequently undergoes fermentation with deposition of ellagic acid, and to avoid this the employment of antiseptics is to be recommended.

Valonia is especially suited for the manufacture of sole leather, and together with gambier and other materials for dressing leather, but is little employed for dyeing purposes (cf. Procter, Principles of Leather Manufacture, 259). A. G. P.

VANADINITE. A mineral consisting of lead chloro-vanadate $(\text{PbCl})\text{Pb}_2(\text{VO}_4)_2$, crystallised in the hexagonal system and isomorphous with apatite and pyromorphite (q.v.). The formula requires 19.4 p.c. V_2O_5 , but this is often partly replaced by phosphoric and arsenic oxides; and the variety *endlicheite* forms a passage to the species *milnesite* (lead chloro-arsenate). The mineral forms small hexagonal prisms usually terminated simply by the basal plane; at times the crystals are curved and barrel-shaped. Globular, warty, and cauliflower-like masses also

occur. The colour is usually yellowish or brownish, but crystals from Arizona are bright scarlet. Sp.gr. 6.6–7.2. When touched with a drop of nitric acid a yellow coating of vanadic oxide is formed on the crystals; this affords an easy test for recognising the mineral.

Vanadinite is a mineral of secondary origin in the upper portions of lodes of lead ore, and it sometimes occurs in association with gold. It was formerly found in some quantity at Wanlockhead in Dumfriesshire and near Klagenfurt in Carinthia; and now abundantly in several of the mining districts of Arizona and New Mexico. It has been met with at Broken Hill in Northern Rhodesia, and in Morocco. Important localities in Arizona are the Red Cloud mine in Yuma Co., the Mammoth gold mine in Pinal Co., the Globe district in Gila Co., and in Pima Co. and Yavapai Co., &c. In New Mexico at the Sierra de los Caballos near Lake Valley in Sierra Co., Magdalena in Socorro Co., Georgetown in Grant Co., &c. It is also of abundant occurrence at Santa Marta in Badajoz, Spain.

In New Mexico and Arizona, and also in Spain, the mineral is mined as a source of vanadium. The concentrate containing the vanadinite, together with descloizite, is treated in lead-lined vats with dilute sulphuric acid heated by steam, and the vanadium obtained in solution as sulphate, the lead remaining in the insoluble residue. The solution is decanted and evaporated, and the vanadium salt heated to give vanadic oxide. The bulk of this product appears to be used in the manufacture of vanadium-steel, and to a limited extent also as a pigment. Other minerals that have been worked for vanadium are carnotite, descloizite, patronite, and roscoelite (q.v.). L. J. S.

VANADIUM. Sym. V. At.wt. 51.0. This element was discovered by Del Rio (Gilbert's Ann. 1801, 71, 7) in a lead ore, *vanadinite*, from Zimapan in Mexico; the discovery was confirmed by Sefström (Pogg. Ann. 1830, 21, 48), and by Wöhler and Berzelius (*ibid.* 1831, 22, 1; cf. Collet-Descotils, Ann. Chim. 1805, [i.] 53, 260). Upon the work of Berzelius was based the view that vanadium was allied to chromium and molybdenum and, like them, yielded an acidic trioxide, and this idea was current till Roscoe, in 1867, showed that the substance believed to be the metal in earlier investigations had been either an oxide or a nitride, and that the compounds of vanadium in general showed that the element belonged to the phosphorus group. According to Aston, vanadium is simple with an atomic weight of 51.

Occurrence.—Minerals containing a large proportion of vanadium are rare, but the metal is very widely distributed in small quantities. Vanadium occurs as vanadic acid in *vanadine* with the native copper of Lake Superior, and in *alaite* (Nenadkevitch, Bull. Acad. Sci. St. Petersburg, 1909, 185); as lead vanadate, with lead chloride, in *vanadinite*; as *descloizite*, a basic lead and zinc vanadate; as hydrated vanadate of lead and copper in *mothramite* and *petitite*; as vanadate of copper in *turnite* (Nenadkevitch, l.c.); as lead vanadate containing zinc and manganese in *degenite*, *crocoite*, and *escravite*; as vanadate of lead and arsenic in *endlicheite*; as bismuth vanadate in *pucherite*; as the basic

oxide V_2O_5 in the vanadium muscovite *roscoelite* (Hillebrand, Turner and Clarke, Amer. J. Sci. 1899, [iv.] 7, 451); as vanadate of copper, barium, and calcium in *colobrothite*; and as vanadium sulphide V_2S_5 with sulphur, in *patronite* (Hillebrand, *ibid.* 1907, [iv.] 24, 141; Hewett, Eng. & Min. J. 1906, 82, 385; Trans. Amer. Inst. Min. Eng. 1910, 40). See also Vanadium Ores [Monographs on Mineral Resources prepared under the direction of the Imperial Institute], John Murray, London, 1924.

Vanadium is present in magnetites and in most other iron ores (Pope, Chem. Soc. Abstr. 1900, ii. 409), and becomes concentrated in the residues from their treatment, especially by the Thomas-Gilchrist process. It is said to be diffused, with titanium, through all primitive granite rocks (Dieulafoy; Hillebrand, Amer. J. Sci. 1898, 6, 209; 7, 294), and has been found by Deville in *bauxite*, *rutile*, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands. Jorissen has found vanadium in the coal of Liège (Bull. Acad. Roy. Belg. 1905, 178). Scacchi has observed its presence in incrustations on the Vesuvian lava of 1631, and Donath has found as much as 0.16 p.c. of vanadic acid in a sample of commercial caustic soda (Dingl. poly. J. 240, 318). It occurs in the sun and has been found in stony meteorites (Hasselberg, Vetensk. Akad. Svenska. 1899, 56, 131).

Extraction.—Ammonium metavanadate was formerly prepared on a commercial scale by the Magnesium Metal Co. at Patricroft near Manchester.

The mineral employed was *mottramite* $(PbCu)_2(VO_4)_2 \cdot 2PbCu(HO)_2$, which occurs in the copper-bearing Keuper beds at Alderley Edge and Mottram St. Andrew's, in Cheshire, as a film on the grains of sandstone. The sand is digested in concentrated hydrochloric acid, and the acid liquid is withdrawn. The solution, with the washings of the residue, is concentrated and evaporated with an excess of ammonium chloride, forming ammonium metavanadate, which, being insoluble in a concentrated solution of ammonium chloride, is precipitated. After being freed from copper and iron by repeated crystallisation, it is gently roasted in a porcelain vessel, with production of vanadium pentoxide. This is suspended in water and subjected to a current of ammonia gas, with formation of ammonium metavanadate, the solution being separated from the silica, phosphates, &c., which are not affected by ammonia, is crystallised until free from phosphates, and gently ignited to produce pure vanadium pentoxide (v. Roscoe, Phil. Trans. 1867, 158, 1).

The chief ores from which vanadium is or may be derived are patronite, carnotite, roscoelite, vanadinite and asphaltite. The chief deposits of vanadium ores, mainly carnotite, in the United States are in South-Eastern Utah and North-Western Colorado, but at present the only vanadium produced from native ore is obtained as a by-product from carnotite worked for its radium content. The principal source of supply at present is in Peru, where deposits occur at *Mina Baja*, about 30 miles to the north-west of the Cerro de Pasco copper mines; here vanadium is found in the coal deposits as a

black mineral resembling slaty coal; it contains about 30 p.c. of free sulphur, with 40 p.c. vanadium sulphide (patronite). After burning out the free sulphur the ore contains from 30 to 52 p.c. of vanadium oxide (V_2O_5). The asphaltite deposits of Peru frequently contain considerable amounts of vanadium, the ash yielding from 25 to 40 p.c. of vanadium oxide.

Vanadium ores are also worked in New Mexico, and carnotite, roscoelite, and vanadinite deposits are found in Colorado, Utah, Nevada, Arizona, and Oklahoma, mainly for the production of ferro-vanadium and vanadium steel. Small quantities of vanadium are also obtained from Argentina (*rafaetite*), Chile (*chileite*), South-West Africa (*mottramite*), and Spain (*vanadinite*).

Two consignments of 25 and 30 tons, respectively, of vanadinite concentrate, averaging 13 p.c. V_2O_5 , from the Kaffir's Krall mine in the Transvaal, constitute the first important shipment of this ore from the Union.

To extract it from vanadinite the mineral is fused with potassium nitrate, alone or mixed with sodium carbonate, the mass is lixiviated, and the solution acidified, or, better, evaporated with ammonium chloride in order to precipitate alumina and silica. From the clear solution barium chloride and ammonia precipitate the barium salts of vanadic, chromic, and molybdic acids, &c., and on treating the product with sulphuric acid, followed by ammonia and water, the vanadium goes into solution as ammonium metavanadate, which is finally precipitated by the addition of ammonium chloride. Vanadic acid may also be separated from mixtures of sodium vanadate and silicate by the addition of more vanadic acid. This precipitates the silica and leaves only fairly pure sodium vanadate in solution (Herrenschmidt, Compt. rend. 1904, 139, 862).

Gin (Proc. Seventh Int. Cong. Appl. Chem. London, 1909) smelts the vanadinite in the electric furnace with 6 p.c. of its weight of carbon, which is sufficient to reduce the base metals, leaving the vanadium in the slag in the form of trioxide. The slag is pulverised and gently heated in a current of air until the trioxide is oxidised to tetroxide; at this stage sodium carbonate and a little nitrate are added to complete the oxidation to vanadic anhydride; the mass is then fused, cooled, pulverised and treated with boiling water, which dissolves the sodium metavanadate together with the phosphate, silicate and aluminate. The cooled solution is treated with carbon dioxide to precipitate silica, and then ammonium carbonate is added and the solution concentrated until ammonium metavanadate is precipitated. This is washed, dried, again washed with water acidified with nitric acid, and calcined to obtain vanadic acid. When electric-furnace treatment is inadmissible, it may be replaced by treatment in a water-jacket furnace, in which case the lead and copper are separated, and the slag is oxidised on the hearth of a reverberatory furnace and mixed with sodium carbonate and nitrate. Or, alternatively, the vanadiferous slag is melted with sodium bisulphate in an iron or steel pan; when the reaction has ceased, the mass is run off on to plates of silicon-steel, pulverised and digested with water in a wooden vessel supplied

with an agitator, steam being introduced during the process. The copper, silver, and arsenic are precipitated from the solution by hydrogen sulphide, ammonia added and the iron and alumina removed. The solution now contains the vanadium in the form of thiovanadate, which is converted into vanadium sulphide by neutralising with dilute acid, and the sulphide is converted into vanadic acid by roasting (J. Soc. Chem. Ind. 1911, 30, 218).

Vanadium can be separated from arsenic or phosphorus by precipitation of vanadic acid from an acidified vanadate solution. A vanadinite concentrate containing 10.24 p.c. V_2O_5 , 0.28 p.c. As, and 0.27 p.c. P, was fused with sodium carbonate, sodium hydroxide, and charcoal. The lead present was reduced to the metallic state and the slag extracted with hot water. After acidifying with sulphuric acid the solution was boiled with live steam for several hours. A 97 p.c. recovery of vanadic acid free from arsenic and phosphorus was obtained (H. A. Doerner, J. Ind. Eng. Chem. 1923, 15, 1014; J. Soc. Chem. Ind. 1923, 42, 1182 A.).

Determination of phosphorus in vanadium ore.—Precipitation of the phosphorus as ammonium phosphomolybdate from a solution containing relatively large quantities of vanadic acid yields an orange-brown precipitate which contains considerable amounts of vanadic acid. The method recommended by Treadwell (Kurzes, Lehrbuch der Analytischen Chemie, 6th ed.), involving previous reduction of vanadic acid to vanadyl sulphate, is also unsatisfactory for determining small quantities of phosphorus in vanadium ores; the precipitate is greenish-yellow, and the results are too high. The most satisfactory of several procedures tested was found to be the following: 10 grms. of finely-divided ore is dissolved in 75 c.c. of hydrochloric acid and 25 c.c. of water, and the solution is oxidised with nitric acid and evaporated with 30 c.c. of sulphuric acid (1:1) until strong, white fumes are evolved. The cold mass is dissolved in 100 c.c. of water, and the sand and lead sulphate are removed by filtration. To the filtrate 50 c.c. of strong nitric acid and 1 grm. of fine tin powder are added, and the mixture is shaken till the latter has dissolved, then set aside overnight in a hot place. The liquid is diluted with 400 c.c. of hot water and filtered. The precipitate is heated in a nickel crucible, and the residue fused with 5 grms. of potassium cyanide, which reduces tin and arsenic to the metallic form. The fused mass is dissolved in water, the solution filtered, and the filtrate boiled with hydrochloric acid to expel all hydrocyanic acid. It is transferred to a graduated flask, treated with potassium ferrocyanide until a spot test gives a brown colour with uranium acetate, when it is diluted to 500 c.c. 450 c.c. is filtered through a dry paper, treated with a solution of an aluminium salt containing about 0.1 grm. of metal, then with a slight excess of ammonia. The precipitate, which contains all the phosphoric acid, is collected, washed free from chloride and ferrocyanide, and dissolved in hydrochloric acid. The solution is evaporated to remove silica, and the filtrate is evaporated with nitric acid to expel chlorine compounds. The phosphoric acid is eventually precipitated as ammonium molybdate and determined in

the usual manner (Kriess, Chem. Zeit. 1923, 47, 177; J. Soc. Chem. Ind. 1923, 314A).

According to Witz and Osmond (Bull. Soc. chim. 1882, [ii.] 38, 49; Compt. rend. 95, 42), the slags produced while working the Thomas-Gilchrist process at the Creusot ironworks contain nearly 1.5 p.c. of vanadium, the quantity of that metal thus concentrated amounting to 60,000 kilos (nearly 59 tons) annually. They recommend the following process for the separation: 1 kilo of the roughly broken slag is treated with a quantity of hydrochloric acid insufficient to attack the whole (about 1 litre of acid of 21°–22°Bé.) without stirring, 3 litres of water being added, and the whole remaining at rest for 2 days. The solution, having a sp.gr. of about 27°Bé. at 36°, is decanted and diluted to 15°Bé., and the silica is removed. The solution contains the vanadium in the hypovanadic condition, and may be used at once for the production of aniline black. If it is desired to produce hypovanadic phosphate, the solution is nearly neutralised and about 250 c.c. of saturated ammonium acetate solution is added. The bluish-grey precipitate produced, containing phosphates of iron, aluminium, and vanadium, is re-dissolved and again treated with ammonium acetate, the precipitate containing about 20 p.c. of vanadium.

If the slag contains less than 1.5 p.c. of vanadium, the hydrochloric acid solution is neutralised by the addition of a further quantity of finely-powdered slag. The solution becomes colourless, and a greyish granular precipitate separates, containing the whole of the vanadium and smaller proportions of the other less soluble phosphates. The precipitate is re-dissolved and re-precipitated as before. For the preparation of ammonium metavanadate, the phosphatic precipitate is roasted at incipient redness, and the ochreous-yellow mass of impure pentoxide is dissolved with the aid of ammonia, boiled until colourless and filtered, the ammonium metavanadate being precipitated by the addition of excess of ammonium chloride. From 4 kilos. of slag containing 1.5 p.c. of vanadium, about 250 grms. of ammonium metavanadate may be produced. It is a colourless transparent salt, or white powder, difficultly soluble in water, insoluble in a concentrated solution of ammonium chloride and in ether. It was formerly used, in conjunction with sodium chlorate, as an oxygen-carrier in the formation of the finest aniline black, only an extremely small quantity of the salt being required for a large amount of aniline.

Später attempted (1896) to employ the ash of an anthracite from Yauli (Peru) containing 28 p.c. of vanadium, but was unsuccessful.

From minerals in which it occurs with uranium, vanadium may be extracted by fusing with potassium hydrogen sulphate, filtrating the mass and concentrating the solution thus obtained. The solution is reduced with zinc and the vanadium precipitated with ammonia and ammonium carbonate (Zin. Elektrochem. Zeit. 1906, 13, 119).

Haynes states (Mines and Minerals, 1909, 30, 139) that vanadium is extracted from caracite, in West Colorado, by dissolving out the uranium and vanadium with hot sodium carbonate solution, precipitating the uranium with oxalic soda, and throwing down the vanadium from the mother liquor as calcium vanadate.

also Barker and Schlundt, *J. Soc. Chem. Ind.* 1916, 35, 175.

Fleck and Haldane recommend that the crushed ore be treated with 15-20 p.c. sulphuric acid, the acid liquid neutralised by the addition of fresh ore, and the clear solution fractionally precipitated with limestone, whereby a complex mixture, rich in vanadium, is obtained, from which the element may be extracted by any ordinary method (U.S. Pat. 890752).

It is probable that in future American carnotite ore will for the most part be delivered to the reduction works as concentrates. The most usual process for dealing with these is as follows: They are first boiled in autoclaves with soda ash and water, with stirring, for 6-10 hours. This converts radium and barium salts into the carbonates, 90 p.c. of the uranium present into sodium uranyl carbonate, and 30 p.c. of the vanadium into sodium vanadate. The treated concentrate is settled, decanted, filtered, pressed, and washed free from sulphate. The filtrate and washings contain the uranium and vanadium salts and are evaporated. The cake is acidified with hydrochloric acid and boiled, pressed in wooden filters, and washed. The cake is discarded. The filtrate contains radium and vanadium, and the former is precipitated as radium barium sulphate and removed on vacuum filters. The cake is washed and boiled with soda ash, caustic soda and water, the resulting carbonates are pressed and washed, converted into chlorides, and are then ready for fractional crystallisation. The utmost care must be taken against contamination by sulphates during the stages of this process. The uranium is separated from vanadium by crystallisation as sodium uranyl carbonate, dissolved in water, acidified, and boiled. Any vanadium present is removed by addition of a small quantity of ferrous sulphate, and the uranium precipitated as ammonium uranate. The vanadium in the acid solution from the barium radium sulphate precipitation is precipitated with lime, and the calcium vanadate added to the solution remaining from the sodium uranyl carbonate crystallisation, and the whole boiled with sodium carbonate and a small quantity of manganese dioxide. The solution, containing 95-98 p.c. of the vanadium, is filtered, almost neutralised with sulphuric acid, and freed from phosphate by precipitation with sodium aluminate. The solution is concentrated and vanadic acid precipitated by boiling with a slight excess of sulphuric acid. By this process a minimum yield of 80 p.c. of each product is obtained from carnotite (K. B. Thews and F. J. Heinle, *J. Ind. Eng. Chem.* 1923, 15, 1159-1161; *J. Soc. Chem. Ind.* 1924, 43, 55 B).

Preparation of metallic vanadium.—Roscoe gave two methods for the preparation of the metal; (a) the reduction of vanadium nitride in hydrogen, which never gives a pure product; and (b) the reduction of anhydrous, oxygen-free vanadium chloride in dry hydrogen. For a long time the latter method was the only one known by which the pure metal could be obtained (v. Roscoe and Schorlemmer, *Treatise on Chemistry*), but it can be also prepared by the reduction of vanadium pentoxide with 'mischmetall,' a mixture of alkaline earth metals extracted from the residues from the manufacture

of thorium (Weiss and Aichel, *Annalen*, 1904, 337, 380). The mixture of mischmetall and pentoxide is placed in a magnesia crucible and fired; the heat of reaction is sufficient to melt the reduced metal, which is afterwards found as a compact mass in the crucible (Muthmann, Weiss and Riedelbauch, *ibid.* 1907, 355, 58).

It was formerly supposed that Goldschmidt's aluminium reduction method would not give pure vanadium from the pentoxide (Koppel and Kaufmann, *Zeitsch. anorg. Chem.* 1905, 45, 352), but under certain conditions Vogel and Tammann have, by this method, obtained a regulus containing 99 p.c. vanadium, with a little silicon and aluminium (*ibid.* 1909, 64, 225).

According to Ruff and Martin (*Zeitsch. angew. Chem.* 1912, 25, 49), vanadium trioxide, melting at about 2000°, gives better results than the pentoxide.

Reduction of the oxide with metallic calcium, according to Muthmann's method, gives a product containing only 91-93 p.c. of vanadium. A purer regulus is obtained by reducing with a mixture of calcium and aluminium (Prandtl and Bleyer, *ibid.* 1909, 64, 217).

Vanadium produced by the reduction of the pentoxide in the electric furnace contains 10-25 p.c. of carbon and consists chiefly of vanadium carbide VC, a silvery-white, highly crystalline and extremely hard substance of sp.gr. 5.405 and m.p. 2705°. A product containing less carbon can be obtained by conducting the operation in an atmosphere of hydrogen (Moissan, *Compt. rend.* 116, 1225; 122, 1297; *Zeitsch. anorg. Chem.* 14, 174).

The pure metal can also be obtained by the electrolysis of a solution of sodium vanadate in hydrochloric acid, using carbon electrodes and a current density of 0.018-0.020 amp. per sq. cm., and maintaining the temperature about 80° (Cowper-Coles, *Eng. and Min. J.* 67, 744; von Bolton, *Zeitsch. Elektrochem.* 1905, 11, 45).

On the small scale it can be obtained by passing a mixture of hydrogen and vanadyl chloride vapour over incandescent platinum wire, when metallic vanadium is deposited as a silver-grey coating, or by passing the chloride over sodium hydride. The reduction of vanadium trichloride with sodium yields a product containing about 96 p.c. of metal and of D_{20} 5.819.

Properties.—Pure vanadium is a silver-white metal, similar in appearance to cast iron, and crystallises in hexagonal rhombohedra, like the other elements of its group. Its hardness is 7.5 on Mohr's scale, and it is as brittle as glass. Its sp.gr. is 5.888 at 18.7 (sp.gr. 5.5 at 15°, 15°, Roscoe), and its specific heat is 0.124 (Matignon and Monnet, *Compt. rend.* 134, 542; Muthmann, Weiss and Riedelbauch, *l.c.*), which, assuming the atomic heat to be 6.4, confirms the atomic weight of 51. Heat of combustion of 1 gm. (to V_2O_5) is 2456 cal.

The melting-point is very high, but the data given by various investigators are not in agreement. Werner von Bolton, using the photometric method of Lammer, found it to be 1680°. Vogel and Tammann give it as 1750°, 1730° (*Zeitsch. anorg. Chem.* 1908, 53, 73); Ruff and Martin 1715°. The melted metal readily dissolves both the trioxide and the pentoxide, and the

mixtures melt at higher temperatures than the metal.

It is stable in moist or dry air at ordinary temperatures, and a polished surface retains its lustre for weeks. It is unacted upon by bromine water, aqueous alkali solutions, hydrochloric acid, or cold sulphuric acid. It is dissolved by hydrofluoric acid or hot sulphuric acid forming green solutions, and is attacked by nitric acid or *aqua regia*. Melted potash or saltpetre rapidly dissolve the metal with formation of an alkali vanadate. Metallic vanadium reduces solutions of mercuric chloride and bromide, cupric chloride and bromide, and ferric chloride to the lower haloid salts, and it precipitates the metal from solutions of auric chloride, silver nitrate, platinum chloride, iridium tetrachloride, &c.

Alloys of vanadium can be prepared in the electric furnace by the reduction of the pentoxide in presence of a second metal or its oxide (Moissan, Compt. rend. 1896, 122, 1297). By fusing vanadic acid with aluminium in the necessary proportions, Czako (Compt. rend. 1913, 156, 140) has prepared alloys of aluminium and vanadium, and has isolated crystals of Al_3V and Al_4V . The hardness of the alloys increases with the vanadium content up to 60 p.c., after which it diminishes. The chief industrial use of vanadium is in the preparation of special steels, which are largely used for motor-car work; it is introduced into the molten steel as *ferro-vanadium*, an alloy prepared by electric-furnace methods. The addition of 0.1-0.25 p.c. of vanadium to chromium, manganese, or other open-hearth or crucible steels greatly increases the elastic limit and the ultimate tensile stress without reducing the ductility (J. Kent Smith, J. Soc. Chem. Ind. 1906, 291; cf. Auchy, J. Ind. and Eng. Chem. 1909, 1, 455).

Colloidal solutions of vanadium have been prepared by Svedberg (Ber. 1906, 39, 1712). According to Prandtl and Hees (Zeitsch. anorg. Chem. 1913, 82, 103) they are best obtained from the solutions of the vanadic esters, especially *tert.* butyl orthovanadate, as the alcohol is easily removed by boiling. Riedel (Chem. Zentr. 1914, i. 1738) found that *iso*-amyl orthovanadate $(C_5H_{11})_2VO_4$, b.p. $161^\circ/19$ mm. is the most convenient ester. This is balled in water until a homogeneous dark red solution is obtained. After removing the amylene hydrate by ether the deep red solution contains about 8 p.c. vanadic acid.

OXIDES OF VANADIUM.

There are five oxides of vanadium, analogous to the oxides of nitrogen—

Vanadium suboxide, V_2O ;

monoxide, hypovanadious oxide, V_2O_3 ;

sesquioxide or trioxide, V_2O_5 ;

dioxide, hypovanadic oxide, $V_2O_4 (VO_2)$;

pentoxide, vanadic anhydride, V_2O_5 .

The first three of these act as basic oxides, forming salts with acids; the last two behave both as weak basic oxides and acid-forming oxides.

Vanadium suboxide V_2O is obtained as a brown powder by the exposure of finely divided

metallic vanadium to the air. No salts of this oxide have been prepared.

Vanadium monoxide V_2O_3 or VO (*vanadyl*) is obtained as a lustrous grey solid by reducing the higher oxides with metallic potassium, or by passing the vapour of vanadyl trichloride with hydrogen over red-hot carbon, or by heating the solid oxychloride $VOCl$ to a red heat in hydrogen. It has sp.gr. 3.64, is brittle and conducts electricity. At a red heat it burns in air to form the trioxide, and it combines directly with chlorine to form the oxytrichloride. This oxide was supposed by Berzelius to be the metal. It is a black amorphous powder D¹⁴ 5-758.

Vanadium monoxide dissolves in acids to form the corresponding salts, which have a blue or violet colour and act as powerful reducing agents. The solution in hydrochloric acid has been suggested as a reagent for the removal of arsenic from hydrochloric acid gas in the process of manufacture, the arsenic being reduced to the free state and remaining suspended in the liquid (D. R. P. 164355).

Vanadium trioxide V_2O_5 , obtained by reducing the pentoxide with hydrogen or carbon at a red heat, is a black powder of sp.gr. 4.7, m.p. 2000° . Heat of formation 302 ± 10 cal. (Ruff and Friedrich). In air it oxidises, slowly at the ordinary temperature, quickly when heated, forming the dioxide V_2O_4 . It is insoluble in most acids.

Vanadium dioxide V_2O_4 or VO_2 is prepared by the oxidation of the trioxide or by the partial reduction of the pentoxide. It is a steel-coloured powder composed of dark indigo-coloured crystals. It dissolves in acids to form solutions of vanadyl salts of a bright blue colour, and in alkalis to form *vanadates* (v.i.). A hydrate, $V_2O_4 \cdot 7H_2O$, or $V_2O_4(OH)_2 \cdot 5H_2O$, is obtained as a greyish-white precipitate by adding sodium carbonate to a solution of a vanadyl salt. At 100° it loses 4 molecules of water, forming $V_2O_4 \cdot 3H_2O$.

Hypovanadic acid (*vanadious acid*) $H_2V_2O_4$ has been prepared by boiling a solution of the dioxide VO_2 in aqueous sulphurous acid. It is a pink crystalline powder (Gain, Compt. rend. 1906, 143, 823; see also *ibid.* 1154), and can exist in a green isomeric form (Gain, *ibid.* 1907, 146, 403; Ann. Chim. 1908, [viii.] 14, 224).

The salts in which VO_2 is the acidic oxide are derived from the partial anhydrides $H_2V_2O_4$ and $H_2V_2O_5$.

Potassium and sodium vanadates

$K_2V_2O_5 \cdot 4H_2O$ and $Na_2V_2O_5 \cdot 4H_2O$

are prepared by adding excess of caustic alkali to a solution of vanadyl sulphate or chloride (v. Koppel and Goldmann, Zeitsch. anorg. Chem. 1903, 36, 281). They form reddish-brown crystalline scales and dissolve in water to dark-brown solutions.

Vanadium pentoxide V_2O_5 is the final product of most commercial processes for the extraction of vanadium from its ores. The pure oxide is best prepared by decomposing vanadyltrichloride with water and fusing the product, or by the decomposition of ammonium metavanadate by heat (Matignon, Chem. Zeit. 1908, 29, 206; see also Beard, Ann. Chim. anal. 1905, 10, 43). Heat of formation 437 ± 7 cal. (Ruff and

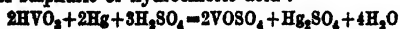
Friedrich, *Zeitsch. anorg. Chem.* 1914, 89, 279.

Vanadium pentoxide forms large rhombic prisms, of a fine ruby-red colour by transmitted light, of sp.gr. 3.35, soluble in about 1000 parts of water with formation of a yellowish, tasteless solution which reddens litmus; this appears to be a colloidal modification of vanadic acid. At 668° (Carnelley) it fuses, forming a red liquid, which recrystallises in needles, with incandescence, on cooling. When the molten acid is poured into water it yields a solution of the colloidal modification (Müller, *Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 302).

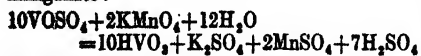
When prepared by heating ammonium metavanadate, treating the residue with nitric acid and drying at a gentle heat, it is a yellow, hygroscopic powder which forms hydrates with 1, 2, and 8 molecules of water, and is soluble in water to the extent of 8 parts in 1000. When the oxide is heated at 440°, or fused, two different sparingly soluble modifications are formed (Ditte, *Compt. rend.* 1885, 101, 698).

The properties of colloidal vanadium pentoxide have been studied by Dumaniski (*J. Russ. Phys. Chem. Soc.* 1924, 54 703; *Chem. Soc. Abstr.* 1924, ii, 195).

Vanadium pentoxide is reduced to V_2O_4 by the action of SO_2 , or by evaporation with hydrochloric acid or hydriodic acid in absence of air; to V_2O_3 by magnesium and hydrochloric acid, or by hydrogen in the dry way; to V_2O_2 by zinc and hydrochloric acid (Glasmann, *Ber.* 1905, 38, 600; Chapman, *Analyst*, 1907, 32, 250); or by shaking with mercury in presence of sulphuric or hydrochloric acid:



If a sufficiency of sodium chloride is present the whole of the mercury is precipitated as mercurous chloride, and a blue solution is obtained which may be quantitatively titrated with permanganate:



(McCay and Anderson, *J. Amer. Chem. Soc.* 1922, 44, 1018). The determination of vanadium by reduction with hydrogen peroxide and titration with permanganate has been studied by Hotherhall (*J. Soc. Chem. Ind.* 1924, 43, 270 T, 853 B). Vanadic acid volatilises with hydrochloric acid or to a slight extent when heated with alkaline chlorides.

The pentoxide was formerly used in the preparation of aniline black, and it acts as a carrier of oxygen in many reactions, e.g. the electrolytic oxidation of organic compounds in acid solution (Meister, Lucius and Brüning, *D. B. Z.* 172654), and the oxidation of sugar to oxalic acid or of stannous to stannic chloride (Ludwig, Moeser and Lindenbaum, *J. pr. Chem.* 1807, [ii] 75, 146; *D. R. P.* 183022).

For the analysis of commercial vanadic acid, see Cheneau (8th Internat. Cong. Appl. Chem. 1913, 1, 123; *J. Soc. Chem. Ind.* 1912, 31, 921).

The Vanadic Acids and their Salts.

Orthovanadic acid H_3VO_4 has not been prepared.

Metavanadic acid HVO_3 may be obtained by boiling copper metavanadate with aqueous sulphurous acid. A mixture of brown and yellow

crystals is first produced, the former being redissolved on continued boiling with excess of sulphurous acid. The remaining yellow crystals consist of metavanadic acid. The acid may also be prepared by addition of a solution of ammonium metavanadate to one of copper sulphate containing excess of ammonium chloride, until a permanent precipitate is produced, and heating for a few hours at 75°. The whole of the vanadium is slowly precipitated, the colour being finer when precipitation is slow (Gerland, *Ber.* 1876, 9, 874). Metavanadic acid forms brilliant golden or orange-coloured scales, which are used as a pigment in place of gold bronze under the name 'vanadium bronze.'

Pyrovanadic acid $H_4V_2O_7$, prepared by the action of nitric acid on an acid vanadate, is a brown precipitate which when air-dried has the above composition (von Hauer, *v.i.*).

Hexavanadic acid $H_6V_6O_{17}$, formed when a solution of pervanadic acid is allowed to stand, is known only in solution (Düllberg, *Zeitsch. physikal. Chem.* 1903, 45, 170).

The following sodium vanadates are known, and may be taken as typical of the vanadates in general—

- Sodium metavanadate, $NaVO_3$;
- " orthovanadate, Na_2VO_4 ;
- " pyrovanadate, $Na_4V_2O_7$;
- " tetravanadate, $Na_8H_4V_4O_{17}$;
- " hexavanadate, $Na_6H_6V_6O_{17}$;

(*v. also* von Hauer, *J. pr. Chem.* 1856, [i.] 69, 385; 1859, 76, 156 and 929; 1860, 80, 324; Carnelley, *Chem. Soc. Trans.* 1873, 323). In solution the metavanadates are most stable, and the orthovanadates least stable, the pyrovanadates being intermediate. This is the reverse of the order of stability of the phosphates. At high temperatures orthovanadates are the most stable salts, being produced, e.g., by fusing alkali carbonates with vanadium pentoxide. The alkali pyrovanadates, prepared by fusing the pentoxide with excess of alkali carbonate and crystallising from water, are soluble, whilst the pyrovanadates of heavy metals are mostly insoluble.

The alkali metavanadates are obtained by boiling a solution of alkali carbonate with the pentoxide, and are colourless salts which give yellowish-red anhydro-salts on treatment with acid. The metavanadates of heavier metals are usually yellow. Pure silver metavanadate is precipitated on addition of silver nitrate to a neutral solution of an alkali vanadate (Browning and Palmer, *Amer. J. Sci.* 1910, 30, 230).

A test which distinguishes between ortho- and meta- vanadates depends on the colour of the copper salts of the acids which are blue-green and light yellow respectively.

A series of double stannates and vanadates of sodium has been described by Prandtl and Rosenthal (*Ber.* 1907, 40, 2125). Mixed alkali tungstates and vanadates by Prandtl and Hecht (*Zeitsch. anorg. Chem.* 1915, 92, 198). Heteropolyvanadates have also been prepared by Rosenheim and Pieck (*Zeitsch. anorg. Chem.* 1916, 98, 223).

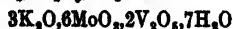
By introducing vanadium pentoxide into a boiling aqueous solution of iodic acid, the salt $V_2O_5 \cdot I_2O_5 \cdot 4H_2O$ and $V_2O_5 \cdot 3I_2O_5 \cdot 16H_2O$ may be formed. By using potassium, sodium, potassium and ammonium salts of the acids

$3R_2O, 3V_2O_5, 3P_2O_5, xH_2O$ are produced. Phosphates give rise to such salts as



and $R_2O, 2V_2O_5, P_2O_5, xH_2O$ (Rosenheim and Yang, *Zeitsch. anorg. Chem.* 1923, 129, 181; *Chem. Soc. Abstr.* 1924, 126, ii, 54).

A number of molybdeno-vanadates such as $4K_2O, 4MoO_3, 3V_2O_5, 7H_2O$ and



have been prepared (Canneri, *Gazz. chim. ital.* 1923, 53, 779; *J. Chem. Soc. Abstr.* 1924, 126, i, 118).

Ammonium metavanadate NH_4VO_3 is the most important salt of vanadic acid. It may be prepared by dissolving vanadium pentoxide in excess of aqueous ammonia and then, by evaporation or by adding alcohol or excess of ammonium chloride, it is thrown out of solution as a white crystalline powder.

Pure ammonium metavanadate (*d* 2.326) is prepared by saturating with ammonia moist vanadium pentoxide and crystallising from a very dilute ammonia solution. One hundred parts of water dissolve 5.18 parts of the salt at 15° and 10.4 parts at 32°; it is only slightly soluble in hot alcohol and in ether. When heated in a vacuum to 135°–210°, the salt yields anhydrous ammonium trivanadate; above 210°, lower oxides of vanadium are formed. On boiling an aqueous solution, soluble ammonium divanadate and the insoluble trivanadate are formed. By the action of 4 p.c. acetic acid on boiling solutions of ammonium metavanadate, the divanadate



is obtained, which on desiccation loses $2H_2O$. Use of 10 p.c. acid gives the trivanadate $3V_2O_5(NH_4)_2O, 2H_2O$ (*d* 2.594), desiccation of which gives an anhydrous red salt (*d* 2.163). The previously described yellow anhydrous trivanadate has *d* 3.029. When the acetic acid is replaced by nitric, hydrochloric, or sulphuric acid, indefinite acid ammonium vanadates are formed, the composition varying with the concentration of the acid added. With a large excess of hydrochloric acid, reduction of the vanadate also takes place (M. Lachatre, *Bull. Soc. chim.* 1924, [iv.] 35, 321; *Chem. Soc. Abstr.* 1924, 126, ii, 409).

A 'vanadium ink' is produced by the addition of gallic acid to a mixture of neutral ammonium metavanadate and gum water. This ink is not destroyed by acids, alkalis, or chlorine but does not appear to be permanent. Soerensen (*J. Soc. Chem. Ind.* 1, 185) recommends the use of a solution of 1 lb. neutral ammonium metavanadate in 10 gals. of water for producing a permanent black dye on leather which has been tanned with nut galls.

A 'drier' for linseed oil may be prepared by heating ammonium metavanadate with rosin or linseed oil. Vanadium is said to be superior to lead in drying power and gives smoother and tougher films than manganese or cobalt. According to Gardner (*Circ.* 149, *Paint Manufacturers Assoc.*, U.S., April, 1923) the time of drying of linseed oil siccatized with vanadium is not markedly different from that of oil siccatized with other known driers.

Perovanadic acid HVO_4 , prepared by adding finely powdered vanadium pentoxide to a solution of hydrogen peroxide acidified with sulphuric acid, forms yellow crystals soluble in water, giving a deep-red solution (Werther, *J. pr. Chem.* 1861, 83, 195; Pissarjewsky, *Zeitsch. physikal. Chem.* 1903, 43, 173). The *potassium salt* KVO_4 forms a yellow microcrystalline precipitate (see also Melikoff and Pissarjewsky, *Zeitsch. anorg. Chem.* 1899, 19, 504; Pissarjewsky, *ibid.* 1903, 32, 341; Melikoff and Kasanezky, *ibid.* 1901, 28, 242; Melikoff and Jelchhaninoff, *Ber.* 1909, 42, 2291; Auger, *Compt. rend.* 1921, 172, 1355).

Vanadioselenious acid $3V_2O_5, 4SeO_3, 4H_2O$ and its salts have been described by Prandl (*Ber.* 1905, 38, 1305).

Vanadium trifluoride $VF_3, 3H_2O$ crystallises in dark-green octahedra from a solution of the trioxide in hydrofluoric acid. Addition of potassium fluoride precipitates the *double potassium salt* $2KF \cdot VF_3 \cdot H_2O$ as a bright green crystalline powder.

Vanadium tetrafluoride VF_4 , a brownish-yellow hygroscopic powder, deliquescent to a blue liquid, is produced by the action of hydrogen fluoride on the tetrachloride.

Vanadyl difluoride VOF_2 is prepared by heating vanadyl dibromide in a current of hydrogen fluoride. It is a yellow powder of sp.gr. 3.396 at 19°.

Vanadyl trifluoride VOF_3 is formed by the action of hydrogen fluoride on vanadyl trichloride. It forms yellowish-white hygroscopic crusts of sp.gr. 2.459, deliquescent to a brownish-yellow solution. Melts at 300° and boils at 490°. May be sublimed in a current of oxygen.

Vanadium pentafluoride VF_5 , obtained as a white sublimate by heating the tetrafluoride in nitrogen. Is readily soluble in water, alcohol, chloroform, acetone and light petroleum. Sp.gr. 2.177; b.p. 111.2°/758 mm (Ruff and Lickfett, *Ber.* 1911, 44, 2539).

Numerous double fluorides have been described (see Petersen, *J. pr. Chem.* 1889, [ii.] 40, 193, 271; Piccini and Giorgis, *Gazz. chim. ital.* 1888, 18, 186; Baker, *ibid.* 1878, 388; Costăchescu, *Ann. Sci. Univ. Jassy*, 1910, 6, 117).

Vanadium tetrachloride VCl_4 is formed by the action of excess of chlorine on the metal or the mononitride. It is prepared by passing the vapour of vanadyl trichloride with chlorine over red-hot sugar charcoal, or by the action of chlorine on the impure metal obtained by Goldschmidt's method (Koppel, Goldmann and Kaufmann, *Zeitsch. anorg. Chem.* 1905, 45, 245), and is separated from admixed oxychloride by fractional distillation. It is readily obtained by the action of chlorine on finely powdered vanadium carbide. It is best prepared by heating the trichloride in a stream of chlorine (Ruff and Lickfett, *Ber.* 1911, 44, 506), or by passing chlorine over heated ferro-vanadium:



(Mertes, *J. Amer. Chem. Soc.* 1912, 35, 671). Heat of formation 165 ± 4 Cal.

It is a deep brown-red, viscous liquid which fumes in air. It boils at 154°, and when heated or exposed to light loses chlorine, forming the trichloride (n.t.). It has sp.gr. 1.8384 at 0° and V.D. 6.66 at 20°. Water decomposes it

with formation of a blue solution of vanadyl chloride. It is soluble in carbon tetrachloride.

The pentachloride does not appear to exist.

Vanadium trichloride VCl_3 is obtained by the decomposition of the tetrachloride, by passing the vapour of the tetrachloride with hydrogen through a red-hot tube, or by heating the trisulphide in chlorine (Halberstadt, Ber. 1882, 15, 1619). It is prepared by passing first the vapour of carbon disulphide and then dry chlorine over heated vanadium pentoxide, or more easily by heating vanadyl trichloride or vanadium tetrachloride with sulphur (Ruff and Lickfett, l.c.). Hydrogen chloride reacts at $300^\circ\text{--}400^\circ$ with vanadium to give the trichloride (Meyer and Backa, Zeitsch. anorg. Chem. 1924, 135, 177). Heat of formation 187 ± 8 Cal.

The trichloride thus obtained forms beautiful purple tabular crystals, resembling chromium trichloride. Heated in air, it decomposes yielding the pentoxide. Heated in nitrogen it is decomposed into the tetrachloride and dichloride. When heated in hydrogen it does not volatilise, but is reduced to the dichloride. Its sp.gr. is 3.0, and it is extremely hygroscopic.

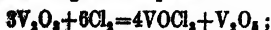
The hydrated salt $\text{VCl}_3 \cdot 6\text{H}_2\text{O}$ is obtained by evaporating *in vacuo* a solution of the trioxide in hydrochloric acid (Loeke and Edwards, Amer. Chem. J. 1898, 20, 594), or by reducing electrolytically a solution of the pentoxide in hydrochloric acid and saturating the resulting solution with hydrogen chloride (Piccini and Brizzi, Zeitsch. anorg. Chem. 1899, 19, 394). It is a green crystalline powder, and when heated begins to decompose before all the water has been driven off.

Vanadium dichloride VCl_2 is prepared by reducing the trichloride, by heating to redness a mixture of the trichloride and hydrogen, or by heating the silicide VSi_2 in chlorine (Moissan and Holt, Compt. rend. 1902, 135, 78; Ruff and Lickfett, l.c.). Heat of formation 14 ± 74 Cal.

It forms deliquescent, apple-green hexagonal plates having a micaceous lustre; it dissolves in water to form a solution which bleaches strongly, and is a more powerful reducing agent even than chromous chloride (Piccini and Marino, Zeitsch. anorg. Chem. 1902, 32, 68).

When the solid is heated in hydrogen the pure metal is obtained (Roscoe).

Vanadyl trichloride VOCl_3 (vanadium oxytrichloride) is prepared (1) by the action of chlorine on the trioxide, some pentoxide being formed according to the equation



(2) by heating the pentoxide to a dull red heat in a stream of chlorine; (3) by heating a mixture of the pentoxide and carbon in a current of chlorine; (4) by passing dry hydrogen chloride over a mixture of vanadium and phosphorus pentoxides at 80° (Ephraim, Zeitsch. anorg. Chem. 1903, 35, 66); (5) by chlorinating a mixture of the pentoxide and sulphur; (6) by heating the trichloride in a current of oxygen. Heat of formation 200 ± 4 Cal.

The product is usually dark-coloured from the presence of the tetrachloride, and is best purified by distillation over metallic sodium in an atmosphere of carbon dioxide.

A solution in acetic acid may be obtained by the action of dry hydrogen chloride on a solution

of the pentoxide in glacial acetic acid (Koppel and Kaufmann, *ibid.* 1905, 45, 352).

Pure vanadyl trichloride is a lemon-yellow mobile liquid; b.p. 127.2° , sp.gr. 1.86534 at $0^\circ/4^\circ$ (Thorpe). In contact with moist air it evolves dense red fumes. Water decomposes it with formation of vanadic and hydrochloric acids, and with a large quantity of water it yields a yellow solution (see Agafonoff, J. Russ. Phys. Chem. Soc. 1903, 35, 649). Heated in a current of ammonia it yields the mononitride. At 70° it combines with ether yielding the compound $\text{VCl}_3(\text{OC}_2\text{H}_5)_2$, crystallising in red needles (Bedson, Chem. Soc. Trans. 1876, i, 309), and it forms a compound with pyridine.

Vanadium may be quantitatively volatilised as the trichloride by heating its compounds in a current of carbon tetrachloride vapour (Jannasch and Harwood, J. pr. Chem. 1909, [ii.] 80, 127).

Vanadyl dichloride VOCl_2 , crystallising in deliquescent green tablets, is formed when the oxytrichloride is heated with zinc at 400° (Thorpe), or with hydrogen at a red heat. The latter method of reduction yields vanadyl monochloride VOCl , a flocculent brown powder, insoluble in water, and divanadyl monochloride $\text{V}_2\text{O}_2\text{Cl}$, a yellow crystalline powder. Double compounds of VOCl_2 , with the hydrochlorides of pyridine and quinoline, have been described (Koppel, Goldmann and Kaufmann, Zeitsch. anorg. Chem. 1905, 45, 345).

Divanadyl tetrachloride $\text{V}_2\text{O}_2\text{Cl}_4 \cdot 5\text{H}_2\text{O}$ is obtained as a brown, amorphous deliquescent mass by the evaporation of a solution of the pentoxide in hot concentrated hydrochloric acid. It dissolves in water to a blue solution which is turned brown by hydrochloric acid or alcohol, possibly owing to the formation of different hydrates (Crow, Chem. Soc. Trans. 1876, ii, 453).

Another oxychloride $\text{V}_2\text{O}_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ is obtained by similar methods as a dark-green deliquescent solid (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium tribromide VBr_3 is prepared by the action of dry bromine on the metal on the mononitride, on vanadium carbide V_4C_3 , or a mixture of the trioxide and carbon at a red heat. It is a deliquescent solid which is very unstable and loses bromine even at the ordinary temperature.

The hydrated bromide $\text{VBr}_3 \cdot 6\text{H}_2\text{O}$ is prepared in a similar manner to the corresponding chloride (*q.v.*).

Vanadyl tribromide VOBr_3 , prepared by passing bromine vapour over the heated trioxide, is a dark-red liquid, sp.gr. 2.967 at 0° , b.p. 130° under 100 mm. Heated to 180° it suddenly decomposes into free bromine and vanadyl dibromide VOBr_2 , a brownish-yellow powder. This on further heating yields VOBr , a violet powder, of sp.gr. 4.0, which is eventually decomposed into vanadium tribromide and vanadium trioxide (Ruff and Lickfett, Ber. 1911, 44, 2534).

Vanadium trisulphide (hydrated) $\text{VI}_3 \cdot 6\text{H}_2\text{O}$ is prepared in the same manner as the corresponding bromide.

Divanadyl tetrachloride $\text{V}_2\text{O}_2\text{Cl}_4 \cdot 8\text{H}_2\text{O}$ is obtained as a dark-coloured deliquescent solid by the action of hydriodic acid on vanadium pentoxide (Ditte, Compt. rend. 1886, 102, 1310).

Vanadium monosulphide VS , obtained by heating the sesquisulphide in hydrogen, is a brown powder soluble in nitric acid.

Vanadium sesquisulphide (*vanadium trisulphide*) V_2S_3 , is prepared by heating the trioxide in a current of hydrogen sulphide or the pentoxide in the vapour of carbon disulphide. It is a greenish-black powder (Kay, Chem. Soc. Trans. 1890, 728; cf. Wedekind and Horst, Ber. 1912, 45, 262).

Vanadium pentasulphide V_2S_5 is obtained as a black powder by heating the trisulphide with sulphur. This sulphide is acidic and gives rise to a series of *thiovanadates*, which are best prepared by passing hydrogen sulphide into cooled solutions of the corresponding vanadates.

Vanadyl sulphite $6\text{VO}_2 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ is obtained as a dark blue crystalline powder by reducing barium vanadate with sulphur dioxide. Gain has described a sulphite $4\text{VO}_2 \cdot 3\text{SO}_3 \cdot 10\text{H}_2\text{O}$, crystallising in silky blue needles (Compt. rend. 1906, 143, 823; see also *ibid.* 1907, 144, 1157).

Vanadous sulphate $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$ is best prepared by acting with sulphur dioxide on a suspension of vanadium pentoxide in sulphuric acid and then reducing the solution electrolytically. On evaporation *in vacuo* the salt is obtained in reddish-violet monoclinic crystals which appear to be isomorphous with ferrous sulphate. The solution of the salt is a powerful reducing agent and bleaches strongly.

Vanadous sulphate forms a series of double salts with the alkali sulphates (see Piccini, Zeitsch. anorg. Chem. 1899, 19, 204; Piccini and Marino, *ibid.* 1902, 32, 55; Marino, *ibid.* 1906, 50, 49; Rutter, *ibid.* 1907, 52, 368; and Zeitsch. Elektrochem. 1906, 12, 230).

Vanadium sesquisulphate $\text{V}_2(\text{SO}_4)_3$, prepared by reducing a solution of vanadium pentoxide in sulphuric acid with magnesium, or by the electrolytic reduction of vanadyl sulphate, forms a green solution from which green crystals of the acid salt $\text{V}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ separate out. By dissolving this salt in water, adding sulphuric acid and heating at 180° in a current of carbon dioxide, the sesquisulphate separates out as a yellow crystalline powder, insoluble in water (Stähler and Wirthwein, Ber. 1905, 38, 3978). Alkali vanadium sulphates of the form $\text{MV}(\text{SO}_4)_2$ have also been prepared (Rosenheim and Mong, Zeitsch. anorg. Chem. 1925, 148, 25; Chem Soc. Abstr. 1925, 128, i, 1411).

Several *vanadium alums* have been prepared.

Vanadyl sulphate $\text{V}_2\text{O}_5(\text{SO}_4)_2$ is prepared (a) in the insoluble form by dissolving the dioxide VO in sulphuric acid and heating the solution at 260° (Gerland, Ber. 1877, 10, 2109; Koppel and Behrendt, Zeitsch. anorg. Chem. 1903, 35, 154); (b) in the soluble form by heating the insoluble form with water at 130° , or by dissolving the dioxide in sulphuric acid, evaporating, and treating the residue with alcohol. Both forms are blue, and by crystallisation of the soluble form under different conditions hydrates with 18, 10, 7, 4, 3, and 2 molecules of water are obtained.

Strongly acid solutions deposit the acid sulphate $(\text{V}_2\text{O}_5)_2\text{H}_2(\text{SO}_4)_2$, crystallising with 5 molecules of water. When heated it gradually loses water, yielding various lower hydrates, and, finally, at 190° , the *anhydrous salt*



which forms microscopic green tetragonal crystals, sparingly soluble in water (Koppel and Behrendt, *loc. cit.*; Gain, Compt. rend. 1906, 143, 1154).

Divanadyl trisulphate $(\text{VO})_2(\text{SO}_4)_3$ is obtained in ruby-red octahedra by boiling the pentoxide with excess of sulphuric acid (see Ditte, *ibid.* 1886, 102, 77). Other basic salts, e.g. $(\text{VO}_2)_2\text{O}(\text{SO}_4)_2$ and $\text{VO}(\text{OH})\text{SO}_4$, have been described (see Gerland, Ber. 1878, 11, 98).

Vanadium pyrophosphate $\text{V}_2(\text{P}_2\text{O}_7) \cdot 30\text{H}_2\text{O}$ is formed as a flocculent green precipitate when an alkaline pyrophosphate solution is added to a solution of vanadium ammonium alum (Rosenheim and Triantaphyllides, Ber. 1915, 48, 582).

Vanadium mononitride VN may be obtained by the direct union of its elements or by heating ammonium metavanadate or the pentoxide to whiteness in a current of ammonia. It is a brown powder, oxidised to the blue oxide when heated in air.

Vanadium dinitride VN_2 is a black powder obtained by the action of ammonia on vanadyl trichloride.

Many phosphovanadic and arsenovanadic acids are known, giving rise to numerous derivatives (see Ditte, Compt. rend. 1898, 102, 757; Gibbs, Amer. Chem. J. 1886, 7, 118, 209; Friedheim, Ber. 1890, 23, 1530, 2600; Gain, Compt. rend. 1907, 144, 1271; Mawrow, Zeitsch. Chem. 1907, 55, 147). Blum has described a series of phosphovanadic molybdates (J. Amer. Chem. Soc. 1908, 30, 1858).

Vanadium boride VB is formed by heating a mixture of its constituents in the electric arc. It is a hard metallic looking substance. Stable towards alkalis and acids but readily decomposed by fused alkali hydroxide.

Vanadium carbide VC , obtained by heating the pentoxide with carbon in the electric furnace, forms hard crystals of sp.gr. 5.405; m.p. 3100°Abs .

Vanadium silicides. Two silicides are known: V_2Si , sp.gr. 5.48; and VSi_2 , sp.gr. 4.42. Both are obtained in the electric furnace from the oxide and silicon. They are hard, crystalline substances, having a metallic lustre (Moissan and Holt, Compt. rend. 1902, 135, 78, 493; Meyer and Backs, Chem. Soc. Abstr. 1924, ii, 558).

A vanadium aluminium silicide $\text{V}_2\text{Al}_2\text{Si}_2$ has been described by Manchot and Fischer Annalen, 1907, 357, 129).

For *vanadic esters and other organic vanadium compounds*, see Hall, Chem. Soc. Trans. 1887, 51, 751; Prandtl and Hess, Zeitsch. anorg. Chem. 1913, 82, 103; Barbieri, Atti R. Accad. Lincei, 1914, [v.] 23, ii, 408; Mertens and Fleck, J. Ind. Eng. Chem. 1915, 7, 1037.

Detection and estimation of vanadium.—Vanadium may be detected *qualitatively* by the behaviour of its compounds on oxidation and reduction, yellow or red solutions of vanadates yielding blue solutions of vanadyl salts on reduction with zinc and acid. Addition of ammonium chloride to a solution of a vanadate precipitates white ammonium metavanadate. The most delicate test known for vanadium consists in adding hydrogen peroxide and ether to a solution of a vanadate acidified with sulphuric acid; a yellow or red colour is produced in the aqueous layer (G. Werther, J. pr. Chem.

1903, [L.] 88, 195; Campagne, Chem. Zentr. 1904, [H.] 1167). Vanadium may also be detected spectroscopically (see Purvis, Trans. Camb. Phil. Soc. 1906, 20, 193; Pollok, Sci. Proc. Roy. Dubl. Soc. 1909, 11, 331).

For the arc spectrum of vanadium, see W. F. Meggers (J. Washington Acad. Sci. 1923, 13, 317-325).

Vanadium is usually estimated volumetrically by oxidation methods after other reducible metals have been eliminated. See art. ANALYSIS, and also Hartmann (Zeitsch. anal. Chem. 1925, 66, 16).

For the volumetric estimation of vanadium in steel, see A. T. Etheridge (Analyst, 1923, 48, 588).

Atomic weight.—The atomic weight of vanadium was estimated by Roscoe (Phil. Trans. 1868, 158, 1) to be 51.23; by Prandtl and Bleyer (Zeitsch. anorg. Chem. 1909, 65, 152; 1910, 67, 257) as 51.07; by McAdam (J. Amer. Chem. Soc. 1910, 32, 1603) as 50.96; and by Briscoe and Little (Chem. Soc. Trans. 1914, 105, 1310) as 50.95.

VANADIUM INK v. VANADIUM.

VANADIUM MICA v. ROSCOELITE.

VANILLA is the dried fermented pod of certain orchids, indigenous to Mexico, but also found in Java, Réunion, the Seychelles, Brazil, Peru, on the banks of the Orinoco, Parahyba and other rivers of South America.

The chief cultivated variety is *V. planifolia* (Andr.), which is grown on a considerable scale in Mexico, Réunion, Mauritius, Madagascar, the Seychelles, and in Java. The long fleshy stem of the plant clings by its aerial rootlets to trees, and bears a greenish-white flower. The fruit is a pulpy pod, about 6-12 ins. long and half an inch thick. In Mexico the plant is cultivated by planting cuttings at the feet of trees left in a clearing of the forest; these root in a few weeks and bear in the third year. In Réunion and in the Seychelles the plants are trained on trellis-work supported by trees, and are fertilised by hand. Care has to be taken to gather the pods at the proper time of maturity, as if over-ripe they split in drying, and if under-ripe they are deficient in flavour.

The fruit is usually gathered in the late autumn when full grown, but just before it ripens.

The curing of the fruits consists essentially of a slow process of drying in warm air, using either artificial or solar heat, but the details vary in different countries; thus in Mexico the gathered pods are allowed to lie in heaps until they begin to shrivel, after which they are heated, either by exposure to the sun or in ovens, when they gradually acquire a dark-brown colour. In Réunion and Madagascar the pods are immersed in boiling water for a few seconds, and then exposed to the sun for a few weeks in woollen cloths until they acquire the proper brown colour. As they become dry, they discharge a viscid liquid from the upper end, and are pressed from time to time to promote its flow. They are usually packed for the market in small bundles of fifty or one hundred in each. The yield of vanilla beans in Madagascar and dependencies for the season 1921-22 was 909,000 lbs., and in Réunion and Mauritius 121,000 and 2000 lb., respectively.

It has also been suggested to use calcium

chloride in the drying of the beans (J. Soc. Chem. Ind., 1898, 180).

For literature on the culture and curing of the vanilla beans, v. *ibid.* 1893, 707; *ibid.* 1896, 679; *ibid.* 1900, 847; *ibid.* 1901, 1048; *ibid.* 1906, 1117; *ibid.* 1909, 1002; Fr. Pat. 367285, 1906.

Those who habitually handle vanilla beans are often subjected to a cutaneous affection in the form of an eruption on the hands, face, or neck, which causes intense irritation; this is probably due to the oily juice which exudes from the beans. To avoid the affection, good ventilation of the factories and thorough washing of the hands are recommended (Claverie, J. Soc. Chem. Ind. 1908, 1082).

Commercial vanilla beans are almost black, 15-20 cm. long and 6-9 mm. thick. They are of a flattened cylindrical shape, tapering towards each end, wrinkled and flexible. The best varieties, chiefly the Mexican, are the largest; they are very dark, glossy, and frost or *givre* (i.e. become covered with white crystals) very quickly. The inferior varieties are shorter, lighter in colour, and do not frost much.

Vanillons are the cured fruits of uncultivated vanilla plants; they are usually of poor quality. The unripe beans are said to contain coniferin and two enzymes, one of which converts coniferin into coniferyl alcohol and glucose, and the other oxidises the former to vanillin (Lecomte, Compt. rend. 1901, 133, 745).

Best Mexican vanilla beans contain 1.60-1.86 p.c. vanillin, Bourbon 1.91-2.90, Java 2.75, German East African 2.16, Ceylon 1.48, Tahiti 1.55-2.02, but the flavour of vanilla does not depend merely on the quantity of vanillin it contains (Busse, Zeitsch. Nahr. Genussm. 1899, 2, 519). The best qualities of vanilla beans contain less actual vanillin than the cheaper varieties.

In addition to vanillin, the beans also contain vanillic acid $C_8H_7(OH)(OCH_3)CO_2H$, resins, fat, sugar, and 4-5 p.c. ash (Winton and Silverman, J. Soc. Chem. Ind. 1902, 1300; U.S. Pat. 931805; *ibid.* 1909, 1062; Gautier and Kling, Ann. Falsif. 1910, 3, 200). Anisyl alcohol and anisaldehyde have also been detected (Walbaum, Chem. Zentr. 1909, ii, 2181).

When the green vanilla pods are exposed to ultra-violet rays, they emit a smell of vanillin, the process being accelerated by a rise in temperature and by previous immersion in dilute manganous chloride (Pouget, Compt. rend. 1911, 152, 1184).

Tincture or essence of vanilla is formed by extracting the ground or cut up vanilla (10 parts) with a mixture of alcohol and water, and mixing the extract with 20 parts of refined sugar, the whole being made up to 100 parts.

The extracts obtained from several varieties of vanilla and tonka beans, using isopropyl alcohol, ether, acetone, and carbon tetrachloride, when compared with that obtained with ethyl alcohol showed that the alcoholic solvents are much superior as regards quality of extract, carbon tetrachloride giving the poorest extract. It is possible, however, that a preliminary extraction with ether or carbon tetrachloride, followed by extraction with a dilute solution of alcohol, may give satisfactory extracts (J. W. Sale, J. Ind. Eng. Chem. 1923, 15, 728-734; J. Soc. Chem. Ind. 1923, 43, 347 A-348 A).

The chief constituent in vanilla extracts is coumarin, either artificial or from tonka beans; good imitation extracts may be obtained from 3 parts of vanilla, and 1 part of tonka beans, but most commercial imitations contain no vanilla, and are made up of artificial vanilla and coumarin and extract of tonka beans, the whole being coloured with caramel (Winton and Silverman, *loc. cit.*). In the preparation of inferior extracts weak alcohol and alkali are employed; these can be distinguished from good extracts by shaking a few c.c. with 3 volumes of water, when, if no alkali has been employed, a flocculent red precipitate will be formed. With hydrochloric acid a good extract should give only a slight turbidity (Hess, *J. Amer. Chem. Soc.* 1899, 21, 719).

Vanilla in the form of its tincture, is employed for flavouring chocolate and confectionery. It is also largely used in the manufacture of liqueurs and perfumes. See also Vanille, Vanilline, Vanille-Extracten. W. L. Utermark, Amsterdam: Kolonial Instituut, 1922.

VANILLIN (4-hydroxy-3-methoxybenzaldehyde $C_8H_8(OH)(CHO)(OCH_3)$) is contained in vanilla beans (*v. VANILLA*); in *Habenaria nigra* (R. Br.) (Lippmann, *Ber.* 1894, 27, 3409); in dahlia tubers (*ibid.* 1906, 39, 4147); in the woody parts of plants (*ibid.* 1904, 37, 4521); in the fruit and roots of *Avena sativa* [L.] (Rawton, *Compt. rend.* 1897, 125, 797). It also occurs in many other plants, in resins, balsams, and other substances (Campani and Grimaldi, *Bull. Soc. chim.* 1890, [iii.] 3, 458; Weld, Tollens and Lindsey, *Ber.* 1890, 23, 2990; Thomas, *Arch. Pharm.* 1899, 237, 271; Knitt, *ibid.* 256; Itallie, *ibid.* 1901, 239, 506). Vanillin may be obtained from vanilla pods by disintegrating the latter with sand and extracting with ether or a mixture of ether and alcohol (Tiemann and Haarmann, *Ber.* 1876, 9, 1287).

Vanillin may be obtained artificially by oxidising coniferin or coniferyl alcohol with chromic acid; by oxidising eugenol or, better, isoeugenol with air (Fr. Pat. 316526, 1902; Eng. Pat. 4909, 1902; *J. Soc. Chem. Ind.* 1902, 722; *ibid.* 1903, 439). According to A. Lowy and Catherine M. Moore (*Am. Electrochem. Soc. Trans.* 1922, 42, 273), contrary to the claim of D. R. P. 92007 (1897), no appreciable proportion of vanillin could be obtained by the electrolytic oxidation of isoeugenol. The latter is highly susceptible to oxidation to a wide variety of possible products and vanillin itself is readily oxidised electrolytically (*Sci. Abstr.* 1924, 27, 575). In the oxidation of the sodium salts of isoeugenol, or of acetyl isoeugenol in presence of aromatic amino carboxylic acids, extracting acetylvanillin from the products of the reaction, converting this into the bisulphite compound and treating successively with acid and sodium hydroxide (Slevers and Givaudan & Co., Swiss Pat. 89053); with ozone or ozonised air (Trillat, *Compt. rend.* 1901, 133, 822; *Bull. Soc. chim.* 1903, 29, 45; Fr. Pats. 326775, 421784, 1909; U.S. Pat. 829300, 1906; *J. Soc. Chem. Ind.* 1903, 819); with peroxides (Eng. Pat. 11952, 1894; 14923, 1896; *J. Soc. Chem. Ind.* 1895, 806; *ibid.* 1897, 633); or electrolytically (Eng. Pat. 1624, 1895; *ibid.* 1895, 48, 322).

These attempts to oxidise isoeugenol by

ozonised air on a commercial scale have not been uniformly successful, owing to the formation of a resin as a result of the reaction being a very rapid one. In the new process the plant consists of a series of four towers partly filled with splash plates or balls. The first two contain a mixture of isoeugenol and aqueous sodium bisulphite, while the third and fourth are smaller and contain sodium carbonate and hydroxide respectively. Ozonised air is drawn through the towers and the vanillin dissolves in the bisulphite solution as formed. After 8 hours the aqueous layer is run off, the bisulphite compound decomposed with the requisite quantity of sulphuric acid (determined by titration of a test sample), rendered slightly alkaline with sodium carbonate, and extracted with benzene. The crude vanillin recovered from the benzene solution is crystallised three times from water, the last crystallisation being from water completely free from iron. The power required for ozonisation is given as $\frac{1}{2}$ kva. per oz. of vanillin (B. G. Wood, *Met. & Chem. Eng.* 1923, 28, 806; *J. Soc. Chem. Ind.* 1923, 42, 626A).

A 95 p.c. yield and a much purer product is said to be obtained by oxidising eugenol, isoeugenol, coniferin, or coniferyl alcohol, simultaneously with air and ultra violet rays at 50°-60° (D. R. P. 224071; *J. Soc. Chem. Ind.* 1910, 1036).

The conversion of isoeugenol to vanillin by ozonised air has been studied by Briner, Patry, and E. De Luserna (*Helv. Chim. Acta*, 1924, 7, 62), by conducting a current of ozonised air at varying concentrations of ozone (5 p.c. to 19 p.c.) into a solution of isoeugenol in carbon tetrachloride, at temperatures from 15°-150°. The highest oxidation efficiency obtained, in terms of ozone consumed, was 20 p.c. at the lowest temperature. At higher temperatures the efficiency falls off rapidly and the quantity of resinous by-product formed increases (*Chem. Soc. Abstr.* 1924, 126, 1, 290).

Vanillin may also be prepared by dissolving 14.2 kilos protocatechuic aldehyde in concentrated sodium carbonate solution, and mixing it with 12.6 kilos of dimethyl sulphate. The whole is heated on the water-bath, acidified, and extracted with ether. The latter is evaporated, and the vanillin extracted from the residue with chloroform (*J. Soc. Chem. Ind.* 1902, 274; see also *ibid.* 1897, 633; *ibid.* 1894, 1218; *ibid.* 1895, 1061).

Pure vanillin may be synthesised by the following method, the yield being 70-80 p.c. of the theoretical: 1 gm. molecule of a methyl or ethyl ester of mesoxalic acid or of any α -diketonic acid (or of the free acid) is added to a solution of 250 grms. of zinc chloride in 500 grms. of glacial acetic acid. The whole is kept at the ordinary temperature for 15 hours, after which it is heated at 50° for some hours, and then diluted with water and shaken with ether. The ethereal extract is washed with dilute aqueous sodium carbonate, distilled with steam to remove guaiacol (if present) and oxidised with copper chloride or acetate, vanilloylcarboxylic acid being formed. The latter, when heated with an equal weight of dimethyl-p-toluidine at 170°, yields vanillin, which is extracted from the acidified mixture by means of ether (Gayot and Gry, *Compt.*

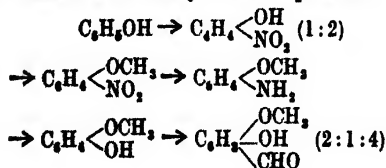
read. 1909, 149, 928). Vanillin may also be synthesised by treating guaiacol with hydrocyanic acid, hydrochloric acid, and zinc chloride in the presence of infusorial earth (D. R. P. 189037; Chem. Zentr. 1908, i, 73).

A nearly theoretical yield of vanillin sodium hydrogen sulphite is obtained when dry hydrogen is passed through a boiling mixture of vanilloyl chloride-*p*-toluenesulphonic ester (154 pts.), dry xylene (1000 pts.), and palladised barium sulphate (5 p.c., 30 pts.) until evolution of hydrogen chloride ceases (Eng. Pat. 131161).

Vanillin has also been prepared by other methods.

The process of the Ozone Vanillin Co. (U.S. Pat. 829100) consists in passing ozonised air into a mixture of isoeugenol and sodium bisulphite solution of 30°Bé. The vanillin produced unites with the bisulphite from which it is easily separated. The production in the United States in 1919 was 134,700 lbs., valued at \$1,365,900 (Census of Industrial Products). Gattefosse and Morel describe a method of producing vanillin from phenol which consists in nitrating the phenol, separating the ortho- and para-derivatives by steam distillation, methylating the ortho-nitrophenol by dimethyl sulphate in presence of caustic soda to produce *o*-nitroanisole, which is then reduced by zinc powder in presence of calcium chloride to *o*-aminoanisole. This is converted by diazotisation into guaiacol, which by treatment with formaldehyde and hydroxylaminobenzenesulphonic acid yields vanillin.

These reactions may be thus represented:

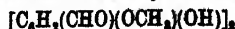


Literature.—Tiemann, Ber. 1891, 24, 2877; Angier and Boissien, Bull. Soc. chim. 1895, 13, 519; Bouveault, *ibid.* 1898, [iii.] 19, 75; Verley, *ibid.* 1901, [iii.] 25, 48; J. Soc. Chem. Ind. 1899, 558, 740; *ibid.* 1902, 68; *ibid.* 1908, 644; Stolz, Ber. 1904, 37, 4149; Frdl. 1877-87, i, 563-590; 1890-94, iii, 894-900; 1894-97, iv, 1272-1291; 1897-1900, v, 101, 110; 1902-04, vii, 755; 1905-07, viii, 1280, 1281; 1907-10, ix, 162, 1130, 1166.

Vanillin forms white needles having a strong characteristic taste and smell, m.p. 80°-81°, b.p. 285° (without decomposition in a stream of carbon dioxide) or 170°/15 mm. It is soluble in 90-100 parts of water at 14°, and in 20 parts at 75°-80°; it is readily soluble in ether, alcohol, and chloroform. Curves of solubility in aqueous alcohol and aqueous glycerol are given by Mange and Ehler (J. Ind. Eng. Chem. 1924, 16, 1258). The aqueous solution is acid, and gives a blue-violet colour with ferric chloride. When treated with ferrous sulphate and bromine water, vanillin is coloured bluish-green, then yellow (Pharm. J. 1897, 58, 187). Vanillin in hydrochloric acid gives characteristic colour reactions with phenols, ketones, and other substances; thus with acetone and its homologues a rose colour is formed, which becomes green on warming (Rosenthal, Zeitsch. anal.

Chem. 1905, 44, 292). A nitric acid solution of vanillin on standing yields a small quantity of hydrogen cyanide (Jorissen, J. Soc. Chem. Ind. 1910, 1638).

When oxidised with ferric chloride, nitric acid, or with fungus extract, or with gum arabic solution, vanillin forms *dehydrodivanillin*.



white needles, m.p. 303°-304° (Tiemann, Ber. 1885, 18, 3493; v. Lerat, Bull. Soc. chim. 1904, [iii.] 31, 270; Bourquelot and Marchadier, *ibid.* 1248; Bentley, *ibid.* 1900, [iii.] 24, 942).

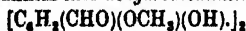
Vanillin may be estimated by converting it into its hydrazone by treatment with a hydrazide (Hann, Zeitsch. Nahr. Genussm. 1900, 3, 531, 657; *ibid.* 1905, 10, 585); or by converting it into its bisulphite derivative, decomposing the latter with sulphuric acid, removing the sulphur dioxide with a stream of carbon dioxide, then extracting the vanillin with ether; the ether is evaporated and the residue weighed (Busse, *ibid.* 1899, 2, 519; Doherty, J. Roy. Soc. N.S.W. 1914, 47, 157). For other methods, see J. Soc. Chem. Ind. 1893, 718; *ibid.* 1903, 514. Or it may be estimated colorimetrically by adding a phosphotungstic phosphormolybdic acid solution to an acid solution of vanillin, and comparing the intensity of the blue colour produced with that formed under like conditions by a standard solution of vanillin. For details, see Folin and Denis, J. Ind. Eng. Chem. 1912, 4, 670. Or 1 c.c. of the vanilla essence is extracted with ether, the extract evaporated over the water-bath, and the aqueous solution filtered and diluted to 50 c.c. in a Nessler glass. Ten drops of freshly prepared bromine water and ten drops of 10 p.c. ferrous sulphate are then added, and the green colour matched against a 0.2 p.c. solution of pure vanillin. Methods for determining vanillin are critically reviewed by Radcliffe and Sharples (Perf. Ess. Oil Rec. 1924, 15, 396, 437; 1925, 16, 20, 51, 87, 156, 197, 271, 353, 387).

A refractometric determination of vanillin in vanilla sugar may be made by shaking 3 grms. of the sugar with 3 c.c. of ether for 1 minute, and allowing to settle. The butyro-refractometer readings of the ether used and that of the ethereal solution of vanillin are then taken. The difference multiplied by 0.4 gives the percentage of vanillin in the sugar. The temperature of the prism should be the same for both readings.

A volumetric method of determining vanillin depends on the formation of a hydro-derivative by the interaction of vanillin and *p*-toluidine dissolved in 80 p.c. alcohol. This compound contains the original hydroxyl group of the vanillin, and is therefore soluble in alkali, giving a yellow solution. A measured excess of standard alkali is added, followed by a comparatively large volume of cold water. The addition of standard acid first neutralises the excess of alkali and then liberates the anhydro-derivative from its sodium salt. The first drop of acid which liberates the derivative produces a yellow turbidity, the free derivative being practically insoluble in the liquid phase. The volume of alkali required for the titration of the vanillin is thus obtained. Accurate results are obtained when benzoic acid is present as an adulterant in quantities up to 10 p.c. but

with higher percentages of acid it is advisable to use a gravimetric method. No sample of first-class vanillin contains more than 1 p.c. of acid (as vanillic acid), though some of the samples had been kept in cardboard containers for 10 years. The gravimetric method suggested comprises the precipitation of vanillin as the semi-carbazone from dilute acetic acid solution. The precipitate is easy to wash and filter and may be dried in a water oven for 6-8 hours, without losing a weighable quantity by volatilisation. The vanillin may be separated from impurities, such as piperonal, by dissolving the semi-carbazone in ammonia solution. Vanillin semi-carbazone, by virtue of its hydroxyl group, forms a soluble ammonium salt, giving a yellow solution, whilst piperonal semi-carbazone is insoluble. Test analyses in which piperonal was added to vanillin gave results agreeing with the actual percentage to within 1 part in 450. The oxidation of samples of purified vanillin exposed to air, moisture, and light was practically negligible. With vanillin in solution, however, oxidation proceeds much more rapidly, while solutions of vanillin in alkali behave similarly to alkaline pyrogallol solution. The following corrected melting-points are given: vanillin semi-carbazone, 232°C.; piperonal semi-carbazone, 218°C.; vanillin-*p*-nitrophenylhydrazones, 148°C. (S. B. Phillips, *Analyst*, 1923, 48, 367-373; *J. Soc. Chem. Ind.* 1923, 42, 948 A).

Oxidising agents, in particular ferric chloride, convert vanillin into *dehydrodivanillin*



m.p. 302°-305°C., and the precipitation of the latter can be observed from aqueous solutions containing as little as 1 in 10,000 of vanillin. 20 c.c. of the solution to be tested is heated in a bath containing a solution of calcium chloride at 130°-140°C., and two fractions of 10 c.c. of distillate are collected. Further quantities of 10 c.c. of water are added to the residue and distilled off, until nine or ten such fractions have been collected. These fractions are tested with ferric chloride, it being easily possible to detect and characterise 0.01 gm. of vanillin in the 20 c.c. of sample taken (*cf.* *Chem. Soc. Abstr.* 1923, ii, 887; H. Herissey and P. Delauney, *J. Pharm. Chim.* 1923, 28, 257-262; *J. Soc. Chem. Ind.* 1923, 42, 1197 A).

For other methods, see Fellenberg, *Chem. Zentr.* 1916, ii, 391; Dox and Plaisance, *Amer. J. Pharm.* 1916, 88, 481; Estes, *J. Ind. Eng. Chem.* 1917, 9, 142.

Vanillin is frequently adulterated with coumarin, acetanilide, and with acetyl isoeugenol (Hess and Prescott, *J. Amer. Chem. Soc.* 1899, 21, 256; see also *J. Soc. Chem. Ind.* 1898, 1076; *ibid.* 1899, 604).

According to Winton and Lott (*ibid.* 1910, 1268) genuine vanillin may be distinguished from imitations by determining the lead number which, for the former, should lie between 0.29 and 0.34.

DERIVATIVES OF VANILLIN.

Vanillin forms salts with zinc, lead, sodium, and magnesium of the type $(C_6H_3O_3)_2M'$ (Tiemann and Haarmann, *Ber.* 1874, 7, 614).

Bromovanillin $C_6H_3Br(OCH_3)(CHO)(OH)$, m.p. 130°-131°, adiates yellow leaflets (Tiemann

and Haarmann, *l.c.*); the corresponding iodo compound has m.p. 174° (Bentley, *Amer. Chem. J.* 1900, 24, 172).

2-Nitrovanillin has m.p. 137°, 5-nitrovanillin, m.p. 176° (Bentley, *l.c.*; Fehorrr and Sumuleanu, *Ber.* 1899, 32, 3405).

Vanillin forms an *aldoxime*, m.p. 121°-122° (Decker and Klausner, *ibid.* 1904, 37, 520); a *phenylhydrazone*, m.p. 105° (Tiemann and Kees, *ibid.* 1885, 18, 1662); an *azine*, m.p. 174°-176° (Knöpfer, *Monatsh.* 1909, 30, 29); an *acetyl* derivative, m.p. 77° (Fehorrr and Sumuleanu, *l.c.*); a *benzoyl* derivative, m.p. 75° (Wörner, *Ber.* 1896, 29, 143); also a *di-* and *trithio* derivative, in which the oxygen of the aldehyde group is replaced by sulphur, m.p. 129°-130°, 235°-237°, respectively (Manchot and Zahn, *Annalen*, 1905, 345, 320; Wörner, *l.c.*). *Vanillinacetic acid* $CHO \cdot C_6H_3(OMe)CO_2H$ has m.p. 188° (Gassmann and Krafft, *Ber.* 1895, 28, 1871).

Vanillin-*p*-phenetidine (*eupyrin*)



is formed by the interaction of vanillin and *p*-phenetidine at 140°; m.p. 97°. It is said to have hypnotic and antineuralgic properties (D. R. P. 91171, 96342; *Frdl.* 1894-97, iv, 1183, 1185).

Benzaldivanillin forms microscopic needles, m.p. 221.5°-222.5° (Rogoff, *Ber.* 1901, 34, 3881; *ibid.* 1902, 35, 1961).

Methyl ether of vanillin (*veratraldehyde*) $(CH_3O)_2C_6H_3CHO$ may be obtained by the methylation of vanillin, and by other methods. It is best to dissolve 1 mol. of vanillin in less than the equivalent quantity of 10 p.c. methyl sulphate on the water-bath, 1 mol. of potash in solution is then added in drops. When the reaction is over the solution is made slightly alkaline when it separates into two layers. The upper layer is extracted with ether, and on distilling off the latter, the pure aldehyde is obtained (Decker and Koch, *Ber.* 1907, 40, 4794). It has m.p. 47° (Juliusberg, *ibid.* 119), and possesses hypnotic properties. The corresponding *ethyl* derivative $CH_3O \cdot C_6H_3(OC_2H_5)CHO$ has m.p. 64°-65° (Tiemann, *Ber.* 1875, 8, 1120). Homologues of vanillin have also been prepared (*Eng. Pat.* 10112, 1895; *J. Soc. Chem. Ind.* 1895, 595).

o-Vanillin (*m*-methoxysalicylic aldehyde) $(CHO : OH : OMe = 1 : 2 : 3)$ is, in the pure state, a solid which crystallises from water in pale yellow needles, m.p. 45.5°, b.p. 265°-266°. It dyes wool and silk from an acid bath a golden or lighter yellow, but the shades are not fast to soap (Noelting, *Bull. Soc. Ind. Mulhouse*, 1909, 79, 401; *J. Pharm. chim.* 1908, 28, 173).

It gives a *phenyl-hydrazone*, m.p. 130°-131°, and a large number of other derivatives. *Cf.* Perkin and Robinson, *Chem. Soc. Trans.* 1914, 105, 2376; Mosimann and Tambor, *Ber.* 1916, 49, 1361.

The root of a species of *CMorocodon* of Uganda, where it is termed *Murundo*, contains an odorous constituent $C_6H_3O_3 \cdot OMe$, m.p. 41°-42°, b.p. 257°-258°, which forms thin, colourless plates, is isomeric with vanillin, and yields an *oxime*, m.p. 138°, and a *phenyl-hydrazone*, m.p. 137°-138° (Goulding and Pelly, *Chem. Soc. Proc.* 1908, 62).

VANTHOFFITE. The presence of this double salt, $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$, in the abraum-salts at Wilhelmshall near Stassfurt, was detected by plotting on curves the results of several analyses of material from an apparently homogeneous specimen, which was found to consist of a mixture of vanthoffite, loewite, apthitalite, halite, &c. Such intimate intermixtures of minerals of different kinds are really of the nature of rocks, and they must be studied by the methods of petrography; namely, by the examination of thin sections in the polarising microscope, and by separating the individual minerals with the help of heavy liquids (e.g. mixtures of methylene iodide and benzene or tetrabromoethane and toluene). Similar mixtures containing vanthoffite have also been found in the Berlepsch mine at Stassfurt. The mineral has also been observed as nodules embedded, with loewite, in bloedite at Hall in the Tyrol. It is colourless with a vitreous lustre, and a flat-conchoidal fracture; sp.gr. 2.7; H. 3½. The mineral is named after J. H. van't Hoff, who, when its occurrence in the salt deposits was discovered, succeeded in preparing it artificially. When crystals of bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) are heated in contact with their mother-liquid to above 70° they are transformed first into loewite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) and then into the anhydrous salt $3\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$. L. J. S.

VAPOUR DENSITY v. SPECIFIC GRAVITY.

VAREC. *Kelp* v. IODINE.

VARIOLARIN v. LICHENS.

VARIISCITE. One of the many minerals consisting of hydrated aluminum phosphate, here with the formula $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$. It forms concretionary and compact nodular masses, sometimes with a minutely crystallised (orthorhombic) surface. The colour is bright apple-green (due to chromium); sp.gr. 2.5-2.6; H. 4-5. It was first found in 1837 in Saxon Voigland (the ancient Variscia), and within recent years has been mined in considerable quantities (3½ tons in 1909, and 2½ tons in 1910) at several places in Utah and Nevada. It is used as a gem-stone, taking the place of green turquoise (D. B. Sterrett, Min. Res. U.S. Geol. Survey, Annual Reports for 1910 and earlier).

L. J. S.

VARNISH (Syn. *Vernis*, Fr.; *Lac*, *Firniss*, Ger.). A varnish may be described as a homogeneous fluid, which, when applied by any suitable means in a thin layer over the surface of any object, dries either by the evaporation of the volatile solvent, or by the combined evaporation of the volatile solvent and the oxidation of the component oils and resins to a more or less impervious elastic film of varying degrees of hardness and of generally good weather-resisting properties.

Varnishes, in the drying of which heat is applied in a well-ventilated compartment to expel the solvent and to complete the oxidation so that the film is uniform like glass, are termed stoving varnishes. The simplest form of varnish is the spirit varnish, which is merely a solution of a more or less elastic solid in a volatile solvent. Spirit varnishes dry the most rapidly, but are liable to be brittle and especially to crack and peel off unless plasticised by the addition of suitable soluble elastic substances. Oil varnishes are, to a large extent,

free from this defect; the drying oils, which they contain, binding and softening the resin, and although they take longer to dry, they are generally more lustrous and durable. When varnish is used as the vehicle or medium for the application of a pigment or a pitch to an object, an enamel is produced. Such enamels dry with a gloss, and save labour by combining painting and varnishing in one operation. The solvents employed in making the various varnishes are chiefly turpentine, naphtha and petroleum spirit, kerosene and white spirit, methylated spirit and, recently, higher aliphatic alcohols, e.g. isopropyl, butyl and amyl alcohols. Linseed oil is the drying oil in most general use, but tung oil (China wood oil) is coming more into demand. Walnut and poppy oils are artists' mediums.

The solids, i.e. resins, &c., mostly employed in oil varnish making are: 1. Copal, including Kauri, Manila and Congo; 2. Rosin, including its glyceryl ester; 3. Asphaltum, including the various pitches. Recently synthetic resins have been tried in the form of coumarons resins and phenol formaldehyde resins incorporated with rosin (Albertols). The resins are solid bodies, generally more or less coloured, amorphous usually with a vitreous lustre, which melt as a rule at comparatively low temperatures often with decomposition. They are insoluble in water, but partially or wholly soluble in a number of solvents, e.g. alcohol, ether, acetone, carbon tetrachloride, benzene, light petroleum, turpentine, &c. In practice the varnish maker is more concerned with the properties of the varnish film than of the original resin, and although, generally speaking, the hardest resin gives the hardest film, the properties of the film are greatly affected by the other ingredients of the varnish and the skill with which they are incorporated.

Resins.—The resins have been classified into hard, medium and soft. Among the hard resins appear Zanzibar and Amber. The medium resins include Kauri, West African and Gold Coast copals. Among the soft resins are Manila (East Indian) and South American resins. Among the spirit varnish resins shellac, dammar, sandarac are hard resins, whereas mastic and rosin are medium, and elemi, oleo-resin turpentine and Burgundy pitch are soft. The solubility of a resin may be said to be in inverse proportion to its hardness. The hard resins and semi-hard resins are but very slightly soluble in their original condition at the ordinary temperature, but they are easily dissolved by turpentine, linseed oil, and other solvents, by previously heating them in such a manner as to cause them to lose by destructive distillation 10-25 p.c. or more of their weight of a resinous oil according to the resin dealt with. This partial destructive distillation of the harder resins is necessary before they will dissolve in oil or other solvents. The temperature to which the resins must be heated before they become soluble, is higher in the case of the hard resins than of the soft resins.

Oil Varnishes.—The first process in preparing an oil varnish is selection of the gum; the pieces are sorted out by hand and graded according to their colour and general soundness, and as the gum gives the hardening properties to the varnish and is the most expensive constituent, great

case is encountered in the solution. The selected gum is heated or 'run' whereby depolymerisation occurs, and then caused to unite with the oil. The gum is heated in a pot of copper, or of iron with a copper bottom, or of aluminium over a rapid fire, until it is perfectly liquid at about 290°-300°C.; a hood or lid is placed over the pot, which is connected to large flues in which the varnish 'fumes' are condensed. The drying oil, specially chosen for varnish making and clarified, is heated and added cautiously at the right moment to the 'run' gum, the whole being kept well stirred, and the heating continued until the mixture is perfectly clear. The driers are added in several ways, either in the form of a lead and manganese soap dissolved in oil or as solid lead and manganese compounds, and the mixture boiled with stirring until the driers are incorporated. The pot is then removed from the fire, and when sufficiently cooled, turpentine or white spirit is added gradually, stirring all the while until the whole is thoroughly mixed. Much inflammable vapour is evolved during these operations, and it is necessary that the varnish house should be so constructed that the vapours do not come in contact with fire.

After the addition of the thinners the varnish is strained into a tank, and allowed to stand until clear for use. The time required for this varies, and as all varnishes improve by age, the longer they are tanked the better. In some cases the driers, consisting of litharge and dry white copperas (cryst. $ZnSO_4$), are churned at the ordinary temperature with the varnish and the excess of undissolved solids is allowed to settle in tanks. Old varnishes produce surfaces of much greater lustre than new ones. The good qualities of a varnish largely depend on the efficient mixing of the gum and oil; if these are thoroughly incorporated the varnish will be free from spots and blemishes on its surface, while, if well boiled, a varnish is said to flow more freely and to dry more rapidly. Excessive boiling, however, causes the varnish to stouten and thus to require more thinners to bring it to a working consistency, and the resulting fluid, being poorer in its non-volatile constituents, yields a thinner and less lustrous coat. No strict rule on this point can be given, as some oils and gums stouten more rapidly than others, and the final result has to be manipulated according to circumstances.

The drying of oil varnishes varies considerably according to composition, and within certain limits to the proportion of metallic driers present as well as to the objects to which they have to be applied; thus a gold size may dry in a few minutes, while body or coach varnishes require 12-24 hours, and even then should be allowed 2 or 3 days to harden.

Of recent years many attempts have been made to prepare oil varnishes without previous fusion of the gum. Only one has led to successful results, viz. that in which naphthalene under pressure is employed. By this process, which was patented by Terence, the copals are dissolved in naphthalene by heating under pressure to 250°-300°C.; linseed oil or other drying oil is added to the solution and the naphthalene is distilled off. The varnishes obtained by this process are satisfactory and of

good hardness. The objections to the antecolore processes are the capital outlay and the length of time taken in rendering the gum soluble. Other special solvents for copals have been proposed, e.g. linseed oil acids, amyl alcohol, terpineol, &c., but they have met with no success. The effect of the solvent materials on the finished product is deleterious, unless they can be completely removed, which is not feasible. The weight of the gum 'run' in one operation has been steadily on the increase, and nowadays the old charge of $\frac{1}{2}$ cwt. is increased to over 1 cwt. and the whole operation can be performed with complete safety, if proper precautions are taken.

The number of varieties of oil varnishes is large; as many as 200 may be listed, each having its own special use. There is no general classification, although long and short oil varnishes, based on the proportion of resin to oil, is the most acceptable. The most important classes are, coachbuilders' varnishes, including those for carriages, motor cars and railway work; boat, marine and spar varnishes; decorators' varnishes for inside and outside work. Other classes include furniture varnishes, clear and black stoving varnishes and black japans containing pitches. Coachbuilders' varnishes (body and carriage varnishes) must give films which are dust dry within 12 hours and do not crack nor show 'bloom'; moreover, they will retain their lustre for several years, if washed from time to time and occasionally polished with wax. Undercoating varnishes, harder than finishing varnishes, must be sufficiently dry in 10-15 hours to admit of being lightly rubbed down previous to the application of an elastic finishing coat. A film of a blooming varnish shows after a time an opacity which may become permanent. Such surfaces have been found to be strongly polar. Blooming is not confined to oil varnish films. The general formulae of coachbuilders' varnishes may be summarised as follows:

	Resin	Oil	Thinners
Finishing body varnish	60 lbs.	15 gals.	15 gals.
Elastic coach varnish	60 "	12 "	12 "
Hard elastic varnish	60 "	10 "	12 "
Quick hard drying varnish	60 "	6 "	12 "

Undercoating varnishes show bloom when not covered by an elastic finish. Boat varnishes should give a water-resisting film and should not become opaque on immersion in water; these, as well as seaplane varnishes, generally contain China wood oil. Whilst a film of linseed oil never attains a degree of hardness to withstand abrasion, China wood oil gives a harder and more weather-resisting coating. Owing to the rapid gelatinisation of wood oil on heating, copals are largely replaced by rosin and rosin glyceride. Decorators' varnishes for inside and outside work differ slightly in the proportions of gum and oil; the inside varnishes must have good flow, be free from bloom, but great weather-resisting power is not required; for outside work, varnishes on the lines of the carriage varieties are employed. The undercoating varnishes are termed *putting on rollers*.

varnishes, drying rapidly so that in 12 hours they may be rubbed down to a flat surface upon which the finishing variety may be applied. The proportions of gum to oil may be 1:1.25. They are liable to bloom and not durable to weathering unless protected by an elastic finishing coat. Other varieties of decorators' varnishes include: church oak, drying with a hard film, not softening appreciably up to 40°C., suitable for church seats; floor varnish, softer than church oak, with a gum and oil proportion of 1:1.4 or 1:1.67; front door varnish, which must combine elasticity with hardness and lustre; furniture varnish containing rosin: oil=1:1.10, in which rosin is often introduced, and thin coats are applied, rubbing down between each coat until the requisite brilliance is obtained.

Black Japans and Bituminous Varnishes occupy a special position, since they have for their characteristic ingredients a bitumen or asphalt. Both gum resin and oil may or may not be present, as the asphaltic substances differ far more widely in their hardness and elasticity than the various gum resins, and their properties can be modified with greater facility. The most important bituminous varnish in the higher branches of the decorative craft is known as black japan. The term "japan," as applied to substances which promote the drying of a paint film, denotes generally liquids which dry to a hard film possessing considerable coherence. Japan driers give a harder film than the oleo-driers, which are elastic and of a drying-oil character, whilst japan driers are of the nature of a resin varnish containing resin, or rosin with lead and manganese. The specific purpose of black japan is in the production of a brownish-black ground of special translucence or depth, thus differing from pigmented preparations (black enamels), which appear to reflect their depth of colour from the surface only. The main use of black japan in the coach-building trade is for panel work. The varnish is obtained by amalgamating specially treated oil of great drying power with suitable bitumens, in the same manner as described in the manufacture of copal varnish. Black japan itself rarely possesses great elasticity or weather resistance, so that it requires a coating of a suitable finishing varnish. The art of the varnish maker consists in the preparation of a mixing of great degree of depth and intensity of colour without employing so high a proportion of bitumen that the solubility of the latter in the ensuing coat takes place, a condition manifesting itself by the appearance on the finished work of a greenish fluorescence. It is difficult to give a general formula for these coatings, as the quality depends on the selection of the materials. The proportions may be roughly stated as equal quantities of hard resin, asphaltum or petroleum pitch, and boiled oil with turpentine, and white spirit thinners.

Air-drying Black Enamels are made on a similar plan to the coachmakers' black japans, but consist of materials which are not so carefully selected, e.g. asphaltum, rosin, boiled oil, and petroleum thinners. Some contain only pitch, boiled oil, and turpentine, and are known as *Russwink* blacks, for which the following formula may be considered as fairly represen-

tative: 45 lb. pitch, 6 galls. boiled oil, and 6 lb. litharge, boiled until stringy and then cooled and thinned with 25 galls. turpentine or petroleum. It is evident that the varieties of blacks will be large in number and will have special names according to their requirements. They may be bright or dead; e.g. Berlin black for grates and fenders, in which the introduction of a black pigment such as carbon black produces a matt appearance. Coach and motor builders require a quick black for iron work, drying in about an hour, a black petrol-resisting varnish of brilliant lustre, drying and hardening quickly, and a dead black metal priming, capable of standing great heat, for the exteriors of cylinders of motor cars.

Black Stoving Enamels are of great variety, and a similar classification holds, as in the case of resin oil varnishes as to elasticity, body or viscosity, and temperature of stoving. One-coating, under-coating and finishing, brushing, dipping and spraying modifications are in use.

The marked difference between clear varnishes and black stoving enamels lies in the presence of bitumen. The remaining components are drying oils with their attendant driers and thinners, chiefly kerosene, since the temperature of stoving is higher than that of resin-oil varnishes, viz. 150°-177°C. Some black stoving enamels contain no resin or rosin, but generally a certain proportion is present; but it is difficult to identify the resins in the presence of a mixture of bitumens, especially if stearine pitches have been used. Flow and surface are important properties. The finishing coat must have a high lustre and hardness, and should show no runs or rivelling at the edges under the conditions of application, dipping, brushing, or spraying. The production of high-quality coatings demands careful selection of the components and of the proportions in the mixings. If an under-coating be used it must be adherent to the surface and be rust preventative, providing also a grip for the finishing coat. The under-coatings possess small elasticity, great hardness, good hiding power, but no lustre. They may contain a pigment such as carbon black instead of bitumen, whose function is to leave a dull uniform surface for the finishing coat. The composition and mode of preparation is variable. Among the many published formulae a mixing containing asphaltum, resin, and boiled linseed oil in the proportions of 10:2.5:50, with petroleum or turpentine may be considered as fairly representative. The proportions will depend on the requirements and on the temperature of stoving. British Specifications for oil, black and shellac varnishes used in the trade have been issued by the British Engineering Standards Association.

Such black stoving enamels, largely used on ironwork, have great weather-resisting power, but recently cellulose air-drying black enamels have been put forward. It is impossible in the space available to consider adequately the great variety of decorative and protective coatings, as well as their advantages and defects.

For further details reference may be made to R. S. Mornell's *Varnishes and their Components*, 1923; H. M. Longton, *Enamels and*

Phocas, 1923; N. Houston, Volatile Solvents and Thinners, 1936; T. H. Barry, A. A. Drummond and R. S. Morrell, Resins, Natural and Synthetic, 1926; The Analysis of Pigments, Paints and Varnishes, J. J. Fox and T. H. Bowles, 1926.

Spirit Varnishes.—The manufacture of spirit varnishes is much less complicated than that of the oil preparations, the former being simply solutions of one or more resins in various solvents. On the evaporation of the solvent a coating of varnish is obtained, consisting practically of the unchanged resins. The resins employed for this purpose are chiefly shellac, sandarac, soluble manila, dammar, acaroid, elemi, benzoin, mastic and rosin. The solution of the resins is affected either cold or hot, as circumstances require, heat presenting the advantages of rapid solution and clearing, while the palest varnishes are obtained by the cold process. To facilitate solution the gum should be kept continually agitated, thus preventing the particles of gum from forming a mass. It will be readily seen that the larger the surface of the gum exposed to the solvent the quicker will be the solution. A revolving churn is used, and the rotation keeps the particles in motion and prevents them from caking together. When the gum is all dissolved the varnishes are set aside to settle, and are ready for use almost immediately. They dry very rapidly and are, generally speaking, harder and more brittle than oil varnishes, and as their drying is merely dependent on the evaporation of the solvent the addition of driers is not required. Within recent years many forms of artificial or synthetic resins have come into use. They may be broadly classified into (1) condensation resins—e.g. the formaldehyde-phenolic resins; (2) polymerisation resins—e.g. the coumarone resins, which are obtained by the treatment of certain distillates from coal tar naphtha. Condensation resins are such as are made by preliminary interaction of at least two chemical substances, generally involving elimination of water. Resinification may be completed by a polymerising action.

Formaldehyde phenolic resins.—The most important condensation resin is made from formaldehyde and phenolic compounds. Bakelite is the typical example. Amongst other trade products of similar character are—in America, Redmanol, Condensite, Amberite, Phenoform, Sibolite, Nuloid, Amberdeen, Abalac, etc.; in France, Melusite, Cerite; in Great Britain, Elo, Bakelacque. There is a marked difference in the properties of the formaldehyde phenolic resins compared with the natural resins. The natural resins can be melted, but not 'run,' and cooled, without great change in their solubility or fusibility, but the phenol synthetic resins on heating may, under certain conditions, pass more or less rapidly into solid infusible resins, charring at 300°C.; moreover, the resin becomes insoluble in all ordinary solvents, and has acquired a remarkable increase in strength. It is this marked change in properties that has made Bakelite products so valuable as shellac substitutes. The formaldehyde phenolic resins are of two distinct types, one of which is chemically analogous to shellac, and the other, in character and solubility,

these form the class of shellac substitutes (called Novolak by Bakeland). They are analogous to shellac in their solubility relationships; they are soluble in alcohol and insoluble in hydrocarbons. The second type of resin is that in which the resin is soluble and fusible only in an intermediate stage and becomes insoluble and infusible on heat treatment, being finally in the *resite* condition, passing through the intermediate *resitol* stage. Bakelite, Elo, and Bakelacque are examples of this latter type. Bakeland terms these latter resins *resinoids*, as they do not possess all the properties common to the natural resins.

For details as to preparation and further application reference must be made to Carleton Ellis, Synthetic Resins and their Plastics, 1923, and to the Chemistry of Natural and Synthetic Resins by Barry, Drummond and Morrell, 1926.

The chemical changes occurring during the manufacture of these substances are not yet understood, although considerable advance has been made during the last few years. The varieties of resin produced is dependent on the amounts of formaldehyde and phenol used and whether the catalyst is acidic or basic in character. Bakeland (J. Ind. Eng. Chem. 1909, 1, 159) uses ammonia as catalyst. An acid catalyst will tend to produce a soluble resin, whereas an alkali favours an insoluble resin. The greatest development of these resins has been in the direction of moulding and insulating compounds.

Formaldehyde-urea Resins.—Condensation products of formaldehyde with urea and thiourea have been used to give viscous products which may be gelatinised in several hours. The reaction takes place in two stages, a condensation phase followed by a polymerisation phase. The solid resins obtained are transparent, colourless, stable, taking a high polish, and may be used as substitutes for glass; Polloplas and the Boettler Products Company resins are examples. In Pollak's Schellian solutions the resin is maintained in water solution by alkali salts of weak acids, e.g. sodium acetate or a borax solution of shellac.

Coumarone Resins are obtained from the fraction of solvent naphtha 150°–200°C., and are polymerised as regards certain of their constituents by sulphuric acid to yield 25–40 p.c. of resin. These resins are not usually soluble in alcohol, and benzene, toluene, solvent naphtha, and turpentine are the best solvents. They are miscible with drying oils. The differences in the technical coumarone resins depend on the variable proportions of indene and coumarone present. The following is a formula for a coumarone oil varnish: China wood oil containing 15 p.c. of linseed oil is incorporated with the resin in the proportion of 5–40 gallons per 100 lbs. resin. The driers used are cobalt or manganese linoleates, and the thinner is a heavy refined coal-tar naphtha, b.p. above 160°C. Typical varnish mixtures containing coumarone are described by King, Bayard and Rhodes, (J. Ind. Eng. Chem. 1920, 12, 626) and R. S. Morrell (Varnishes and their Components, 1923).

Cellulose Ester Varnishes.—Only two of cellulose are of any importance in the

industry, viz. the nitrate and the acetate, formed by combination of cellulose with nitric acid and acetic acid respectively. These substances are soluble in certain mixtures of organic liquids, which have a comparatively high rate of evaporation, and when the solutions are spread on solid surfaces they rapidly become dry, leaving the cellulose ester in the form of a continuous film. By making certain additions to the original solutions, the hardness and adhesiveness of the films may be modified. Owing to the rapidity with which the solutions dry, they may be applied at ordinary temperatures, although a warm room is advantageous. As a rule a coating is dry under an hour. All organic protective coatings consist of highly polymerised structures. The degree to which the original cellulose is depolymerised or degraded in structure before and during the manufacture of the ester determines to a considerable extent the properties of the resulting varnish.

Nitrocellulose Varnishes.—The cellulose ester varnishes may be either transparent or opaque. The transparent varnishes may be coloured in practically any tint so as to give a coloured transparent lacquer coating. The opaque varnishes containing pigments may also be obtained in any colour, and are usually termed enamels. It is customary to include all solutions of cellulose esters used for protective or decorative coatings under the general term of cellulose varnishes. They may be applied by brush, but better results are obtained by dipping or by use of an air spray. Under proper conditions the solutions dry with a high polish, and the films resist water, petrol, soap, turpentine, weak acids and weak alkalis.

Cellulose nitrate lacquers.—The common metal lacquer usually contains not more than 5 p.c. of cellulose nitrate, in a mixture of solvents, and serves to delay the tarnishing of metal, not acting as a finishing material. In order to increase the solid content it was necessary to produce cellulose nitrate, which, when dissolved in suitable solvents, gave a solution of low viscosity. The addition of natural resins was found to impart adhesion and rubbing properties in varying degrees according to the resin employed and the amount used. The constituents of finishing lacquers may be: cellulose nitrate of low viscosity, resins to make the film glossy and hard, solvents which control the rate of drying, degree of gloss and viscosity of the lacquer, and plasticides to remain in the film after the solvents have evaporated and so to give it elasticity. Scrap celluloid as a substitute for cellulose nitrate has many drawbacks, and its use is not to be recommended. The resins are either of the soft or medium hard varieties. Butyl alcohol, ethyl, butyl and amyl acetates, ethyl lactate and amyl formate may be used as solvents. D. B. Keyes classifies the solvents into three groups: (1) low boiling solvents, reducing the viscosity of the lacquers and permitting a high rate of evaporation; (2) medium boiling, giving the lacquers the property of flow; (3) high boiling, acting as a non-solvent, preventing the precipitation of nitrocellulose or the resin.

The lacquers are best applied by spraying, but good results may be brushed on. In

the order of application of the cellulose coatings careful consideration of their elasticity must be taken, so as to prevent subsequent cracking of the film. Pigmented lacquers and enamels have been used for many years as protective coatings for bathroom fittings, cycle and motor lamps and furniture. The following proportions of cellulose nitrate, resin and plasticide have been found satisfactory for interior lacquer enamels: cellulose nitrate 12 parts; resins 6 parts; plasticide 2 parts. This ratio will give a hard and elastic film provided too much pigment is not added. For further details reference may be made to F. Sproston, *Cellulose Ester Varnishes*, 1925.

Cellulose acetate varnishes.—Solutions of cellulose acetate in a mixture of high and low b.p. solvents are used for tanning and weather-proofing linen fabric composing the wing surfaces of aeroplanes. A typical three-coat formula would be cellulose acetate 8.5 parts, acetone 50, alcohol 24, benzene 24, benzyl alcohol 2 and triphenyl phosphate 1.5. For durability the dopes must be specially pigmented and generally require a protective coating of a seaplano oil varnish.

Natural varnishes or lacquers.—Japanese lacquer is the milky juice exuding from the trunk of *Rhus vernicifera* (Tsi-chou, varnish tree). The tapping of the tree resembles that of *pinus* for turpentine oleoresin. The raw varnish, which is frequently adulterated with tung and perilla oils, is known in Japan as Ki-urushi. The peculiarity of the varnish is that it hardens only in a moist atmosphere and remains in a tacky condition to sunlight and heat. It is the most durable varnish known and resists the action of air and water excellently. It is stated to be the best protective coating for aeroplane propellers. The application of the lacquer is said to be dangerous to western workers owing to the peculiar poisonous properties of the *urushiol* in the resin. The resin has been investigated by Japanese chemists, who have synthesised hydrourushiol, the reduction product of the active principle of Japan lac. A concise account of Chinese and Japanese manufacture will be found in the Bulletin of the Imperial Institute, 1910, 8, 32; and in Stewart Dick's *Arts and Crafts of Old Japan*, 1908.

R. S. M.

VARVICITE. *Hydrated manganese ore*
 $\text{MnO}_2 \cdot \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Rammelsberg), or



(Phillips) (v. MANGANESE).

VASOTONIN. Trade name given to a combination of yohimbine and urethane which produces a fall of blood pressure, and appears to have considerable therapeutic value (*China. Soc. Abstr.* 1910, ii, 725).

VAT DYES. The term 'vat dye' is applied to those dyestuffs which, like indigo, are insoluble in water, dilute acids, and alkalis, but which, on being treated with suitable reducing agents, yield leuco compounds which are soluble in the hydroxides of the alkalis or of the alkaline earths, and in dyeing are taken up as such by textile fibres. By subsequent exposure to the air the leuco compound is oxidised and

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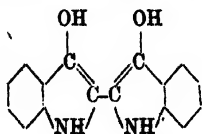
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and in the fibre, with the re-formation of the original colouring matter. The characteristic fastness of the colours thus produced is, in a large measure, due to the insolubility of the dyestuff.

Indigo (*g.v.*), which was formerly the only known vat dye, is by far the most important of this series of colouring matters, and has been used in dyeing from time immemorial. A blue, dyed with it on cotton, is still referred to as a 'vatted blue,' whilst in the woollen industry the term 'wooded blue' means a blue which is dyed either wholly or in part with indigo.

In preparing or 'setting' the indigo vat, various methods are employed in practice to bring about the reduction of the indigotin. This is effected either by purely chemical or by bacteriological means, but in either case the product of the reaction is the same, viz. indigo white, $C_{16}H_{12}N_2O_2$, or graphically,



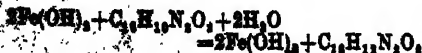
which dissolves in caustic soda with the formation of either the mono- or di-sodium salt ($C_{16}H_{11}N_2O_2Na$ or $C_{16}H_{10}N_2O_2Na_2$), according to the amount of caustic soda present in the bath. It has been shown that indirubin and thioindigo red also require 2H for reduction, and by analogy it is presumed that the other indigoid dyestuffs behave similarly. In aqueous solution, the mono-sodium salt of indigo white has been shown to be an electrolyte, though it is not so strongly ionised as sodium chloride (Knecht and Batey, *J. Soc. Dyers*, 1910, 171).

The so-called chemical vats are distinguished, according to the reducing agent employed, as the copperas, the zinc, and the hydrosulphite vats. They are used in cotton dyeing, but the hydrosulphite vat also finds a limited application in wool dyeing. In the setting of any indigo vat, it is essential that the indigo should be in a finely divided state. The 20 p.c. artificial indigo paste contains the colouring matter in a sufficiently finely divided condition for the purpose, but the natural product must be ground, before use, to an impalpable powder.

The copperas vat depends upon the reducing action of ferrous hydroxide, and is made up of indigo, copperas and slaked lime. The lime reacting with the copperas forms ferrous hydroxide:



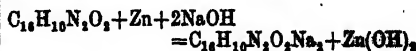
which in turn reduces the indigotin to indigo white:



which then dissolves in the excess of lime present to form the soluble calcium salt. In the copperas vat, there is always a large amount of sediment, and to prevent this coming into con-

tact with the goods during dyeing, deeper vessels are required than with the other chemical vats. At the present time, the copperas vat is not largely used in this country, the main reasons being that its use involves a considerable loss in indigo, and the sediment in the vat is very bulky. On the other hand, the blues obtained in the copperas vat are faster than those obtained in the zinc or hydrosulphite vats.

In the zinc vat, zinc powder is the reducing agent. For satisfactory working, this should contain not less than 80 p.c. of metallic zinc. The vat is set with indigo, zinc powder and lime (or caustic soda). The reduction may be regarded as taking place as follows:



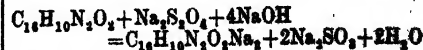
although, according to Binz (*Chem. Ind.* 11, 1902), it is probable that combination of the indigotin with the alkali takes place first, with the formation of a compound



which then reacts with the zinc, forming the same products as shown in the above equation.

This vat is the one which is most largely used in cotton dyeing.

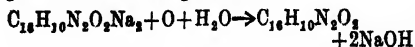
The hydrosulphite vat depends upon the reduction of the indigotin by sodium hydrosulphite, which is usually prepared by stirring zinc dust into commercial sodium bisulphite, in the proportion of a pound of the former to a gallon of the solution; and after allowing to stand for some time, adding to the solution an excess of milk of lime. The so-called 'stock vat' or concentrated vat is made by dissolving the indigo in this muddy liquid. (A product of this kind, containing about 3 p.c. of indigotin, was formerly sold under the name of 'reduced indigo.') This stock vat serves either for making up or for replenishing the dye vat proper. The reduction by means of sodium hydrosulphite may be regarded as taking place according to the following equation:



By employing artificial indigo paste, caustic soda, and the solid commercial sodium hydrosulphite, which is now placed on the market in an almost pure condition and at a reasonable price, it is possible to obtain a vat practically free from sediment.

The dyeing of cotton in the indigo vat is in itself a comparatively simple operation, although the management of the vats requires careful supervision and considerable practical experience. In hank dyeing, the wetted-out hanks are immersed in the vat and turned by hand under the surface of the liquid until thoroughly impregnated with the vat liquor, after which they are withdrawn and wrung, the liquor being returned to the vat. The hanks are then exposed freely to the air, in order to allow of the oxidation of the indigo white to indigotin. By repeating this operation several times, the shade becomes successively darker, and its depth will therefore depend upon the number of 'dips' in

one and the same or in different vats. Although it is possible to obtain a dark shade by a single dip in a strong vat, this is not practised, because it would result in a large proportion of the indigo being loosely fixed and much of it would be lost in washing off; besides, the resulting blue would 'rub off' very badly. The oxidation of the indigo white taken up by the fibre from the vat is usually regarded as taking place in the following manner:—



though under chosen conditions it has been shown by Herzog and Manchot that auto-oxidation may take place, resulting in the formation of equal molecular proportions of indigotin and hydrogen peroxide (Annalen, 316, 318). This interesting observation may account, according to Crowther, for the presence of isatin in the hydrosulphite vat (J. Soc. Dyers and Col. 1911, 146). It is further evident that the dyed cotton material removes a considerable amount of alkali from the vat. Where lime is used in the vat in place of caustic soda, an accumulation of calcium carbonate on the fibre occurs through air exposure, and the goods therefore soured, after dyeing, in dilute sulphuric acid. In the dyeing of cotton warps and of piece goods, the material is guided through the vat by means of submerged rollers, so that it passes many times up and down between the time of entering and leaving; excess of liquor is expressed at the point of exit by means of a pair of squeezing rollers. In case it is desired to give the pieces two or more 'dips' in the same vat, they are stitched together, end to end, so as to form a continuous band, and, after leaving the vat, are passed up and down over a series of loosely running wooden rollers (which are usually placed immediately above the vat in order to economise space) for a sufficient length of time to allow of the oxidation of the indigo white before they re-enter the vat.

The reason why indigo white should be taken up from its aqueous solution by the cotton fibre is imperfectly understood. It has been suggested that it is a case of mutual precipitation between colloids, but as it has been definitely shown (see above) that indigo white lacks some of the most essential properties of a colloid, this theory cannot hold good. In any case, the affinity of indigo white for cotton is but slight, as, when once taken up, it can be completely removed by continued washing with cold, air-free water, whereas a boiling solution of dilute caustic soda removes it from the fibre almost instantaneously. The affinity of indigo white for cotton appears to be similar in character to that of tannic acid for this fibre (Knecht and Nair, *ibid.* 1912, 28).

If the cotton to be dyed in indigo or other vat dyes has been previously mercerised, darker shades are obtained than on untreated cotton. The same applies with regard to indigo and certain indigoid dyestuffs if the cotton has been previously dyed manganese bronze or has been steeped for some time in strong nitric acid (see *Mercerising*). In the latter case, the increase in depth is due in a greater measure to alight nitration of this fibre than to the mercerising effect of the acid.

Indigo dyed on cotton is sometimes associated with other colours. Thus, if a light shade of indigo is 'topped' or subsequently dyed chrome yellow, pleasing and very fast shades of green result. The old-fashioned 'fast black' was obtained by a combination of a heavy shade of indigo and catechu brown. The dyeing of a black of this description was practised by the Incas of Peru prior to the Spanish invasion.

Indigo dyed on cotton is usually regarded as fast to washing and to light. Strictly speaking, however, these qualities are only relative, for by repeated washing in soap or continued exposure to light, the colour (especially in light shades) gradually fades. But in fading it always retains the characteristic colour of indigo and does not change, as is the case with most other blues, to an unsightly grey or drab. It is noteworthy that the fastness of indigo to light may be considerably enhanced by treating the dyed fabric for a few minutes in a boiling dilute solution of copper sulphate.

In Egypt, Persia, India, China, Japan, and other Eastern countries, where dyeing is still almost entirely a household industry, fermentation vats are generally used for cotton dyeing. Such vats are occasionally used in this country for the dyeing of goods for certain markets. The fermentation vat imparts a certain peculiar smell to the goods dyed in it, and unless they possess this smell, the natives in some markets will not accept them as indigo-dyed. A product known as indigo essence, consisting of a mixture of the methyl ethers of α -naphthol and β -naphthol, is put on the market for the purpose of imitating this smell on material dyed blue with dyes other than indigo.

The dyeing of wool with indigo differs from the dyeing of cotton in that whereas cotton is invariably dyed cold, the temperature of the vat for wool dyeing must be maintained at from 50° to 55°. Another point of difference is that in the case of wool, the time of immersion in the vat has to be much longer than in the case of cotton.

For wool dyeing, especially where fermentation vats are used, natural indigo is generally preferred to the artificial product.

Only one of the vats generally used in cotton dyeing can be used with advantage in wool dyeing, viz. the hydrosulphite vat. This is set with indigo, sodium hydrosulphite and ammonia. Although the cost of working this vat is greater, as far as materials are concerned, than that of the fermentation vats, this is more than compensated by its greater output. It is, however, only suitable for light to medium shades of blue.

The fermentation vats, of which a considerable variety are in use in different countries and sometimes in one and the same country, might appear at first sight to depend for their action upon different principles. But it is probable that in all cases the action depends upon a bacterial decomposition (butyric acid fermentation) of the carbohydrates, in which hydrogen is generated. Various substances containing carbohydrates, such as bran, flour, sugar, treacle or dates, are used along with lime, potash, or soda for the purpose. The setting and management of fermentation vats require considerable skill and experience, and in all large works these matters are under the sole

control of the 'blue dyer,' upon whose intelligence and efficiency the prosperity of the works largely depends.

The fermentation vat mostly used in this country is the so-called *woad vat*, which is set in a vessel having a capacity of from 1600 to 3000 gals. with indigo, woad, bran, madder and lime, the temperature being maintained at 60°. The fermentation will have set, as a rule, in from three to five days, and the vat will then be ready for use. Once set, a woad vat simply requires replenishing, from time to time, with the necessary additions of indigo, lime, and bran, and may remain in use continuously for many years. It should be explained that in this vat the woad, which in former times (before the introduction of indigo from India) was the only indigo-bearing dyestuff used in this country and on the Continent, now acts solely by virtue of the bacteria which it contains, for in commercial woad there is, at the present day, no indigotin, the whole of the colouring matter having been destroyed by bacterial action.

Dyed on wool, indigo resists the action of light better than when dyed on cotton.

The disulphonic acid of indigotin, which is obtained by heating the dyestuff to about 100° with excess of concentrated sulphuric acid, is known commercially as indigo extract or, in the form of its sodium salt, as indigo carmine. It dyes wool 'at the boil' from a bath containing sulphuric acid and Glauber salt a much brighter shade of blue than that obtained in the vat, but the colour is neither fast to light nor to soap, and goods so dyed cannot be classed as being dyed with indigo.

Silk is seldom dyed in the indigo vat, although fast and pleasing shades can be obtained in this way.

Indigo in printing.—In textile printing, notably in calico printing, indigo may be regarded as the most important individual dyestuff in use at the present time. This is partly due to the favour which it finds with the public as being pleasing to the eye and relatively fast, and partly to the variety of styles to which it lends itself in this branch of textile colouring. Effects are obtained with indigo in printing in three entirely different ways, viz. by direct printing, by the discharge process, and by the resist process.

In direct printing, the indigo is not printed on to the fabric in the reduced condition (a process which would obviously suggest itself at once to any one acquainted with its properties and its application in dyeing) owing to practical difficulties which this mode of application entails. The process in actual use is the so-called *glucose process*, in which glucose and caustic soda serve as the reducing agent. The pieces are first prepared by padding in a solution of glucose and are then dried. The finely ground indigo is made up with strong caustic soda thickened with maize starch and British gum. This is printed on to the prepared calico and the goods are run through a rapid ager containing air-free moist steam, the time required for this treatment being about half a minute. During the steaming, the indigo is reduced to indigo white which dissolves in the caustic soda and penetrates into the fibres. By subsequent exposure to air, the indigo white slowly oxidises

back to indigo blue. The operations of preparing in glucose and drying may be dispensed with by adding to the printing colour a suitable reducing agent such as the formaldehyde compound of sodium sulphonylate (hydrosulphite NaF.). This has no action on indigo in the cold, but reduces it on steaming for two to three minutes. The goods are then exposed to the air as in the glucose process.

Indigo may also be produced on the fibre in printing (or in dyeing) by means of *indigoool*, a product discovered by Messrs. Sunder and Bader, and recently introduced by Messrs. Durand and Huguenin. The new product is a comparatively stable compound of indigo white, soluble in water and in caustic soda. The printed or padded pieces are run through a weak bath of nitrite of soda and acid, when the indigo instantly develops on the fibre. The blues obtained in this way are faster to rubbing than those obtained in other ways.

In the discharge process, which lends itself to a greater variety of effects, the whole piece is first dyed to the required depth of blue in the vat and the colour is then removed locally either by destroying it by means of oxidising agents or by reducing it to the leuco compound and removing this by means of boiling dilute alkali. The former process, which is the one chiefly employed, consists in printing sodium chromate, suitably thickened, on to the blue fabric. After printing, the goods are run through a warm solution of sulphuric and oxalic acids, when in consequence of the liberation of chromic acid, the indigo is oxidised to isatin and this is removed in the subsequent washing, a white pattern on a blue ground resulting. For coloured discharges, the chromate is mixed with albumen and a suitable pigment, such as vermilion or chrome yellow, and the goods are run, after being printed, through the mixture of acids at a temperature high enough to coagulate the albumen. The fixation of the pigment and the destruction of the indigo thus take place simultaneously. The process is capable of many modifications. Thus, in order to obtain a bright scarlet on a blue ground, the indigo-dyed fabric is padded first with an alkaline solution of β -naphthol, dried and printed with a colour containing diazotised *p*-nitraniline and sodium dichromate. The *p*-nitraniline red thus formed resists the action of the chromic acid formed when the pieces are run through acid and a bright red on a blue ground results.

Indigo may also be discharged by printing on sodium nitrate and running the goods through warm sulphuric acid of 100°Tw. (Freiberger's process).

In the reduction discharge process, the pieces are printed with the formaldehyde compound of sodium sulphonylate with or without the addition of a catalyst such as anthraquinone. They are then steamed in the rapid ager to reduce the indigo and immediately run through a boiling bath of caustic soda, soda ash, or sodium silicate. The indigo white is thus completely removed and there is no tendering of the discharged places, as is invariably the case when the chromate discharge is used.

In the resist process, the fabric is first printed with a mechanical or with a 'chemical resist' and is then dyed in the vat. Wherever the resist

has been printed no colour is fixed, and a white pattern on a blue ground results. In the East, and also to some extent in European print works, wax is used as the resist. After dyeing it is removed by soap and alkali. When the goods are handled (as in dyeing) after the wax has been printed on, the latter cracks in places so that in the dyeing some of the reduced indigo liquor penetrates through the fissures, with the result that fine blue veins are afterwards seen in the pattern. This defect is characteristic of all true Battick work, which the modern printers are at pains to imitate.

The 'chemical resist' mostly used at the present time is a very thick colour containing copper sulphate, lead nitrate, and China clay, usually thickened with flour and British gum and with or without the addition of such mechanical resists as tallow or rosin. As with the wax resist, the dyeing is best conducted in the zinc vat. By increasing the amount of lead nitrate in this resist so as to exceed its equivalent in copper sulphate, and running the goods after dyeing through sodium dichromate, lead chromate is formed in the resisted parts and a yellow pattern on a blue ground results.

VAT DYES OTHER THAN INDIGO.

Although it has long been known that indirubin (an isomeride of indigotin which occurs in almost all natural indigos) can be dyed in the same manner as indigo, it has never found any technical application, partly on account of the shade it yields being undesirable and partly for other reasons. The tetrabromo (5:7:5':7') derivative, obtained by brominating the artificially prepared dyestuff in nitrobenzene solution is, however, a useful vat dye, and comes into the market under the designation *Ciba Heliochrome B. Indophenol*, which was discovered in 1882 by Koechlin and Witt, is also a vat dye, and although it was a commercial article in the '90's it was never much used, mainly because it produced loose colours, and it is now entirely obsolete.

The enormous development in the vat colour industry that has taken place during the last few years may be traced, on the one hand, to the discovery of indanthrene blue by Bohn in 1901, and on the other hand to the synthesis of thioindigo red by Friedländer in 1905. At the present time there are well over one hundred individual dyestuffs which may be strictly classed as vat dyes, without taking into account the large number of sulphide colours (*q.v.*) which, in a sense, might also be classed as vat dyes. It would obviously be out of place to embody the whole of our present knowledge of the vat dyes in this work, as that would require an amount of space which would not be commensurate with the general interest attaching to the subject. In the following, it will therefore be understood that the examples given are only typical of the various classes. For further information on the subject of vat dyes, see Engi, *Chem. Zeit.* 1908, 1178; Bohn, *Ber.* 1910, 987; Staebli, *Chem. Zeit.* 1910, 731 *et seq.*; Friedländer, *ibid.* 1911, 640; Masera, *Färber-Zeit.* 1911, 336; Grandmougin and Battagay, *Ela. Text. Bl.* 1910; Maffoch, *J. Soc. Dyers*, 1910, 26; Ermen, *ibid.* 1910, 56 and 236; E. de Barry Barnett,

ibid. 1913, 183; L. E. Vlies, *ibid.* 1914, 22; Truttwin, *Enzyklopädie der Küpenfarbstoffe*, 1920; J. F. Thorpe and C. K. Ingold, *Vat Colours*, 1923; The 'Colour Index' of the Society of Dyers and Colourists, edited by F. M. Rowe, 1924; Knecht, Rawson and Loewenthal, *A Manual of Dyeing*; Knecht and Fothergill, *The Principles and Practice of Textile Printing*, 1924.

These vat dyes may be classed under two headings, viz. as (a) indigoid dyestuffs, and (b) anthraquinonoid dyestuffs. The former come into the market under various trade names such as indigos of various brands, the Durindope colours (British Dyestuffs Corporation), Alizaranthrene colours (British Alizarine Co.), and the Ciba colours (Soc. of Chem. Ind., Basel), while the latter are represented by the Duranthrene colours (British Dyestuffs Corporation), the Caledon colours (Solway Dyes Co.), and the Cibanon colours (Soc. of Chem. Ind., Basel) *V. INDIGOID DYESTUFFS*, Vol. III, p. 620.

The bromo derivatives of indigotin are brought into the market under different designations, such as indigo pure R.B.N., *ciba blue*, indigo K2B, and generally yield, in dyeing and in printing, either redder or greener shades of blue than indigo itself, according to the amount of bromine which they contain. Thus *indigo R* is 5 bromoindigo, *ciba blue 2B* is 5:7:5':7'-tetrabromoindigo, and *indigo KG* consists mainly of 4:5:7:4':5':7'-hexabromoindigo. There is no object to be gained in substituting more than five hydrogen atoms in the indigo molecule, as the leuco compounds of the more highly halogenated derivatives are so sparingly soluble as to preclude their practical application. The 6:6'-dibromoindigo synthesised by Friedländer, and shown by him to be identical with the *Tyrian purple* of the ancients, is not a commercial article. It is interesting to note that the 6:6'-dibromoindigo dyes an amethyst shade (Tyrian purple) whereas the isomeric 5:5'-dibromoindigo (*indigo RB*) dyes blue. The position occupied by the halogen atoms in the molecule is of importance in other instances. Thus the entrance of the halogen atoms in the para-position with reference to the nitrogen atoms causes but little alteration in the colour, although the shades are brighter than those from indigo itself. If the halogen atoms occupy the para-position to the CO groups, the dyes obtained are redder in shade than indigo.

Of homologues of indigo, the 7:7'-dimethylindigo (*methyl indigo B*), and the 5:5'-dimethylindigo (*methyl indigo R*) are the most important commercial representatives. The former dyes cotton a greener and the latter a redder shade of blue than indigo itself.

Thioindigo red B or thionaphthene indigo



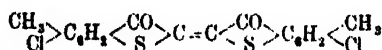
was discovered in 1905 by Friedländer and is obtained by fusing *o*-carboxyphenylthioglycollic acid with caustic potash to form thioindoxyl, which is then oxidised to the dyestuff. This dye results from the action of dichloroethylene on thioacetylic acid, followed by treatment with sulphuric chlorohydrin. The discovery of this product marked the beginning of

a new era in the history of organic colouring matters, for it opened up a new field and has resulted in the introduction of a large number of new and valuable vat dyes. Like artificial indigo and most other commercial vat dyes, thioindigo red B comes into the market in the form of a 20 p.c. paste. The pure colouring matter is readily obtained from the dried paste by crystallisation from benzene or toluene in well-defined dark red crystals. Its solution in benzene is red and shows a characteristic intense yellow fluorescence. In concentrated sulphuric acid it dissolves with a bluish-green colour; but on pouring the solution into water, the original dyestuff separates. By warming with fuming sulphuric acid, it is sulphonated and the soluble sulphononic acid thus obtained dyes wool from an acid bath a full bluish shade of red. Unlike indigo, thioindigo red is not affected by oxidising agents, remaining unaffected by chromic acid, alkaline ferrocyanide and bleaching powder; whilst, on the other hand, it is more readily reduced than indigo. It has been shown that the reduction of thioindigo red to its leuco compound is analogous to that of indigo, two atoms of hydrogen or their equivalent being required for one molecular weight of the dyestuff (Knecht, J. Soc. Dyers, 1906, 156). Like indigo white, the leuco compound dissolves readily in caustic alkalis, forming a yellow vat from which it is taken up by the cotton fibre, the red reappearing on exposure to the air.

Of derivatives of thioindigo red, the following may be mentioned:

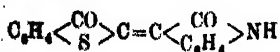
Thioindigo red B.G (dichlorothionaphthene indigo) $C_6H_3Cl_2 \langle \begin{smallmatrix} CO \\ S \end{smallmatrix} \rangle C=C \langle \begin{smallmatrix} CO \\ S \end{smallmatrix} \rangle C_6H_3Cl_2$; *thio-*

indigo red 3B (dichlorodimethylthionaphthene indigo)



thioindigo violet 2B (dichlorodimethyldimethoxythionaphthene indigo); *thioindigo orange R* (6:6'-diethoxythionaphthene indigo); and *thioindigo gray* (7:7'-diaminothioindigo). In general it may be said that the introduction of substituents such as OH, OCH₃, OC₂H₅, SCH₃, SC₂H₅, NH₂, &c., in the para- position to the sulphur atoms produces a deepening of the shade to blue-violet, greenish-black, &c. Substitution in the meta- position to the sulphur atoms produces yellower shades—orange, orange-brown and scarlet. Halogenation darkens the shade of thioindigo red.

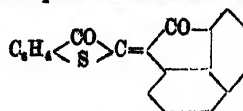
Thioindigo scarlet R



obtained by the action of thioindoxyl on isatin contains the characteristic groupings of thioindigo red and of indirubin. When acted upon by bromine in sulphuric acid solution it yields a dibromo derivative which is placed on the market under the name of *thioindigo violet K*. The tribromo-amino derivative represents *thioindigo brown G*.

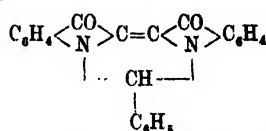
Ciba scarlet G (also known as *thioindigo scarlet 3G*) is a non-nitrogenous product, ob-

tained by the condensation of thioindoxyl with acenaphthene quinone and has the constitution



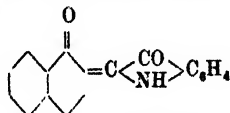
By the bromination of this dyestuff, *Ciba red R* results.

Of other indigoid dyestuffs, mention may be made of *Ciba yellow 3G*, which is obtained by boiling indigo with benzoyl chloride and copper powder in nitrobenzene, and to which the constitution



has been described. The complete change from blue to yellow is remarkable.

By the condensation of α -naphthol with α -isatinchloride, a compound is obtained with the following *ortho*quinonoid structure



and is, in a sense, also indigoid in character. The tribromo derivative is known as *Alizarin indigo 3R*. The corresponding compound from alpha anthrol and dibromoisatin is known as *Alizarin indigo G*.

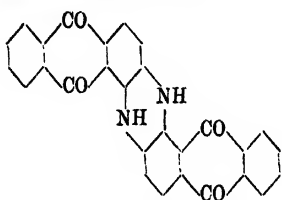
The indigoid dyestuffs all behave very much like indigo towards reducing agents, i.e. they yield leuco compounds (corresponding to indigo white) which dissolve readily in caustic alkalis, and in this condition show affinity for the textile fibres. The affinity of the different dyestuffs for the cotton fibre varies, however, in each case, so that their successful application, especially in the production of mixed shades, requires a considerable amount of practical experience. The reducing agent employed for these colouring matters (in fact for all vat dyes other than indigo) is invariably sodium hydrosulphite, for although it is not the most economical, it is the most effective and convenient reagent for the purpose and yields vats which are free from sediment. In principle, the dyeing of cotton with these dyestuffs is the same as the dyeing of indigo in the hydrosulphite vat. The optimum temperatures vary, however, according to the individual dyestuff, from the ordinary temperature (as used for indigo) to temperatures as high as 70°. The range of shades obtainable contains almost every colour of the spectrum, and some of these vie in brilliancy with the basic colours. Most of the colours are characterised by great fastness, and are in this respect superior to indigo. Hitherto no indigoid black has been produced.

Although originally applied to dyeing and printing on cotton and other vegetable fibres, methods have been devised by which these colouring matters can be successfully applied in wool dyeing, by substituting ammoniacal

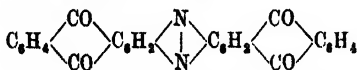
the caustic soda in the vat or neutralising the effect on the fibre of the caustic soda by the addition of some soluble oil (see H. Kämmerer, J. Soc. Dyers, 1913, 68).

In calico printing, the indigoid dyestuffs can be applied by methods similar to those employed for indigo, with the exception of the chromic acid discharge, which cannot be used owing to these dyestuffs being either not affected at all by chromic acid, on the one hand, or yielding imperfect discharges on the other. They can, however, be discharged by means of the formaldehyde compound of sodium sulfoxylate. For further information on the use of these colours in calico printing, see N. Evans, J. Soc. Dyers, 1913, 144.

Anthraquinonoid dyes.—The first of these dyestuffs brought into the market was *indanthrene blue*, a product formed by the action of molten caustic potash on β -aminoanthraquinone, and possessing the constitution



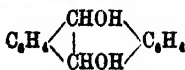
It is a dark blue compound insoluble in water, dilute acids, alkalis and most ordinary organic solvents. It can be obtained in well-defined crystals from its solution in quinoline or by sublimation. Oxidising agents convert it into the yellow azine



(containing 2 atoms of hydrogen less), but this is readily reconverted into the dyestuff by the action of reducing agents. Acted upon by hydrosulphite in presence of an excess of caustic soda, indanthrene blue yields a blue vat from which cotton and other vegetable fibres can be dyed in exceedingly fast shades of blue. The composition of the leuco compound of indanthrene blue and other anthraquinonoid vat dyes is not known with certainty, but it is evident from the behaviour of anthraquinone, alizarin and the non-nitrogenous anthraquinonoid dyes that reduction takes place in the $-\text{CO}-$ group, resulting in the formation of compounds analogous to oxanthranol



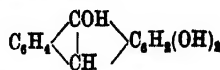
or the isomeric anthrahydroquinone



where in either case 2H would be required for the reduction. The further reduction to anthranol



requires 4H or its equivalent. In this connection it may be mentioned that in the quantitative estimation of alizarin by titration with titanous chloride in presence of sodium tartrate (J. Soc. Dyers, 1915, 241) the analogous reduction to desoxyalizarin

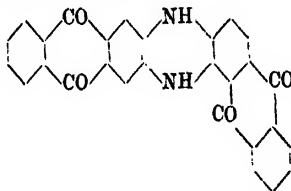


takes place, 4H being required.

To what extent the four $-\text{CO}-$ groups of indanthrene blue suffer reduction in the formation of a 'vat' is not known at the present time, and this applies also to the other anthraquinonoid dyes.

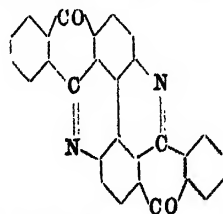
Halogen derivatives (Cl and Br) of indanthrene blue are also commercial articles and yield in dyeing greener shades of blue which are faster to bleaching powder than ordinary indanthrene blue (v. INDANTHRENE), as the introduction of halogen atoms renders the oxidation to the azine less easy. *Indanthrene blue GCD* an *dindanthrene blue GC* are the dichloro and dibromo derivatives respectively of indanthrene blue.

By the condensation of alizarin with 2:3-diaminoanthraquinone, a compound having the following constitution



is obtained, halogen derivatives of which come into the market under the names *algol blue* and *algol green*.

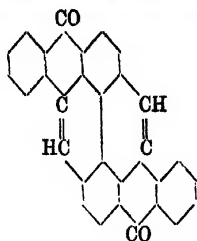
Flavanthrene or *indanthrene yellow* is formed as a by-product in the manufacture of indanthrene blue, but is obtained in much better yield, according to D. R. P. 138119, by the oxidation of β -aminoanthraquinone with antimony pentachloride in boiling nitrobenzene, or by the action of manganese peroxide in nitric acid solution (D. R. P. 141355). Flavanthrene has been shown to possess the constitution



and comes into the market in the form of a yellow paste. With caustic soda and hydrosulphite (or other reducing agents) it yields a deep cobalt-blue vat from which cotton takes up the leuco compound and is dyed, after exposure to the air, a fast yellow. The halogen derivatives of flavanthrene dye redder shades than flavanthrene itself.

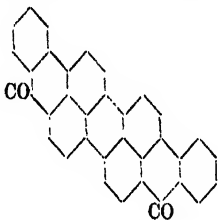
That nitrogen and sulphur are not essential

constituents of vat dyes is shown by the fact that *pyranthrone* or *indanthrene golden orange G*

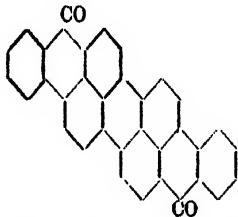


obtained by the condensation of two molecules of 2:2'-dimethyl-1:1'-dianthraquinonyl behaves in exactly the same manner towards reducing agents and in dyeing as the other vat dyes of this series. By the introduction of halogens into this dyestuff the shade is altered towards red. Thus, the brominated product represents *indanthrene scarlet G*.

By the alkaline condensation of two benzanthrone molecules, vat dyes are obtained, the simplest representative of which (*violanthrene BS*) is represented by the constitution

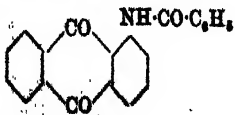


which, when nitrated, yields *indanthrene green*. This vat dye produces a green on cotton which is not very fast to light. *Indanthrene violet RT*, which dyes very fast shades, is a halogenated violanthrene. *Violanthrene R extra* is obtained by fusing halogen derivatives of benzanthrene with alcoholic potash. It is represented by the constitution

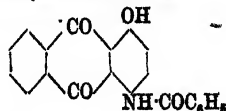


Indanthrene violet RR and *indanthrene violet B* are the dichloro and dibromo derivatives of this violanthrene.

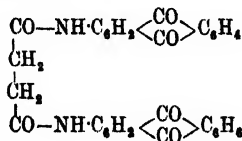
Some of the dyestuffs of this series are derivatives of aminoanthraquinones and are represented by comparatively simple constitutional formulae. Thus, *algal yellow WG* is α -benzoylaminoanthraquinone



whilst *algal pink R* is the benzoyl derivative of a hydroxyaminoanthraquinone

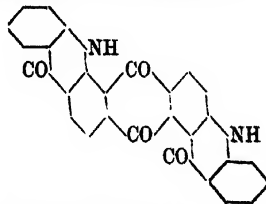


A variety of shades are produced by the introduction of further groups such as OCH_3 , NH_2 , additional OH groups, &c., into the anthraquinone molecule, followed by benzoylation. Succinyl derivatives are also used. An example of these is the dyestuff known as *algal yellow 3G*, which is the succinyl compound of diamino-dianthraquinone



It is noteworthy that the arylaminoanthraquinones do not act as vat dyes for cotton, although some of them are, in the form of the sulphonic acids, valuable wool dyes. In this connection it may be mentioned that whereas alizarin is quantitatively reduced by titanous chloride in presence of Rochelle salt to desoxy-alizarin, alizarin orange cannot be reduced further than to β -aminoalizarin.

Another class of anthraquinonoid dyes, the anthraquinone acridones, are obtained by condensing 1:2 chloroanthraquinone carboxylic acids with aromatic amino compounds, followed by treatment with concentrated sulphuric acid. *Indanthrene violet 2B* is a member of this class. It is represented by the constitution



Some of the *sulphide colours* (q.v.) are also classed as vat dyes, though they do not appear to bear any relationship to the indigoid or anthraquinonoid dyestuffs as far as constitution is concerned. The points of similarity are the use of hydrosulphite to form a vat and the fastness of the resulting colours on cotton. Of these dyestuffs the best known is *hydron blue*, which is obtained by melting the indophenol of carbazol (from *p*-nitrosophenol and carbazol) with a sodium polysulphide rich in sulphur. The dyeing is done at an elevated temperature ($50^\circ\text{--}70^\circ$), and shades are obtained which resemble indigo, though they are claimed to be faster. Some vat dyes obtained from anthracene or its derivatives, such as *algal brown B*, *indanthrene olive G*, and the *cibacron* colours are also sulphide dyes of unknown constitution.

The anthraquinonoid dyes are employed in cotton dyeing much in the same way as the indigoid dyes. Generally speaking, they require, however, a much larger amount of caustic soda in the vat and are not dyed cold, but at a

temperature of 50°-60°. In dyeing light shades, the dye-bath is generally exhausted under these conditions. After dyeing, the goods are soaped hot, a process which in most cases considerably enhances the brilliancy of the colour. With some of the colours, the fastness to bleaching powder is increased by steaming under pressure after dyeing. Although no black anthraquinonoid dyestuff is known, a black of extraordinary fastness can be obtained on cotton by dyeing it first indanthrene green and then subjecting the dyed material to the action of bleaching powder. The colours obtained with the dyes of the anthraquinoid series are generally somewhat faster to light than those obtained with the indigoid dyes. They are not applicable to wool dyeing owing to the necessity of keeping the vat strongly alkaline with caustic soda, with the inherent risk of damaging or destroying the fibre. It has been suggested that a preliminary treatment of the wool with formaldehyde would obviate this difficulty.

In calico printing, the anthraquinonoid dyes are largely used for some of the best classes of work. The usual method of using the indanthrene colours is to print a colour containing the vat dye, stannous chloride, ferrous sulphate and thickening, and after drying to pass rapidly through a hot strong solution of caustic soda. The fixation may also be effected in one operation by using a printing colour containing the vat dye, hydrosulphite-formaldehyde and soda ash, after which the goods are steamed for 5-7 mins. in air-free steam. The glucose process, as described for indigo, is also applicable to vat dyes in general.

In steaming or 'ageing' the vat dyes, it sometimes happens that the colours do not develop satisfactorily on subsequent exposure to the air, and faulty goods thus result. This is due to over-reduction of the vat dye to a stage at which neither air contact nor oxidising agents will develop the colour. See Reinking: Exothermic reactions in the rapid ager, J. Soc. Dyers, 1922, 306.

By the introduction of the vat dyes the public demand for fast colours, especially in dyes and printed cotton and linen fabrics, has been met, and it is now possible to obtain by means of them almost any shade fast to washing, light, perspiration, rubbing, and even bleaching powder. It should, however, not be taken for granted that a vat dye is of necessity a fast colour. Those on the market have, however, generally been carefully tested and selected by the makers and usually possess this attribute. Many of the vat dyes are so fast that they can be put through the full bleaching process for cotton pieces without suffering any material diminution of intensity and brilliancy, and advantage is taken of this in the production of white fabrics with coloured stripes or figures. Whereas it was formerly necessary, in order to obtain these effects, to bleach both warp and weft before weaving, the bleaching is now largely effected in the piece and considerable economy is realised. With the exception of indigo, the vat dyes are still too expensive to admit of their being employed for any but the best class of work. This is due in part to the high cost of manufacture, but more especially to the fact that most of them are tinctorially weak, as com-

pared with, for instance, the basic and direct cotton colours. Even indigo itself shows this drawback, but most of the other vat dyes show it to a greater extent.

For the identification of the vat dyes in dyed and printed fabrics, see A. G. Green and G. H. Frank (J. Soc. Dyers, 1910, 83), also G. E. Holden (*ibid.* 1909, 47), A. G. Green, W. Gardner, L. Lloyd, and G. H. Frank (*ibid.* 1913, 227), and J. I. M. Jones and W. Kilby (*ibid.* 1925, 127). Indigo can readily be distinguished from the other vat blues by dissolving the fabric in warm 80 p.c. sulphuric acid. The solution is poured into water and filtered through a small asbestos filter. After washing and drying, the residue on the filter is heated to about 100° with concentrated sulphuric acid and again poured into water and filtered. Under these conditions, the indigo is sulphonated and passes into the filtrate with a bright blue colour, whereas the other vat blues remain unaffected. E. K.

VAUQUELINITE. Native lead and copper chromate.

VAUXITE AND PARAVAUXITE. These occur on wavellite in brecciated tin-veins in rhyolite at Llallagua, Oruro. Vauxite occurs as radiating aggregates of sky-blue, tridinic crystals with $a:b:c=1.1510:1:1.2624$, $\alpha=99^{\circ}32'$, $\beta=102^{\circ}14'$, $\gamma=110^{\circ}14'$; $d\ 2.375$, $H\ 3\frac{1}{2}$; refractive indices $\alpha\ 1.551$, $\beta\ 1.555$, $\gamma\ 1.562$, optically positive. Paravauxite forms colourless, triclinic crystals of prismatic habit with good $b\ (010)$ cleavage; $a:b:c=0.5058:1:0.6882$, $\alpha=97^{\circ}42'$, $\beta=110^{\circ}22'$, $\gamma=100^{\circ}56'$; $d\ 2.291$, $H\ 3$; refractive indices $\alpha\ 1.554$, $\beta\ 1.558$, $\gamma\ 1.573$, optically positive. Analyses by J. E. Whitfield gave I for vauxite and II for paravauxite.

				H ₂ O at 104°	H ₂ O above 104°
FeO	MnO	Al ₂ O ₃	P ₂ O ₅	104°	104°
I. 19.34	0.18	14.89	31.33	3.68	30.24
II. 15.47	—	17.89	29.80	16.40	20.34

The minerals are readily soluble in hydrochloric acid. The water content of the paravauxite varies considerably with the humidity of the atmosphere. Formulas:

Vauxite: $4\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 24\text{H}_2\text{O} + 3\text{H}_2\text{O}$.

Paravauxite:

$5\text{FeO} \cdot 4\text{Al}_2\text{O}_3 \cdot 5\text{P}_2\text{O}_5 \cdot 26\text{H}_2\text{O} + 21\text{H}_2\text{O}$.

(Samuel G. Gordon, Proc. Acad. Nat. Sci. Philadelphia, 1923, 75, 261-270; Chem. Soc. Abstr. 1923, 124, ii. 646).

VEGETABLE BUTTER v. **BASSIA OILS**; also **OILS, FIXED, AND FATS**.

VEGETABLE ETHIOPS. A form of charcoal obtained by the incineration of *Fuci*.

VEGETABLE FATS v. **OILS, FIXED, AND FATS**.

VEGETABLE IVORY. The fruit of *Phytelephas macrocarpa* (Ruiz. and Pav.) found in Colombia, South America.

VEGETABLE PARCHMENT v. *Parchment paper*, art. **CELLULOSE**.

VEGETABLE SPERMACEYL. *Insect wax*, v. **WAXES**.

VELOCITY OF REACTION v. **CHEMICAL AFFINITY**.

VELLOSINE v. **PERIBO BARK**.

VENETIAN CHALK v. **STREATITE**.

VENETIAN LAKE. *Crimson lake* v. **PREMENTS**.

VENETIAN RED. Ferric oxide.

VENETIAN WHITE. A white lead pigment containing a large percentage of barium sulphate.

VENTILAGO MADRASPATANA (Gerten.) is a large climbing shrub belonging to the order *Rhamnaceae*, the root-bark of which furnishes a dyestuff much valued in Southern India. It is very common in the Western Peninsula from the Konkan southwards, as well as in Ceylon and Burma, and, according to Lostard, it is collected in Mysore at certain periods of the year and exported to other districts of India.

The following are a few of its vernacular names: pitti (*Hindi*); raktapita (*Bengali*); pappili-chakka, surralpattai (*Tamil*); popli-chukai (*Kan*); lokandi, kanwai (*Bomb*).

The root-bark appears as dark purplish-brown scales, ribbons, or filaments, the dust from which, when it is ground to powder, irritates the throat in a marked manner. When treated with boiling water or alcohol it gives a red solution, which on addition of caustic alkali, changes to a deep crimson.

Perkin and Hummel (Chem. Soc. Trans. 1894, 65, 923), who examined this dyestuff, extracted the root-bark with carbon disulphide, and obtained in this manner a resinous colouring matter, *ventilagin*, together with the crystalline non-tinctorial substances described below.

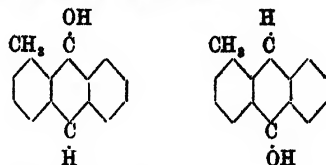
Ventilagin $C_{11}H_{14}O_4$ consists of a reddish-brown brittle resin which, when distilled with zinc-dust, gives *a*-methyl-anthracene, and when treated with zinc-dust in alkaline solution behaves as a derivative of *methyl-anthraquinone*. Dilute alkalis dissolve it with a purple-violet coloration, and the corresponding salts are obtained as violet precipitates on adding sodium or potassium chlorides to these solutions. According to Perkin and Hummel, ventilagin is possibly allied to alkanannin $C_{13}H_{14}O_4$, the colouring matter of alkanet, *Anchusa tinctoria* (Lam.), and may differ from this merely by the possession of two additional hydroxyl groups.

Emodin monomethyl ether $C_{15}H_{12}O_5$, m.p. 200°, consists of orange-red needles, and is identical with that subsequently isolated from the root of the *Polygonum cuspidatum* (Sieb. and Zucc.) (Perkin, Chem. Soc. Trans. 1895, 67, 1064). A similar, if not identical, substance was isolated by Schwabe (Arch. Pharm. 1888, 26, 569), and by Thorpe and Miller (Chem. Soc. Trans. 1892, 64, 6) from the bark of the *Rhamnus frangula* (Linn.), and it is also present in rhubarb and the *Rumex ecklonianus* (Lc.) and Goa powder.

Trihydroxy-a-methyl-anthranol monomethyl ether (A), $C_{15}H_{12}O_6$, colourless needles, decomposes about 260° before melting, and is soluble in alkaline solutions with a yellowish-brown coloration. On gentle oxidation with chromic acid it is converted into emodin methyl ether, m.p. 300° (Lc.), and the same reaction takes place when its alkaline solution is oxidised with hydrogen peroxide. It closely resembles the dehydro-emodin-anthranol monomethyl ether, subsequently isolated from Goa powder by Tatin and Clewer (Chem. Soc. Trans. 1912, 101, 280).

Trihydroxy-a-methylanthranol monomethyl ether (B), $C_{15}H_{12}O_6$, pale yellow needles, m.p. 173°, when oxidised with chromic acid is also

converted into the emodin methyl ether, m.p. 200°. As two methyl anthranols are capable of existence, the isomerism of these compounds may possibly be thus explained:—



Substance $C_{15}H_{12}O_5$, orange-red crystalline powder, m.p. 275°–280°, is soluble in alkaline solutions with an orange-red coloration, and when heated with zinc-dust gives a hydrocarbon which resembles *a*-methyl-anthracene.

Substance $C_{17}H_{12}O_5$? is a chocolate, crystalline powder, soluble in dilute alkali with a yellow coloration, and this solution, on exposure to air, deposits a blue amorphous precipitate.

Dyeing Properties.—On striped printed calico the root-bark gives with alumina mordant a claret-red, not unlike that of alizarin bordeaux; with iron mordant a greyish-lilac, which in strong colours approaches a black; and with a mixture of the two a very purplish dark chocolate. The colours are moderately fast to soap, although considerably behind the alizarin colours in this respect. On oil-prepared calico ventilago gives with alumina mordant a rich claret-brown, with chromium mordant a very black-purple, and with iron mordant a good purplish-black shade. On wool chromium mordant gives a good purplish-brown, alumina a bordeaux red, tin a brighter red similar to an alizarin red, and iron mordant gives dark dull purple and black. On silk similar colours are produced. No difficulty is experienced in dyeing with ventilago, and no additions to the dye-bath are necessary, except in the case of wool, with which it is desirable to add calcium acetate in order to correct the strong acidity of the mordanted fibre. Owing to the slight solubility of the colouring matter in water, the dyeing does not commence until the temperature reaches 70°–80°. The root-bark appears to contain from 8–10 p.c. of ventilagin.

A. G. P.

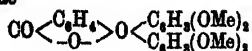
VERATRALBINE, VERATRIDINE, VERATRINE v. CEVADINE.

VERATROLE (*o*-dimethoxybenzene)



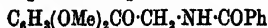
is best obtained by dissolving catechol (100 grms.) in methyl alcohol (200 grms.) mixed with 75 grms. of methyl sulphate. The mixture is cooled to –5°, and 150 grms. of potash dissolved in 350 grms. of water are then added all at once. In 3 mins. the methylation is complete. The product is diluted with water, extracted with ether, and the extract is dried and distilled (Perkin and Weizmann, Chem. Soc. Trans. 1906, 1856). Veratrole is also formed by the distillation of guaiacol with lead oxide (Fischer and Silberbach, Ber. 1904, 37, 2149). Veratrole forms a crystalline mass, m.p. 15°, b.p. 205°. It yields a number of halogen derivatives (Cousin, Compt. rend. 1898, 127, 759; 1902, 135, 987; Ann. Chim. 1898, [vi] 13, 483); also nitro derivatives (Cousin, Compt. rend. 1902, 134, 290; 135,

967; Salway, Chem. Soc. Trans. 1909, 1163), a *phthalide*



(Perkin and Weizmann, l.c.) and other compounds (Kropp and Decker, Ber. 1909, 42, 1184).

Veratrole reacts with hippuryl chloride in presence of aluminium chloride, forming a crystalline product, m.p. 155°



from which valuable therapeutic products are said to be obtained (D. R. P. 185596; Frdl. 1905-1907, 1184).

For other literature, see Simonsen, Chem. Soc. Trans. 1917, 111, 69, 220; 1918, 22, 782; Jones and Robinson, *ibid.* 1917, 111, 903.

VERBENALIN. A crystalline glucoside found in *Verbena officinalis* (Linn.), m.p. 181.5°; $\alpha_D = -180.3^\circ$. Hydrolysed by emulsin, yielding dextrose (Bourdier, J. Pharm. Chim. 1908, 27, 49, 101).

VERDIGRIS, VERT-DE-GRIS, VERT DE MONTPELIER. Basic acetates of copper v. ACETIC ACID.

VERDITE. An ornamental stone of a rich green colour consisting mainly of hydrated magnesium silicate coloured by chromium. It represents a serpentine rock more or less completely altered to talc. The chromium is probably present as the chrome-mica fuchsite, which was no doubt derived from chromite. The rock shows mottlings of yellowish-green and bluish-green with splashes of brown and yellow, and it takes a high polish. Sp.gr. 2.8; H. 3½. It occurs in the Jamestown series (Swaziland system) of chloritic and talcose schists; and is obtained from small quarries at several places on the banks of the Kaap and North Kaap rivers near Barberton in the Transvaal, and more particularly at the Verdite mines at Jamestown near Barberton, which are worked for talc with gold as a by-product (A. L. Hall, The Geology of the Barberton Gold Mining District, Union of South Africa, Geol. Survey, 1918, Mem. No. 9). L. J. S.

VERDITER, GREEN AND BLUE, v. COPPER.

VERIDIAN. Guignet's green v. CHROMIUM.

VERJUICE. A kind of vinegar containing malic acid made from the juice of the crab-apple.

VERMILION v. MERCURY.

VERMILIONETTE. A red pigment made by adding eosin to white lead, barium sulphate or zinc white.

VERNINE $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_5\cdot 2\text{H}_2\text{O}$ found by Schulze (Zeitsch. physiol. Chem. 1885, 9, 420) in seedlings of *Vicia sativa*, and later in a number of other plants. Is identical with *guanosine*, obtained by Levene and Jacobs (Ber. 1909, 42, 2469) by the hydrolysis with water of guanylic acid. M.p. 237°, $[\alpha]_D^{20} = -60.52^\circ$ in alkaline solution. It is hydrolysed by acids to guanine and a pentose, presumably *d*-ribose (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 70, 143).

From the green leaves and berries of the coffee tree a pentoside has been isolated, containing guanine, which is probably identical with *guanosine* obtained by Schulze and Trier from other plants and from 'nucleic acid' by Levene and Jacobs. It is suggested that the

caffeine in the leaves and berries of the coffee tree is derived from *guanosine*, the latter being converted successively into *guanine*, *xanthine*, and *caffeine* by the action of enzymes (T. de A. Camargo, J. Biol. Chem. 1924, 58, 831; J. Soc. Chem. Ind. 1924, 43, B. 312), v. **ESGOT**.

G. B.

VERONAL. Trade name for diethylmalonyl-urea ($\text{C}_2\text{H}_5\text{O}_2\text{C}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$), prepared by the condensation of urea and diethyl-malonyl chloride. A white crystalline powder of bitter taste, m.p. 191°. Soluble in water, ether, acetone, acetic ester. Used as a soporific (v. **SYNTHETIC DRUGS AND PYRIMIDINES**). For the chemical detection of veronal poisoning, v. Macadie, Pharm. J. 1913, 90, 134; Richards, Analyst, 1919, 44, 192; van Itallie and van der Veen, Pharm. Weekblad, 1919, 56, 1142; J. Pharm. Chim. 1919, [vii.] 20, 337. Veronal and the malonylureas generally readily condense with xanthidrol to form crystalline dioxanthyl derivatives which may be used for the characterisation and identification of the malonylureas by observation of their melting-points (Fabre, J. Pharm. Chim. 1922, 26, 241). The veronal derivative melts at 245°-246°. Thus, if a solution of 1 gm. of veronal and 2 grms. of xanthidrol in acetic acid is boiled for a few seconds and cooled a crystalline precipitate of a dioxanthylated derivative is formed which can be purified by washing with boiling alcohol and its melting-point determined. In toxicological investigation the veronal has first to be isolated from the viscera. From 100 to 150 grms. of material are digested on a water-bath for 3 hours with a mixture of 95 p.c. alcohol and 5 grms. of tartaric acid, cooled, filtered and concentrated by distillation. The residue is dissolved in 50 c.c. of distilled water, and after being made slightly alkaline, the solution is shaken up several times with ether to eliminate fatty matter. After acidulation with dilute sulphuric acid the liquid is evaporated, and the residue taken up three times with ether which dissolves the veronal. The residue from the extract is purified by dissolving it in water, heating with animal charcoal, filtering and crystallising the filtrate. After several crystallisations the melting-point can be determined. The search for these hypnotic compounds may also be made in the urine, since 60 to 65 p.c. of the veronal absorbed can be found in the urine excreted during the four following days (Analyst, 1922, 47, 523).

VEROPYRIN. Trade name for a mixture of ethylmorphine hydrochloride, veronal-sodium and calcium acetylsalicylate.

VERT DE GUIGNET v. CHROMIUM.

VERVAIN. Cymylacetic aldehyde (1-isopropyl-4-ethanalbenzene



possesses a strong odour resembling vervain, but not of such delicacy as that of the plant. As it may be easily and economically prepared, it is anticipated that it will be extensively used in synthetic perfumery. It is obtained by condensing magnesium cymyl chloride with ethyl orthoformate, hydrolysing the product with dilute sulphuric acid, and separating the aldehyde by means of its bisulphite compound. It is a pale yellow liquid, b.p. 245°C. (L. Bert.

Comptes rend. 1923, 177, 550-551; J. Soc. Chem. Ind. 1923, 42, 1099 A).

VESALVINE. Syn. for hexamethylenetetramine.

VESIPIRIN. Trade name for phenyl acetosalicylate, v. SALICYLIC ACID and SYNTHETIC DRUGS.

VESTORIEN v. EGYPTIAN BLUE; also ENAMELS.

VESUVIANITE or **IDOCRASE.** A mineral consisting of a complex silicate of calcium and aluminium, together with iron, magnesium, water, fluorine, boron, &c. F. W. Clarke's formula is $R'_4Al_2Ca_2Si_4O_{24}$, where $R'_4 = Ca_2, (AlOH)_2, H_2$, &c. Crystals are tetragonal and usually green or brown in colour; sp.gr. 3.35-3.45; H. 6½. The mineral is of common occurrence in contact-metamorphic rocks, particularly crystalline limestones. Lustrous, brown crystals are common at Monte Somma, Vesuvius (hence the name vesuvianite). Green crystals from Ala in Piedmont are cut as gems at Turin. A compact, massive variety has been found abundantly as blocks and boulders, measuring up to 6 by 3 ft., at several places in California (Siskiyou, Butte, Fresno, and Tulare counties). This has been called *californite* (G. F. Kunz, 1903), and is much used as a gemstone and for larger ornamental objects. It is somewhat translucent, takes a high polish, and ranges from bright green to yellowish-green and white in colour, thus closely resembling jade in appearance (D. B. Sterrett, Min. Res. U.S. Geol. Survey, annual reports for 1909 and 1910.)

L. J. S.

VICINE $C_{10}H_{16}O_4N_4H_2O$ was discovered by Ritthausen (J. pr. Chem. 1870, [ii.] 1, 336; 1873, [ii.] 7, 374; 1881, [ii.] 24, 202) in the seeds of *Vicia* spp. According to Levene (J. Biol. Chem. 1914, 18, 305; Levene and Senior, *ibid.* 1916, 25, 607) it is a mononucleoside, or glucoside of 2:5-diaminotetrahydropyrimid-4:6-dione (2:5-diamino-uracil) of the following constitution:



It forms needles, m.p. 242°, $[\alpha]_D^{25} -11.7^\circ$. It is hydrolysed by 20 p.c. sulphuric acid at 100° to dextrose and *divicine* (of Ritthausen) = 2:5-diamino-uracil $C_4H_4O_2N_4$. Compare also Johnson, J. Amer. Chem. Soc. 1914, 36, 337; Johnson and Johns, *ibid.* 1914, 36, 545; Fischer, Ber. 1914, 47, 2611; Winterstein, Zeitsch. physiol. Chem. 1919, 105, 258.

Convicine $C_{16}H_{14}O_4N_4H_2O(?)$ was also found by Ritthausen in vetch seeds and yields on hydrolysis alloxantin, ammonia and a hexose.

G. B.

VIGANIN v. GLUCOSIDES.

VIGANOSE v. CARBOHYDRATES.

VICTORIA YELLOW. *Gold yellow, Aniline orange, Saffron surrogate.* This colouring matter, introduced by Mottenswei, under the name of *Victoria yellow* or *aniline orange* (Wag. Jour. 1869, 583), consists of the potassium or ammonium salt of a dinitrocresol (Martius and Wichelhaus, Ber. 2, 206; v. Sommaruga, *ibid.* 2, 579). It is prepared by heating cresol, with three times its weight of sulphuric acid at 100°, until the product is soluble in water. After removing the excess of sulphuric acid by

means of barium carbonate, the cresol-sulphonic acid is converted into potassium salt, which in the dry state is nitrated by introducing it rapidly into about three times its weight of dilute nitric acid (sp.gr.=1.2), and is then poured into water, neutralised with potassium carbonate, and the resulting potassium dinitrocresol crystallised out. Obtained in this way, the colouring matter is a mixture of the potassium salts of dinitro-*o*- and dinitro-*p*-cresol, and varies in colour according to the proportions of these. Thus Victoria yellow is yellowish in colour, and consists chiefly of the potassium salt of dinitro-*o*-cresol (m.p.=86°), which crystallises in yellow needles (Wichelhaus, *ibid.* 7, 176; Piccard, *ibid.* 8, 685), whereas saffron surrogate is distinctly reddish in colour, and consists chiefly (80 p.c. according to Piccard) of the potassium salt of dinitro-*p*-cresol (m.p.=84°), which crystallises in red needles (Armstrong and Field, Chem. News, 27, 318; Hofmann and v. Miller, Ber. 14, 567; Staedel, *ibid.* 14, 900, 906; Nölting and Salis, *ibid.* 14, 986).

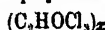
Victoria yellow is soluble in water and dyes wool and silk orange, but owing to the fugitive nature of the colour is no longer employed for this purpose. Saffron surrogate is still used to some extent as a colouring matter for butter, margarine, vermicelli, cheese, &c. (Piccard), but this is to be deprecated, since Weyl's experiments show that the compound is poisonous (Ber. 20, 2835; 21, 512). Cf. NITROPHENOLS AND THEIR HOMOLOGUES.

VIENNA BLUE. Cobalt blue v. PIGMENTS.

VIENNA GREEN. Emerald green v. PIGMENTS.

VIENNA PASTE. A mixture of lime and potash used as a caustic to extirpate malignant growths.

VIFERRAL. A polymerised chloral



A white powder, m.p. 153°-155°, sol. in water. Used as a hypnotic.

VIMOPYRIN. Trade name for *p*-phenetidine tartrate.

VINASSE v. SUGAR.

VINE BLACK. Blue black v. PIGMENTS.

VINEGAR, AROMATIC, v. ACETIC ACID.

VINEGAR PLANT. v. ACETIC ACID; FERMENTATION.

VINOLINE. A mixture of coal-tar reds, mostly rosaniline salts, used for colouring wines.

VINOPYRIN v. SYNTHETIC DRUGS.

VIOFORM. Trade name for iodochloro-hydroxyquinoline. A greyish-green powder used as a bactericide and antiseptic, and as a substitute for iodoform (v. SYNTHETIC DRUGS).

VIOLANE. A variety of the pyroxene (q.v.) group of minerals of a rich violet colour, and occasionally used as an ornamental stone. It is a silicate of calcium, magnesium, aluminium, sodium, iron, and manganese (about 2 p.c. MnO, to which the colour is due). It sometimes forms prismatic crystals of the monoclinic system, but more often compact masses with a lamellar or fibrous structure. It is found, together with other silicates coloured by manganese, in the manganese mines at San Marcel in the Aosta valley, Piedmont. L. J. S.

VIOLANIN v. ANTHROCYANINS.

VIOLANTHRENE v. INDANTHRENE.

VIOLET DE PARIS or VIOLET DIRECT.
Methyl violet v. TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET 5B, 6B, v. TRIPHENYLMETHANE COLOURING MATTERS.

VIOLET R and RR and 5R. *Hofmann's violet v. TRIPHENYLMETHANE COLOURING MATTERS.*

VIOLIN. An emetic substance contained in the common violet, supposed to be identical with emetine from ipecacuanha root.

VIOLINE or VIOLEIN. A synonym for mauve or aniline purple.

VIOLONES. Coloured anhydro-bases obtained by acting upon pyrylium salts with *p*-hydroxylated phenyl radicals by weak alkalis Dilthey and Burger, Ber. 1921, 54 [B], 825).

VIOLURIC ACID v. PYRIMIDINES.

VIRIDIAN. Hydrated chromium sesquioxide, v. CHROMIUM.

VIRIDINIC ACID v. TANNINS.

VIRIDITE v. THURINGITE.

VISCOSE v. SILK, ARTIFICIAL.

VITAMINS. To deal seriously from a standpoint strictly chemical with substances which have never been isolated in a pure condition is, of course, impossible. The constitution of the peculiar dietary constituents which have been called Accessory Food Factors (Hopkins), or Vitamines (Funk) is as yet entirely unknown. They are not, however, merely hypothetical substances. The evidence for their objective existence is ample enough, but as this evidence is in part, so to speak, of a negative kind, and in any case depends upon studies in which impure preparations have been perforce employed, it calls for critical consideration. The fundamental facts which make necessary a belief in the existence and physiological importance of nutrients differing in kind from those which until lately were alone recognised, can, however, be quite briefly enumerated.

Until fifteen years ago it was generally believed that the efficacy of a diet could be determined by three essential criteria. The first was the obvious one that it should provide enough potential energy for the current dynamic needs of the body. The second was that it should contain a certain minimum of protein, to exercise specific functions which the non-nitrogenous foodstuffs cannot subserve, and the third called for a balanced mineral supply. We now know that these criteria are insufficient. Although data from highly quantitative studies of human and animal nutrition have long existed in great numbers, these data were obtained during the administration of natural food materials. The fats, carbohydrates and proteins contained in these diets were accurately calculated and the effects of their variation evaluated; but that these constituents (with the necessary minerals) were alone responsible for the successful maintenance of the body was an unjustifiable assumption. Quantitatively they account for nearly the whole of the necessary supply, but hundreds of recent experiments and observations have shown that there are other substances in natural foods which, though present in only very small quantities, are yet absolutely essential for proper nutrition. These are the substances which,

pending a knowledge of their nature, it is agreed to call vitamins.

The assumption mentioned in the last paragraph was unjustified, because the food constituents which were thought to cover all needs were never administered in a pure form. It can be shown with the greatest ease that if an animal be supplied with purified protein and pure fats and carbohydrates, together with a salt mixture proved in other associations to be efficient, the food may be well eaten, well digested, and even fully metabolised, yet the animal's nutrition fails, and it finally dies. What, however, endows the phenomena we are considering with their fullest significance is the circumstance that the purified foodstuffs just mentioned become wholly efficient and fully maintain growth, health and activity when material is added to them in amounts so small compared with the whole quantity of food consumed that it would seem almost negligible. This material must comprise at least three and probably more vitamins. The extraordinary importance of their nutritional effects and the remarkably small concentration in which these effects are produced are the characteristics which supply the only definition of vitamins at present available.

While, during the first decade of the present century, the facts just mentioned were being established by feeding experiments done mainly upon animals, evidence giving precisely similar indications arose from a new and enlightened study of certain human diseases. It was almost a pure coincidence that these two lines of evidence should have become available contemporaneously. Clear indications showing that the disease, Beri Beri, which mainly—though by no means exclusively—attacks rice-eating populations, is intimately related to diet, was indeed brought forward by Eijkman so far back as 1897. He showed that a condition very similar to the human malady could be induced in fowls by feeding them upon an exclusive diet of polished white rice, while a cure was at once established by adding rice polishings to the diet, or by replacing the polished grain by whole grain. The suggestion given by these experiments was followed up and observations made upon a great number of prisoners in the gaols of Java, and the fact established that Beri Beri is far more frequent among these eating rice deprived of the grain cortex than among those receiving the whole grain. This work was fully confirmed by that of W. Fletcher, published in 1907-8 (Lancet, 1907, 1776). The time was not even then ripe, however, for the simple interpretation of the facts. Only when later studies were published, and in particular those of Frazer and Stanton (Studies from the Inst. for Med. Research, Federated Malay States, No. 12, 1911) did the clear conception arise that the cortex of rice grain, unlike the endosperm, contains a specific substance of unknown nature, but certainly essential to life. It can be supplied in many other foodstuffs besides cereals, but the circumstance that it has a local distribution in grains, together with the one-sided character of Eastern dietaries, conspired to bring the facts to light. The disease scurvy yields even clearer evidence that healthy nutrition calls for a supply of a substance, or substances, not comprised in the ordinary categories of foodstuffs. Its

incidence and cure might, it would seem, have led long ago to a conception of what we should now call a vitamin. Preconceptions and prejudices led, however, to other explanations of the disease. Ultimately, however, though not until about 1912, the convergence of the pathological evidence and that obtained from feeding experiments led to a somewhat sudden emergence of the belief that nutrients must exist with the potent qualities now attributed to vitamins.

Though all attempts to isolate the substances with which we are concerned have so far failed, preparations have been made in a highly concentrated form, and work which, in a limited sense at least, is quantitative, has been done upon them. Certain of the properties of the vitamins are well characterised in a chemical sense, and there is every reason to believe that they will ultimately be isolated. It is as yet impossible, as already admitted, to define them except in terms of their physiological properties. They arise during the growth of the plant. For the animal they are essential, indispensable nutrients. There is clear evidence that at least three distinct members of the class exist and strong suggestions for the existence of a fourth. Each has its own peculiar influence in the body. While we are ignorant of their nature any scheme of nomenclature must be unsatisfactory. It is best to use names without special connotations, and to speak simply of the A-, B- and C-vitamins, respectively, is a justifiable custom.

The B-Vitamin.—Although this substance has received as a prefix the second letter of the alphabet, it will be convenient to deal with it first. It is the so-called 'water soluble vitamin,' or anti-neuritic factor. If it be absent from the diet, a young animal fails to grow, and soon, like the adult animal, develops symptoms which depend upon the occurrence of degenerative changes in the nervous system. In the human individual these symptoms in their more extreme form constitute the picture of Beri Beri. The substance, as its earliest name betokens, is freely soluble in water. It is also soluble in 80 p.c. alcohol, though much less so, if at all, in absolute alcohol. Acidified methyl alcohol extracts it from many tissues containing it. Insoluble in other ordinary organic solvents, it shows a rather remarkable solubility in oleic acid or olive oil (Myers and Voegtlin, *Proc. Nat. Acad. of Sc.* 1920, 6, 3). It is precipitated from aqueous solution by precipitants which throw down organic bases: phosphotungstic acid, for instance, or silver nitrate plus barium hydroxide. This behaviour, together with the fact that very active preparations obtained by the use of these precipitants contained nitrogen, led Funk to believe that the active substance was a base, and, in consequence, he suggested the name *vitamine*, which is now attached to all members of the class. Such precipitation may not be specific, however, but may be due to adsorption. The substance is freely adsorbed, for instance, by fuller's earth, and may be concentrated by its use. This property also allows of its separation from other vitamins (Harden). A silver compound has been prepared with high physiological potency (Seidell, *Pub. Health Reports*, Washington, 1921). The B-vitamin is a relatively stable substance, showing considerable

resistance to destruction by heat. It also resists the effects of acids, but is much more sensitive to alkalis (McCollum and Simmonds, *J. Biol. Chem.* 1918, 33, 55; Daniels and McClurg, *ibid.* 1919, 37, 201). Several attempts to isolate it have been described. Funk obtained, from extracts of rice polishings and yeast, crystalline products capable of curing birds suffering from polyneuritis due to feeding exclusively upon polished rice (*J. Phys. Chem.* 1913, 46, 173). Such results proved, indeed, the potency of almost infinitesimal quantities of the active substance, but unfortunately did not lead to its isolation. Funk believed at first that he had proved it to be a pyrimidine derivative, but when his crystalline preparations were fully purified they were found to be inactive and to consist largely of nicotinic acid, which itself is certainly without the characteristic activity. The purine base adenine has been stated to possess the properties of this vitamin, the remarkable statement being made that this base exists in two forms—one a physiologically active form, which by molecular rearrangement may pass over into a second and inactive form. Certain synthetic α -hydroxy-pyridines have been said to have similar properties (Williams, *J. Biol. Chem.* 1916, 25, 437; Williams and Seidell, *ibid.* 26, 431). These statements have been controverted, however (Harden and Zilva, *Bio-Chem. J.* 1917, 11, 172; Voegtlin and White, *J. of Pharm. and exp. Ther.* 1916, 9, 155). It must be admitted that all attempts to isolate the vitamin or to relate it to known substances have hitherto failed.

The B-vitamin is widely distributed in the tissues of plants, and is stored, though in low concentration, in many animal tissues. In the yeast cell it is especially abundant. As already pointed out, in the grains of cereals it has a local distribution, being present in the germ and pericarp, but not in the endosperm. The relative amounts present in various natural foods have been ascertained by determining on standard lines the minimum quantity of each food which is capable of preventing or curing polyneuritis in birds. The available data will be found in the Report upon Vitamins issued by the Medical Research Council. Such experiments consume much time. Endeavours to use its supposed effects upon the rate of growth of yeast as a measure of its amount have on the whole proved disappointing (*cf.* Funk and Dubin, *J. Biol. Chem.* 1920, 44, 487; McDonald and McCollum, *ibid.* 1921, 46, 525). No chemical means for its estimation are yet available.

Vitamin C.—This is the antiscorbutic substance which, while present in most uncooked foods, is found in exceptionally high concentration in certain fruits and in other vegetable tissues. The very fact that it is an unstable substance—easily destroyed by heat at temperatures not exceptionally high, prone to oxidation, and possibly destroyed under the influence of catalysts present in the tissues themselves—has been in itself the direct cause of much human suffering. Scurvy follows almost automatically when the substance is absent from the diet, and is often a devastating disease in communities cut off from a supply of fresh foods. The tentative efforts which have so far been made to

isolate the antiscorbutic agent, though without success, have served the useful purpose of making it clear that there is a definite substance to look for. We have not to deal with some vague 'property' of fresh foods, nor, as has been thought, with the influence of known constituents such as citrates, malates, or inorganic potassium salts. Because of its great importance to the body and the low concentration in which it is efficient the anti-scorbutic substance must certainly be recognised as a vitamin.

In the endeavour to study its distribution among foodstuffs, and the rate of its destruction by this or that agency, physiological methods have hitherto been perforce employed. For an account of methods whereby highly concentrated preparations of this vitamin are obtained and its main properties demonstrated the papers of Zilva should be consulted (*Bio-Chem. J. passim*). The discovery of even a purely empirical chemical method for estimating the vitamin would certainly be of the utmost practical importance. Determinations of its relative concentrations have been made by observing for each kind of material under study the minimal curative or preventative dose for scurvy in the guinea-pig. This animal reacts in a highly characteristic way when it is deprived of the factor in question, and also when after deprivation a supply is again provided (Axel Holst). Elaborate and careful experiments have been made on these lines (Chick and Hume, 1917, *et al.*). The vitamin is absent from dry cereal foods and from pulses, but appears suddenly in grains, beans, &c., during even the earlier stages of germination. It is present in all fresh vegetables though in varying concentrations. It is usually destroyed when these are dried, though it is stated that very rapid sun drying (an industry in Beluchistan) leaves it largely intact. Its concentration in fruits varies considerably. Those of the genus *Citrus* contain it in relatively large amount—as the long established empirical treatment of scurvy with lime juice would itself suggest. The fact that the concentration differs, however, in the juices of different varieties of citrus has affected the history of anti-scorbutic treatment. On several occasions in the past, and even during the war, 'lime juice' has appeared to fail and faith in its efficacy has consequently wavered. This occurred long ago when in the British Navy the juice of the West Indian lime was substituted for the lemon juice previously used. The explanation came when it was shown that the first-mentioned juice contained no more than one-fourth of the active substance present in the latter. Orange juice, on the other hand, contains about the same proportion as lemon juice (Chick, Hume and Skelton, *Biochem. J.* 12, 131; Davey, *ibid.* 1921, 15, 83). Orange juice retains its activity when wholly freed from its colloids and from citric acid and calcium (Harden and Zilva, *Bio-Chem. J.* 1918, 12, 259; McClendon, *J. Biol. Chem.* 1921, 46, ix). Orange or lemon juice evaporated to a syrup under reduced pressure at 40°C. or concentrated by rapid methods at higher temperatures, retains its activity (Harden and Robison, *Bio-Chem. J.* 1920, 14, 171). The condition of the vitamin in the tomato is apparently such as to make it exceptionally stable. In all cases a slightly acid reaction in the material makes

for stability. Fresh tomato juice, for instance, boiled for one hour lost 50 p.c. of its activity; boiled for four hours it lost 70 p.c. When the juice was first made slightly alkaline, boiling destroyed it much faster (La Mer, Campbell and Sherman, *Proc. Soc. exp. Biol. and Med.* 1921, 18, 122). In the case of vegetables (cabbage) heating for twenty minutes at 100°C. may destroy 70 p.c. of the anti-scorbutic power (Delf, *Bio-Chem. J.* 1918, 12, 416). Oxidation plays a part in the destruction of this vitamin (Zilva, *Lancet*, 1921, i, 478; Anderson and others, *Science*, 1921, 53, 446). It would seem to be especially rapid in the case of some tissues. Fresh potato has marked anti-scorbutic power, but the juice, unless made acid, quickly loses it even at ordinary temperatures (Berzsonoff, *Compt. rend.* 1921, 173, 417). The anti-scorbutic value of milk, even when fresh, is relatively low, important as the function must be to the infant. The actual concentration of this vitamin (and, indeed, of the other vitamins in cows' milk) depends, however, upon the nature of the food supplied to the cow (Hess and others, *Proc. Soc. exp. Biol. and Med.* 1920, 18, 39; Drummond and others, *Bio-Chem. J.* 1921, 15, 540). The vitamin is largely destroyed by Pasteurisation, and it is becoming well recognised that infants receiving heated milk should be given a ration of fruit juice.

Vitamin A.—The 'Fat soluble' accessory factor. If animals be fed on a synthetic dietary such as that earlier described there may be complete failure of nutrition, even when Vitamins B and C are duly supplied, unless at the same time regard is paid to the nature of the fat comprised in the diet. Most vegetable fats, whether purified or not, prove unable to support nutrition in the circumstances mentioned, while most animal fats are found to be efficient, though in varying degrees. This is of course not due to any differences in the fats as fats. As a source of energy for the animal one type of fat differs but little from any other type. The difference, as abundant evidence proves, is due to the fact that associated with animal fats and not (at least as they appear on the market) with vegetable fats, is a specific substance, not itself a fat or other ester, which is essential to life. While actually made by the plant and present for instance in relative abundance in green leaves, it for some reason does not accompany vegetable oils when those are expressed from plant tissues. When, on the other hand, it is eaten by the animal in its food the substance tends to accumulate in its fatty tissues. It is stored in exceptionally large relative amounts in the livers of fish, but takes its origin from the marine vegetable organisms on which the fish feeds (Hjort, *Proc. Roy. Soc.* 1922, B). As in the case of other vitamins, its relative distribution has been in the main studied by means of standardised feeding experiments, but evidence is accumulating to show that its concentration in a fat is measured by the intensity of a colour reaction produced on the addition of arsenic chloride and certain other reagents (Rosenheim and Drummond, *Bio-Chem. J.* 1925, 19, 753). It is soluble in alcohol, ether, and benzene, and may be extracted, for example, from green leaves by these solvents. The vitamin is stable towards heat, and highly

resistant to the processes involved in saponification. It appears therefore greatly concentrated in the unsaponifiable residue from any fat which contains it. On the other hand, it is easily oxidised, and loses all activity when a fat or oil containing it is thoroughly aerated (Hopkins, Bio-Chem. J. 1920, 14, 725). Drummond and his co-workers have shown that when the unsaponifiable material from cod-liver oil is freed as far as possible from cholesterol and distilled in a high vacuum the active vitamin is found in fractions distilling at 184°-220° at pressures of 1 to 2 mm. (Bio-Chem. J. 1925, 19, 1047). An ethereal extract of green leaves has been prepared (Osborne and Mendel), of which a daily dose of 30 milligrammes contained enough of the vitamin (doubtless greatly diluted with other substances) to supply the needs of the rat, an animal highly sensitive to deprivation of the substance. Concentrations much greater than this have been obtained from the unsaponifiable residues of cod-liver oil prepared with avoidance of oxidation. Of one such preparation a daily dose of no more than 0.004 mgm. was sufficient to maintain a rat (Paulsen), and very small amounts of such concentrates will serve the purposes of the whole oil in therapeutic practice. The variation in animal fats is great. It has been estimated that cod-liver oil may be 250 times richer in the substance than butter (Zilva and Miura). For the influence of storage and emulsification on the vitamin A in cod-liver oil, see Drummond, Zilva and Coward (J. Soc. Chem. Ind. 1924, 43, 236 T).

The following figures have been obtained, representing the relative amount of the fat needed to supply a growing rat with its necessary supply of the vitamin. Crude cod-liver oil 2 mgms., haddock-liver oil 10 to 15 mgms., refined cod-liver oil on sale in this country 10 to 15 mgms., butter 500 mgms. (Zilva and Drummond, Lancet, 1921, ii. 753). The effects which follow upon an absence of this vitamin from the food, or a considerable deficiency in the supply, are failure of growth and maintenance, together with a specific form of degenerative changes in the eye, constituting what is known as xerophthalmia. It was for some time believed that the deposition of lime salts in growing cartilage on the lines necessary for the normal formation of bone called for a supply of vitamin A. The work of E. Mellanby has indeed shown clearly that something present in natural animal fats exerts an important influence on this process. When this substance is absent from its food a child becomes prone to develop rickets. It would seem, however, as McCollum and his co-workers were the first to suggest (J. Biol. Chem. 1922, 53, 293), that the dietary factor which prevents rickets, while usually associated with vitamin A, is not identical with it. It is a substance less readily oxidised. A fully aerated animal fat will fail to promote growth, but it may efficiently protect the young animal from rickets. It would seem that at least one other vitamin may therefore exist in addition to the three which have been discussed, and it is now usual to speak of this substance as Vitamin D. The remarkable relations between the activity of this food constituent and the effects of light

cannot be here discussed. It is probable that the list of existing vitamins is not exhausted by those discussed. Already there is evidence that a quite specific constituent in the diet is necessary for the maintenance of reproductive functions (Evans and Burr, Proc. Nat. Acad. Sc. 1925, 11, 334). F. G. H.

VITELLIN v. PROTEINS.

VITEXIN. The *Vitex littoralis* (A. Cunn.) or 'Puriri' is a large tree, 40-60 feet high, and 3-5 feet in diameter, which grows only in the northern portion of the North Island of New Zealand. The wood affords a very durable timber, and is chiefly used for house blocks, fencing posts, piles for bridges, railway sleepers, &c.

Vitexin, the main colouring matter, is present in the wood in the form of a glucoside which has not yet been isolated. It is prepared by digesting a purified extract of the dyestuff with boiling dilute hydrochloric acid, and by this means separates in the form of a yellow viscous mass. By extracting this crude product with boiling alcohol, a pale yellow crystalline powder remains undissolved, and this, owing to its sparing solubility, is most readily purified by acetylation, and the subsequent hydrolysis of the pure acetyl derivative (Perkin, Chem. Soc. Trans. 1898, 74, 1020).

Vitexin consists of minute canary-yellow prismatic or fine hair-like needles, soluble in alkaline solutions with a pale yellow coloration, and from these solutions when boiled it is deposited by acidification in a crystalline condition.

On fusion with alkali vitexin yields *phloroglucinol* and *p-hydroxybenzoic acid*, and when digested with boiling 50 p.c. potassium hydroxide solution *p-hydroxyacetophenone* is also produced. Boiling 15 p.c. nitric acid gives dinitro-*p*-hydroxybenzoic acid, together with a small quantity of *tetranitroapigenin*, m.p. 239°-241°. The formula first assigned to vitexin by Perkin was $C_{18}H_{14}O_8$, and the *acetyl derivative*, colourless prismatic needles, m.p. 251°-256°, was consequently represented as $C_{18}H_{12}O_7(C_2H_3O)_2$. In a later communication in view of its apparent relationship to apigenin, and the difficulty of accounting for the large number of hydroxyl groups which are present, it is suggested by this author (Chem. Soc. Trans. 1899, 77, 422) that vitexin is probably a very stable glucoside of apigenin represented by the formula $C_{15}H_{10}O_6$. Vitexin is a somewhat feeble colouring matter, and dyes shades similar to those given by apigenin; these, employing woollen cloth mordanted with chromium, aluminium, and tin, are respectively greenish-yellow, pale bright yellow, and pale brown.

In addition to vitexin the wood of the *Vitex littoralis* contains (as glucoside) a small quantity of a second colouring matter, *homovitexin*. It was obtained as a pale yellow powder, m.p. 245°-246°, and is distinguished from vitexin by its ready solubility in alcohol. Fused with alkali it gives *phloroglucinol* and *p-hydroxybenzoic acid*, and is possessed of feeble dyeing property. The analytical figures approximate to $C_{18}H_{14}O_8$ or $C_{18}H_{12}O_8$.

According to Barger (Chem. Soc. Trans. 1906, 89, 1120) the glucoside saponarin, which is present in *Saponaria officinalis* (Linn.), yields on hydrolysis glucose, saponaretin and a small

quantity of vitexin. It is possible that saponarin and homovitexin are identical. A. G. P.

VITRIFIABLE PIGMENTS v. POTTERY; also PORCELAIN.

VITRIOL (*vitrum*, 'glass'). An old name for a sulphate, and still frequently applied to the sulphates of certain common metals on account of their vitreous lustre, e.g. white or zinc vitriol $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; blue or copper vitriol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; green or iron vitriol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; red or cobalt vitriol $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. Basic ferric or ferroso-cupric sulphates obtained in the extraction of copper sulphate from ferruginous minerals are known as Admont, Bayreuth, Salzburg vitriols, &c.

VITRIOL, OIL OF. *Vitriolic acid*. Sulphuric acid (*q.v.*).

VITRIOL STONE and **COLCOTHAR**. Vitriol is the material from which the so-called fuming or Bohemian sulphuric acid was formerly manufactured, and it is obtained from the rock known as vitriol slate ('Vitriolschiefer') in the following manner. Large masses of pyritous slate (which belongs to the Silurian formation, and consists of a quartzose matrix containing pyrites, carbon, and clay) are exposed to the weathering action of the atmosphere for three years. The products of oxidation so formed are ferrous sulphate and sulphuric acid, which latter acts upon the clay, yielding aluminium sulphate and other sulphates. The ferrous sulphate at first formed becomes by oxidation ferric sulphate, which, together with the aluminium sulphate, is the principal product of the weathering of the vitriol slate. Ferrous sulphate remains only in small quantities. The next operation is lixiviation of the mass with water, after which the liquor obtained is concentrated to a density of 40°B , and finally evaporated in pans until, on cooling, a crystalline cake of vitriol stone is obtained. The vitriol stone is now calcined, in order to remove the greater part of its water. The resulting product, when heated to a high temperature in clay retorts, yields sulphur trioxide; and a residue, termed *colcothar*, remains in the retorts. The composition of vitriol stone and colcothar may be seen from the following analyses:—

Vitriol stone.— Fe_2O_3 , 20.07, Al_2O_3 , 4.76, FeO 0.64, MnO traces, CaO 0.14, MgO 0.39, K_2O 0.07, Na_2O 0.05, CuO 0.10, SiO_2 0.10, P_2O_5 traces, SO_2 40.51, As traces, H_2O 32.58. Total 99.32; or combining acid oxides and bases: $\text{Fe}_2(\text{SO}_4)_3$, 50.17, $\text{Al}_2(\text{SO}_4)_3$, 11.94, FeSO_4 , 1.35, MgSO_4 , 1.17, CaSO_4 , 0.33, CuSO_4 , 0.20, K_2SO_4 , 0.13, Na_2SO_4 , 0.11, H_2SO_4 , 1.49, MnO , As , and P_2O_5 traces, SiO_2 0.10, H_2O 3.31—99.29.

Colcothar.— Fe_2O_3 , 7.62, Al_2O_3 , 12.53, MgO 3.23, CaO 0.82, SO_2 , 5.17, SiO_2 , 1.17, CuO 0.20, H_2O 1.30—99.04 (F. Stolba, B. Königl. Böhm. Gesells. 1885; J. Soc. Chem. Ind. 6, 30).

VIVIANITE. Hydrated ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, crystallised in the monoclinic system. The crystals have a perfect cleavage in one direction, parallel to the plane of symmetry; they are quite soft (H , 1½–2), sectile, and easily bent, being flexible but not elastic. Sp.gr. 2.58–2.68. Crystals from freshly opened rock

cavities are colourless, but on exposure to the air they very soon acquire a greenish-blue tinge, darkening to a characteristic deep indigo-blue. This change in colour is due to a partial oxidation of the iron, which in the black kertschenite $(\text{Fe}, \text{Mn}, \text{Mg})\text{Fe}^{++}(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, from the Kerch peninsula, Crimea, is almost complete. Vivianite is the commonest of the several iron phosphate minerals. The best crystals are found in metalliferous veins, e.g. at Wheal Jane, in Cornwall, with pyrrhotite, and at Leadville in Colorado. Crystals are also found in the interior of fossil shells, e.g. in the iron ores of the Kerch peninsula, Crimea; and also sometimes in bones and horns buried in peat deposits. More often the mineral has the form of a blue earthy powder ('blue iron-earth'), and it is in this form that phosphorus is present in bog iron-ore and other limonitic ores of iron. L. J. S.

VOLBORTHITE. Hydrated basic copper vanadate $(\text{CuOH})_2\text{VO}_4 \cdot 6\text{H}_2\text{O}$, with the copper in part replaced by calcium, barium, and magnesium. It forms olive-green or citron-yellow, pearly scales, which are often aggregated in globular forms. As a dissemination in sandstones of Permian age it occurs over a wide area in Govt. Perm in Russia.

Calciovolborthite is a mineral of very similar appearance and mode of occurrence. It contains, as a rule, rather more calcium and has no water of crystallisation; the composition approximates to the formula $\text{Cu}_2(\text{CuOH})_2(\text{VO}_4)_2$. This is found as golden-yellow or greenish-yellow pearly scales and rosettes on the surfaces of sandstone in Utah, Colorado, and Oregon, and also at Friedrichroda, near Gotha, in Thuringia. On the significance of these occurrences of vanadium and copper minerals in sandstones v. PSITTACINITE. L. J. S.

VOLCANIC GLASS v. OBSIDIAN.

VOLCANIC TUFF v. TUFF.

VOLEMITOL v. CARBOHYDRATES.

VOLUMENOMETER v. SPECIFIC GRAVITY.

VOROBYEVITE v. BERYL.

VRAIC. *Varech*. The French name for kelp, v. IODINE.

VRBAITE. Thallium sulph-arsenite and antimonite $\text{TlAs}_2\text{SbS}_5$ or $\text{Tl}_2\text{S}_2\text{As}_2\text{S}_5\text{Sb}_2\text{S}_5$, containing Tl 32.15 p.c., crystallised in the orthorhombic system. It is greyish-black with metallic lustre, but in thin splinters dark red, and the powder is light red with a yellowish tinge. Sp.gr. 5.3. The small crystals are found embedded in realgar and orpiment, at Allichar, in Macedonia. Another mineral containing thallium as an essential constituent yielded by this locality is lorandite (*q.v.*). L. J. S.

VULCANISED OILS v. OILS, FIXED, and FATS.

VULCANITE v. RUBBER. Also applied to a nitroglycerin explosive.

VULCAN POWDER v. EXPLOSIVES.

VULPIC or **VULPULIC ACID** v. LICHENS.

VULPINITE. A variety of anhydrite mixed with silica. That from Vulpino near Bergamo, known as the *Marmo Bardiglio di Bergamo*, takes a fine polish and is used for ornamental purposes.

W

WAD or **BOG-MANGANESE**. A black, earthy mineral consisting mainly of hydrated manganese dioxide, but of variable composition, barium and various other constituents being often present. Many varieties have consequently been distinguished by special names. *Asbolite* or 'earthy cobalt' is a cobaltiferous variety, and *lampadite* contains copper. The mineral may be regarded as an earthy form of psilomelane (*q.v.*); it is so soft and sooty that it soils the fingers, and is sometimes so porous that it floats on water. It has resulted from the weathering and decomposition of other manganese minerals, and is sometimes deposited from solution by springs and in swamps. It is of wide distribution and is mined at many places together with other oxides of manganese. *Asbolite* is of importance as an ore of cobalt (up to 35 p.c. CoO), as much as 5000 tons per annum having been exported from New Caledonia. L. J. S.

WALNUT HUSKS (*Brous des noix*. Fr.) are employed by the French dyers to give dun colours. The green shells contain *juglone* or *hydroxy-[α]-naphthaquinone*; *v. NAPHTHALENE*.

WALNUT OIL *v. OILS, FIXED, AND FATS*. Walnut oil is obtained from kernels of the walnut tree (*Juglans regia*), which contain from about 65 to 66 p.c. of oil. The best oil is separated by cold expression and from its pale colour is a favourite medium for white paints, and is commonly termed 'nut oil' by artists. It dries more slowly than linseed oil, but yields a more elastic film. In the bromination test it yields from 1.5 to 2 p.c. of an insoluble bromide, which appears to be that of a mixed glyceride.

An oil of similar character is obtained from the seed of the North American walnut, *Juglans niger*. This oil is termed *pecan oil*.

The fruit of *Juglans Siboldiana* gave 26.54 p.c. of kernel, which contained 4.99 p.c. of water, and gave 59.58 p.c. of oil by pressing. The oil has a light yellow colour and no odour, and has the following characters: sp.gr. 0.9332 at 15°; $n_D^{20} = 1.4800$; acid value 0.68; Hehner value 92.3; saponification value 191.1; Reichert-Meissl value 0.62; and iodine value (Hübl.) 150.8, and has the properties of a drying oil. C. A. M.

WALSRODE POWDER *v. EXPLOSIVES*.

WARAS, also called 'wars' and 'wurrus,' consists of a purplish resinous powder which covers the seed pods of *Flemingia congesta* (Roxb.), an erect woody shrub growing in the thickets and forests of the warmer parts of India. According to Watt (Dictionary of Economic Products in India, iii. 482), it is collected also in Africa in the neighbourhood of Harrar, and is sent to Arabia, chiefly to Yemen and Haddramant, where it is used as a dye, as a cosmetic, and as a specific against colds. According to Wardle, waras is distinctly inferior as a dye to kamala, which it closely resembles, and contains only a small amount of colouring matter compared with the yellow vegetable dyes of commerce. It is suitable as a dye for silk rather than for wool, but is quite useless with cotton. It has been

introduced into England from Aden as an adulterant or substitute for kamala (Flückiger and Hanbury's Pharmacographica, 1879, 576). Under the microscope waras appears as orange-brown lumps, frequently circular and closely resembling kamala.

Flemingin $C_{13}H_{12}O_4$ (provisional) is a dull orange-red crystalline powder consisting of star-shaped groups of minute prismatic needles, which melt at 171°–172°, and closely resembles the rottlerin of kamala. Solutions of the alkali hydroxides dissolve it with an orange-brown tint, but these solutions when boiled do not deposit resinous matter, as is the case with rottlerin. On fusion with alkali *salicylic acid* and acetic acid are produced.

Silk suspended in a solution of *flemingin* in dilute sodium carbonate, and the whole gradually raised to the boiling temperature, is dyed golden yellow, slightly duller than the shade given by rottlerin; but, on the other hand, *flemingin* possesses much the stronger dyeing power of the two.

In addition to *flemingin* waras contains a trace of a yellow crystalline colouring matter, *homoflemingin*, m.p. 165°–166° ($C = 69.97$; $H = 5.75$), together with some quantity of two resinous substances: (a) $C_{12}H_{12}O_3$ (?), m.p. 162°–167°, and (b) $C_{13}H_{14}O_3$ (?), melting below 100°. Fused with alkali these latter gave *salicylic* and *acetic acids*, and appear to be allied to *flemingin*.

Added to a boiling solution of its own weight of sodium carbonate, waras dyes silk golden yellow shades, which are brightened by rinsing in very dilute acetic acid. Contrary to the statement of Wardle, it is to be regarded as a decidedly superior dyestuff to kamala (Perkin, Chem. Soc. Trans. 1898, 73, 659). A. G. P.

WASH. The name given to the fermented wort of the distiller.

WATER.

ITS PHYSICAL AND CHEMICAL PROPERTIES.

Purification.—Because of its solvent action on solids and gases, water is difficult to purify and still more difficult to keep in a pure state. It may be partially freed from dissolved salts by freezing, the ice separating from any unsaturated salt solution containing only the small quantity of the dissolved salt present in the mother liquor included in the ice crystals. The ice separating from, say, sea-water, is fairly free from saline matter. It is not known whether this method of purification eliminates, partially or completely, dissolved gaseous impurities. The method is relatively troublesome and costly, and has not been practically applied.

Water is commonly purified by distillation under atmospheric pressure. When adequate arrangements are made to prevent carrying over of entrained droplets of water formed upon the bursting of steam bubbles, the condensed steam contains only the solid and gaseous impurities it dissolves after condensation. Assuming dust to be excluded, the non-volatile impurities in the distillate will be confined to such traces of

lime, silica, alkalis, tin oxide, etc., as may be derived from condensers and containers, and the volatile impurities, which generally are much the more serious in amount and effect, will comprise volatile organic matter, ammonia, carbon dioxide, oxygen, nitrogen, and the like, originally contained in the raw water and carried over with the steam or dissolved from the atmosphere with which the condensate is in contact.

The proportion of non-volatile impurities may be reduced to insignificance by using suitable material for condensers and containers. Hot, newly condensed water has a much greater solvent action than when cold; therefore a material suitable to contain water for a given purpose may not serve for its condensation. Good resistance glass vessels, which have been freed from superficial soluble matter by blowing steam into them for some hours in such a way that the condensate drains away continuously, after long standing in cold water will yield little impurity to pure water during several weeks. Such glass, so treated, is suitable for the preservation for short periods of cold pure water for all but a few very special purposes. It is unsuitable for condensers, which are usually made of pure block tin or heavily tinned copper. The risk of introducing non-volatile impurity may be reduced by using pure fused silica, or, better, pure tin or silver as the material of condenser and receiver. Occasionally water has been condensed and kept in vessels of gold or platinum, but for all ordinary and most special purposes water condensed in pure tin and kept a short time in steamed resistance glass is quite satisfactory. Water kept in ordinary glass bottles for some weeks or months may dissolve sufficient silica, &c., from the glass to render it unsuitable for ordinary precise analytical work, especially that in which small amounts of silica must be determined.

In the estimation of ammonia in water and for work upon conductivity of dilute solutions, the volatile impurities are much the more serious. Fortunately simple precautions suffice to eliminate them. Organic matter may be destroyed by adding to the raw water in the still a small proportion of potassium permanganate or manganate, with sufficient caustic soda or potash to make the water distinctly alkaline (Stas, *Mém. Acad. Belg.* 1865, 35, 1; *Chem. News*, 1861, 4, 207; 1867, 15, 204). Practically the whole of the carbon dioxide and ammonia will come over with the first 20-30 p.c. of the distillate, and if this be rejected the remaining two-thirds will be pure water.

Many procedures have been described, in which the acidic and basic impurities are retained in the still by added reagents, e.g. aluminium sulphate, potassium hydrogen sulphate or phosphoric acid to retain ammonia, or lime or baryta to retain carbon dioxide (see, e.g. Hulett, *Zeitsch. physikal. Chem.* 1896, 21, 297; Walker and Cormack, *J. Chem. Soc.* 1902, 77, 5; W. R. Bousfield, *ibid.* 1905, 87, 740; 1912, 101, 1443). Some workers have obtained fair conductivity water by redistillation of laboratory distilled water without added reagents (see Bousfield, *loc. cit.*; Hartley, Campbell and Poole, *J. Chem. Soc.* 1908, 93, 428; Thole, *ibid.* 1912, 101, 207).

In a simpler method for the positive chemical elimination of basic and acidic impurities in one operation, a large glass flask containing an aqueous solution of 10 p.c. potassium dichromate and 5 p.c. sulphuric acid is heated, raw water is run in at a rate equal to the rate of evaporation, and the steam is led through a second flask, also heated, containing saturated baryta solution and then condensed in tin (Moseley and Myer, *J. Amer. Chem. Soc.* 1918, 40, 1409: this method was partially employed by Paul, *Zeitsch. Elektrochem.* 1914, 20, 179).

But still simpler methods are effective. It has long been known that ordinary 'conductivity' water, having a conductivity about 1.0×10^{-6} mho (1 gemmho) is materially improved by contact with an atmosphere freed from carbon dioxide, e.g. by enclosure over lime or even by passing through it clean air from the open, whilst it deteriorates markedly in contact with air contaminated by human breath or by flames (Kohlrausch, *Zeitsch. physikal. Chem.* 1902, 42, 193).

If a current of purified air be passed through such water heated nearly to its boiling-point in a quartz still, and the water distilling under these conditions be condensed in block tin and collected in quartz, it has a conductivity of $0.05-0.07 \times 10^{-6}$ mho at 18° (Weiland, *J. Amer. Chem. Soc.* 1918, 40, 131). Such water compares favourably with the purest conductivity water prepared by distilling repeatedly *in vacuo* in sealed glass vessels and had a conductivity of 0.043×10^{-6} mhos at 18° (Kohlrausch and Heydeweller, *Zeitsch. physikal. Chem.* 1894, 14, 317; Kohlrausch, *Proc. Roy. Soc.* 1903, 71, 338). This method is applicable only to those cases where carbon dioxide is the sole impurity, but the same principles have been applied in a method, applicable to all types of water, first described by Bourdillon (*J. Chem. Soc.* 1913, 103, 791) and elaborated by Clevenger (*J. Ind. Eng. Chem.* 1919, 11, 964). Raw water containing potassium bisulphate or phosphoric acid is distilled, and the steam is carefully scrubbed and separated from spray and led into a long vertical tube through which a current of purified air passes from the bottom upward. The upper end of this tube is surrounded by a water-jacket maintained nearly at 100°, which, therefore, condenses, but does not cool, the major portion of the steam; the uncondensed steam escapes either to the air or to a second condenser. The hot condensate which flows down the walls of the tube in contact with pure air, is cooled by a cold-water jacket surrounding the lower part of the tube and passes away by a syphon. The apparatus is best constructed wholly of copper heavily tinned and soldered with pure tin. Thus it is not difficult to prepare water having a conductivity about 0.05×10^{-6} mho, but it cannot be preserved save under rigid exclusion of atmospheric carbon dioxide. In contact with clean air its conductivity increases to a limiting value of about 0.75×10^{-6} mho, which is that of a solution of carbonic acid in equilibrium with the 0.035 (± 0.004) volume p.c. of carbon dioxide present in air (Kendall, *J. Amer. Chem. Soc.* 1916, 38, 1490). Kendall has suggested that as such a solution is permanent it is preferable to use it and correct for its

known conductivity rather than to use water of lower conductivity, the correction for which must be uncertain (Kendall, J. Amer. Chem. Soc. 1916, 38, 2460; *g.c.* also for a full discussion and bibliography of previous work on the preparation of conductivity water).

Pure water has been prepared in other ways. Baker found that pure water prepared by the union of pure and dry hydrogen and oxygen differs in some respects from ordinary pure water. If steam from pure water be passed through a red-hot silica tube and then condensed in silica and Jena glass, the condensate acts upon pure 1 p.c. sodium amalgam much more slowly than do other types of water. This inactivity is independent of the conductivity of the water, and there is evidence that it is due to the absence from such water of traces of hydrogen peroxide which constitute a normal impurity in ordinary pure water (Baker and Parker, J. Chem. Soc. 1913, 103, 2060; Parker, *ibid.* 2071).

Pure water may also be prepared by dehydrating pure hydrates, *e.g.* hydrated barium chloride or telluric acid, H_2TeO_4 , by heat; but the method has usually been applied to obtain very small, accurately known, amounts of water in closed apparatus, and little or nothing is known of the properties of such water.

THE RELATION OF PRESSURE AND TEMPERATURE FOR STEAM, WATER, AND ICE.

The pressure, temperature, volume, and state of aggregation of water are, of course, interdependent, and it is thus difficult to discuss separately the effect of variation of any one or two of these factors. Possibly the simplest method is to discuss first the relations of pressure and temperature for the various states of aggregation, and then consider the effect upon volume of varying temperature and pressure considered separately.

Fig. 1 is the complete pressure-temperature diagram for water, except that to save space the steam-line ΔJ is not continued to the critical point at which it terminates, viz. 374°C. and 217 atm. The diagram is defective also in that the line ΔLM stands for the vapour-pressure curves of both ice and supercooled water, which are in fact distinct but by an amount entirely inappreciable on the scale of pressure necessarily adopted. The line ΔL represents the vapour pressure of supercooled water, which has been measured down to -16.3° and is given in Table 1; the line ΔM shows the vapour pressure of ice which has been measured down to about -70° , and is given in Table 2 from -60° to 0° . The maximum difference between the vapour pressures of ice and supercooled water is 0.200 mm. at -11.7° .

The vapour pressure of water has been the subject of much accurate experimental work. The data given in Table 3 from 0° – 100° and in Table 4 from 100° – 370° , and represented on the diagram by the line ΔJ , are the values regarded as most probable.

The area below the line ΔJ represents the vapour phase, and water as we know it at or near atmospheric pressure, is, on the scale of Fig. 1, represented by little more than the thickness of that line.

For many purposes the changes in the boiling-point of water attending small changes of pressure are of great practical importance. At pressures in the neighbourhood of 1 atm. the value of dt/dp for $dp=1$ mm. of mercury is 0.0376° (Wiebe, *Zeitsch. für Instrumentkunde*, 1893, 13, 329); and the precise values of the boiling-point of water at pressures from 720–800 mm. of mercury are given in a form convenient for reference in Table 5.

Our knowledge of the rest of the PT diagram, covering a range of temperature from -80° to $+80^\circ$ at pressures from 1 to over 20,000 kgm./cm.², rests upon the work of Tammann as confirmed and extended by Bridgman. The principal numerical data are given in Tables 6 and 7, which show respectively the variations in the melting-points and transition-points of the various forms of ice with variation in pressure; their significance is evident from a consideration of Fig. 1. The line ΔB represents the equilibrium between water and ordinary ice, Ice I. At pressures above about 2000 kgm./cm.², whatever the temperature, Ice I cannot exist, but changes into one of the denser forms of ice, II or III, the equilibria between which and Ice I are represented respectively by $\kappa'GB$ and κGB . The line $\kappa'G$ represents stable equilibrium between Ice I and Ice II, whereas κG is the locus of equilibrium between Ice I and Ice III in a metastable condition. Ice III has a stable existence only in the range of temperature and pressure denoted by the area $BCFG$, within which are smaller areas (shown on a larger scale in the upper part of Fig. 1) in which labile modifications of Ice I and Ice III, called respectively Ice I' and Ice III', can exist. The inter-relation of these forms is not as yet well understood.

Two other still denser forms of ice exist at higher pressures. Ice V is in equilibrium with Ice III at about 3500 kgm./cm.² over a small range of temperature in the neighbourhood of -20° ; its equilibrium with Ice II has been followed over a small range only, the point x being conjectural. The stable equilibrium between Ice V and water, indicated by the line CD , has been traced some distance into the area of Ice III as shown, Ice V being here metastable. Above a pressure of about 8500–8000 kgm./cm.² Ice V and Ice II are converted into Ice VI, the only form observed at higher pressures. Its equilibrium with liquid water is represented by the line DH , and it is remarkable that at the highest pressures this form is stable at temperatures up to 75° . The existence of metastable Ice VI in equilibrium with liquid water has been traced along the line DD' for a considerable distance in the area of Ice V. The estimated densities of the different forms of ice are:—Ice II 1.03; Ice III 1.04; Ice V 1.06; Ice VI 1.09; as compared with ordinary ice 0.92 and water=1.00.

It must be understood that the evidence for the separate existence of these solids is simply the abrupt change of volume, manifested by a sudden drop of pressure, observed in a mass of water subject to isothermal compression. The conclusion that these are solid forms of water is supported by the fact that Ice III formed at about 2500 kgm./cm.² and -20° to -30° , if cooled first to -80° and then

to -190° , is so stabilised that it is unchanged on release of pressure and can be examined in the open. At temperatures of -120° or higher under atmospheric pressure, the clear trans-

parent Ice III breaks down into a bulky powder of Ice I (Tammann, *Zeitsch. anorg. Chem.* 1909, 63, 285; *Zeitsch. physikal. Chem.* 1910, 72, 609; 1913, 84, 257).

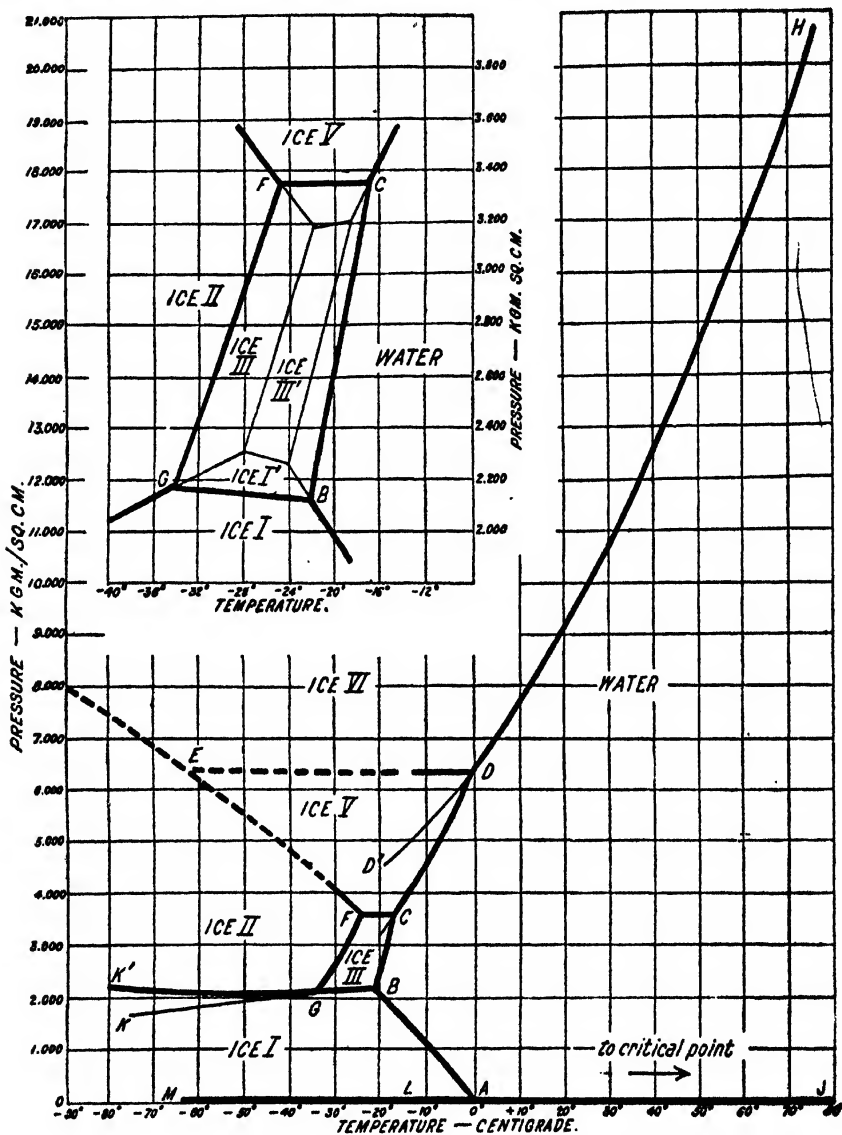


Fig. 1.

The extent and direction of the line DH are of great theoretical interest, inasmuch as they lend no support to the hypotheses which have been formulated (Poynting, *Phil. Mag.* 1881, [5], 12, 32; Ostwald, *Lehrbuch der allgemeinen Chemie*, 1902, 2, ii. 373, 391; Tammann, *Kristallisieren und Schmelzen*, Leipzig, 1903, 29; Planck, *Wied. Ann.* 1882, 15, 446) that the melting-point curve of a solid should, with increase of pressure, terminate at a critical end-point analogous to that of the boiling-point curve, or pass through a maximum.

Critical data for water have been determined as follows:

Authority	Crit. temp.	Crit. press.	Crit. vol.	Crit. density
1	358.1°	—	0.001874	0.429
2	364.3°	194.6 atm.	0.003864	—
3	374.0°	217.0 atm.	—	—

(1) Nadejdine, *J. Russ. Phys. Chem. Soc.* 1885, 9, 721.
 (2) Battelli, *Mem. Torino*, 1890, [II.] 41.
 (3) Holborn and Baumann, *Ann. Physik.* 1910, 31, 945.

TABLE 1.

VAPOUR PRESSURE OF SUPER-COOLED WATER.

Millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

Temp. degrees	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
-16	—	—	—	—	—	—	—	—	—	1·315
-15	1·326	1·337	1·349	1·360	1·371	1·383	1·394	1·406	1·417	1·429
-14	1·441	1·453	1·465	1·477	1·489	1·501	1·513	1·525	1·538	1·551
-13	1·564	1·577	1·590	1·603	1·616	1·630	1·643	1·657	1·670	1·684
-12	1·698	1·712	1·726	1·740	1·754	1·768	1·783	1·797	1·812	1·826
-11	1·841	1·856	1·871	1·886	1·901	1·917	1·932	1·948	1·963	1·979
-10	1·995	2·001	2·028	2·044	2·060	2·077	2·093	2·109	2·126	2·143
-9	2·160	2·177	2·195	2·212	2·230	2·248	2·266	2·284	2·302	2·320
-8	2·338	2·357	2·375	2·394	2·412	2·431	2·450	2·469	2·489	2·509
-7	2·529	2·549	2·569	2·589	2·609	2·629	2·650	2·670	2·691	2·712
-6	2·733	2·754	2·775	2·797	2·818	2·840	2·862	2·884	2·906	2·928
-5	2·950	2·972	2·994	3·017	3·040	3·063	3·086	3·110	3·134	3·158
-4	3·182	3·206	3·230	3·254	3·278	3·303	3·328	3·353	3·380	3·404
-3	3·429	3·455	3·481	3·508	3·534	3·561	3·588	3·615	3·642	3·669
-2	3·697	3·724	3·752	3·780	3·808	3·836	3·865	3·894	3·923	3·952
-1	3·981	4·011	4·041	4·071	4·101	4·131	4·162	4·193	4·224	4·256
-0	4·287	4·318	4·350	4·382	4·414	4·447	4·480	4·513	4·546	4·579

Scheel and Heuse, Ann. Physik. 1909, [iv.] 29, 723.

TABLE 2.

VAPOUR PRESSURE OF ICE IN MILLIMETRES OF MERCURY.

Measured at 0°C. and at sea-level in latitude 45° over a range of temperatures on the constant volume gas-thermometer (Reichsanstalt scale).

Temp. °C.	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
-60	mm. 0·006	mm. 0·006	mm. 0·006	mm. 0·006	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007	mm. 0·007
-59	0·007	0·007	0·007	0·008	0·008	0·008	0·008	0·008	0·008	0·008
-58	0·008	0·008	0·009	0·009	0·009	0·009	0·009	0·009	0·009	0·009
-57	0·009	0·010	0·010	0·010	0·010	0·010	0·010	0·011	0·011	0·011
-56	0·011	0·011	0·011	0·012	0·012	0·012	0·012	0·012	0·013	0·013
-55	0·013	0·013	0·013	0·014	0·014	0·014	0·014	0·014	0·015	0·015
-54	0·015	0·015	0·015	0·016	0·016	0·016	0·016	0·017	0·017	0·017
-53	0·017	0·018	0·018	0·018	0·018	0·019	0·019	0·019	0·019	0·019
-52	0·020	0·020	0·020	0·020	0·021	0·021	0·021	0·022	0·022	0·022
-51	0·022	0·023	0·023	0·023	0·024	0·024	0·024	0·025	0·025	0·025
-50	0·026	0·026	0·027	0·027	0·027	0·028	0·028	0·029	0·029	0·029
-49	0·030	0·030	0·030	0·031	0·031	0·031	0·032	0·032	0·032	0·033
-48	0·033	0·034	0·034	0·034	0·035	0·035	0·036	0·036	0·037	0·037
-47	0·038	0·038	0·039	0·039	0·040	0·040	0·041	0·041	0·042	0·042
-46	0·043	0·043	0·044	0·044	0·045	0·045	0·046	0·046	0·047	0·047
-45	0·048	0·048	0·049	0·049	0·050	0·050	0·051	0·051	0·052	0·052

TABLE 2.—VAPOUR PRESSURE OF ICE IN MILLIMETRES OF MERCURY (continued)

Temp. °C.	Tenths of a degree									
	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1	0·0
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
-44	0·053	0·053	0·054	0·054	0·055	0·055	0·056	0·057	0·057	0·058
-43	0·059	0·059	0·060	0·061	0·062	0·063	0·064	0·065	0·065	0·066
-42	0·067	0·068	0·068	0·069	0·070	0·071	0·072	0·072	0·073	0·074
-41	0·075	0·076	0·077	0·078	0·079	0·079	0·080	0·081	0·082	0·083
-40	0·084	0·085	0·086	0·087	0·088	0·089	0·090	0·091	0·092	0·093
-39	0·095	0·096	0·097	0·098	0·100	0·101	0·102	0·103	0·104	0·105
-38	0·106	0·107	0·109	0·110	0·112	0·113	0·115	0·116	0·117	0·119
-37	0·120	0·122	0·123	0·125	0·126	0·127	0·129	0·130	0·132	0·134
-36	0·135	0·137	0·138	0·140	0·142	0·144	0·145	0·147	0·148	0·150
-35	0·152	0·153	0·155	0·156	0·158	0·160	0·162	0·163	0·165	0·167
-34	0·169	0·171	0·172	0·174	0·176	0·177	0·179	0·181	0·183	0·185
-33	0·187	0·189	0·191	0·193	0·195	0·197	0·199	0·201	0·203	0·205
-32	0·207	0·209	0·211	0·213	0·215	0·217	0·220	0·222	0·225	0·227
-31	0·229	0·231	0·234	0·236	0·239	0·242	0·244	0·247	0·249	0·252
-30	0·255	0·258	0·260	0·263	0·266	0·269	0·272	0·274	0·277	0·280
-29	0·283	0·286	0·289	0·292	0·295	0·298	0·301	0·305	0·308	0·311
-28	0·314	0·318	0·321	0·325	0·328	0·331	0·335	0·338	0·342	0·345
-27	0·349	0·353	0·356	0·360	0·364	0·368	0·372	0·375	0·379	0·383
-26	0·387	0·391	0·395	0·399	0·403	0·407	0·411	0·416	0·420	0·425
-25	0·429	0·435	0·439	0·443	0·448	0·453	0·457	0·462	0·466	0·471
-24	0·476	0·481	0·485	0·490	0·495	0·500	0·505	0·511	0·516	0·521
-23	0·526	0·532	0·537	0·543	0·548	0·554	0·559	0·565	0·570	0·576
-22	0·582	0·588	0·594	0·600	0·606	0·612	0·618	0·624	0·630	0·636
-21	0·642	0·648	0·652	0·661	0·667	0·674	0·681	0·687	0·694	0·701
-20	0·708	0·715	0·722	0·729	0·736	0·743	0·750	0·758	0·765	0·772
-19	0·780	0·787	0·795	0·802	0·810	0·818	0·826	0·834	0·842	0·850
-18	0·858	0·867	0·875	0·884	0·892	0·901	0·909	0·918	0·926	0·935
-17	0·944	0·953	0·962	0·971	0·980	0·989	0·998	1·008	1·017	1·027
-16	1·037	1·047	1·057	1·067	1·077	1·087	1·097	1·108	1·118	1·128
-15	1·139	1·150	1·160	1·171	1·182	1·193	1·204	1·216	1·227	1·238
-14	1·250	1·261	1·273	1·284	1·296	1·308	1·320	1·333	1·345	1·357
-13	1·369	1·382	1·394	1·407	1·420	1·433	1·446	1·460	1·473	1·486
-12	1·500	1·514	1·527	1·541	1·555	1·569	1·584	1·598	1·613	1·627
-11	1·642	1·657	1·672	1·687	1·702	1·718	1·733	1·749	1·764	1·780
-10	1·796	1·812	1·828	1·845	1·861	1·877	1·894	1·911	1·928	1·946
-9	1·963	1·981	1·999	2·016	2·034	2·052	2·070	2·088	2·106	2·125
-8	2·145	2·164	2·183	2·203	2·222	2·241	2·261	2·281	2·301	2·321
-7	2·342	2·362	2·383	2·404	2·425	2·446	2·467	2·489	2·510	2·532
-6	2·554	2·577	2·599	2·622	2·645	2·668	2·691	2·714	2·738	2·761
-5	2·785	2·809	2·833	2·857	2·881	2·906	2·931	2·956	2·982	3·006
-4	3·034	3·060	3·086	3·112	3·139	3·166	3·193	3·220	3·248	3·276
-3	3·304	3·332	3·361	3·390	3·419	3·448	3·477	3·507	3·536	3·566
-2	3·597	3·627	3·658	3·689	3·720	3·751	3·783	3·815	3·847	3·879
-1	3·912	3·945	3·979	4·012	4·045	4·079	4·113	4·147	4·182	4·216
0	4·251	4·286	4·322	4·358	4·395	4·431	4·468	4·505	4·542	4·579

WATER.

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TABLE 3.

VAPOUR PRESSURE OF WATER FROM 0° TO 100°.

In millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

(Landolt-Börnstein: *Physikalische-Chemische Tabellen.*)

Temp. degrees	Tenths of a Degree									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	4·579	4·613	4·647	4·681	4·715	4·750	4·785	4·820	4·855	4·890
1	4·926	4·962	4·998	5·034	5·070	5·107	5·144	5·181	5·219	5·256
2	5·294	5·332	5·370	5·408	5·447	5·486	5·525	5·565	5·605	5·645
3	5·685	5·725	5·766	5·807	5·848	5·889	5·931	5·973	6·015	6·058
4	6·101	6·144	6·187	6·230	6·274	6·318	6·363	6·408	6·453	6·498
5	6·543	6·589	6·635	6·681	6·728	6·775	6·822	6·869	6·917	6·965
6	7·013	7·062	7·111	7·160	7·209	7·259	7·309	7·360	7·411	7·462
7	7·513	7·565	7·617	7·669	7·722	7·775	7·828	7·882	7·936	7·990
8	8·045	8·100	8·155	8·211	8·267	8·323	8·380	8·437	8·494	8·551
9	8·609	8·668	8·727	8·786	8·845	8·905	8·965	9·025	9·086	9·147
10	9·209	9·271	9·333	9·395	9·458	9·521	9·585	9·649	9·714	9·779
11	9·844	9·910	9·976	10·042	10·109	10·176	10·244	10·312	10·380	10·449
12	10·518	10·588	10·658	10·728	10·799	10·870	10·941	11·013	11·085	11·158
13	11·231	11·305	11·379	11·453	11·528	11·604	11·680	11·756	11·833	11·910
14	11·987	12·065	12·144	12·223	12·302	12·382	12·462	12·543	12·624	12·706
15	12·788	12·870	12·953	13·037	13·121	13·205	13·290	13·375	13·461	13·547
16	13·634	13·721	13·809	13·898	13·987	14·076	14·166	14·256	14·347	14·438
17	14·530	14·622	14·715	14·809	14·903	14·997	15·092	15·188	15·284	15·380
18	15·477	15·575	15·673	15·772	15·871	15·971	16·071	16·171	16·272	16·374
19	16·477	16·581	16·685	16·789	16·894	16·999	17·105	17·212	17·319	17·427
20	17·535	17·644	17·753	17·863	17·974	18·085	18·197	18·309	18·422	18·536
21	18·650	18·765	18·880	18·996	19·112	19·231	19·349	19·468	19·587	19·707
22	19·827	19·948	20·070	20·193	20·316	20·440	20·565	20·690	20·815	20·941
23	21·068	21·196	21·324	21·453	21·583	21·714	21·845	21·977	22·110	22·243
24	22·377	22·512	22·648	22·785	22·922	23·060	23·198	23·337	23·476	23·616
25	23·756	23·897	24·038	24·182	24·326	24·471	24·617	24·764	24·912	25·060
26	25·209	25·359	25·509	25·660	25·812	25·964	26·117	26·271	26·426	26·582
27	26·739	26·897	27·055	27·214	27·374	27·535	27·696	27·858	28·021	28·185
28	28·349	28·541	28·680	28·847	29·015	29·184	29·354	29·525	29·697	29·870
29	30·043	30·217	30·392	30·568	30·745	30·923	31·102	31·281	31·461	31·642
30	31·824	32·007	32·191	32·376	32·561	32·747	32·934	33·122	33·312	33·503
31	33·695	33·888	34·082	34·276	34·471	34·667	34·864	35·062	35·261	35·461
32	35·663	35·865	36·068	36·272	36·477	36·683	36·891	37·099	37·308	37·518
33	37·729	37·942	38·155	38·369	38·584	38·801	39·018	39·237	39·457	39·677
34	39·898	40·121	40·344	40·569	40·796	41·023	41·251	41·480	41·710	41·942
35	42·175	42·409	42·644	42·880	43·117	43·355	43·595	43·836	44·078	44·320
36	44·563	44·808	45·054	45·301	45·549	45·799	46·050	46·302	46·556	46·811
37	47·067	47·324	47·582	47·841	48·102	48·364	48·627	48·891	49·157	49·424
38	49·692	49·961	50·231	50·502	50·774	51·048	51·323	51·600	51·879	52·160
39	52·442	52·725	53·009	53·294	53·580	53·867	54·156	54·446	54·737	55·030
40	55·32	55·61	55·91	56·21	56·51	56·81	57·11	57·41	57·72	58·03
41	58·34	58·65	58·96	59·27	59·58	59·90	60·22	60·54	60·86	61·18
42	61·50	61·82	62·14	62·47	62·80	63·13	63·46	63·79	64·12	64·46
43	64·80	65·14	65·48	65·82	66·16	66·51	66·86	67·21	67·56	67·91
44	68·26	68·61	68·97	69·33	69·69	70·05	70·41	70·77	71·14	71·51
45	71·88	72·25	72·62	72·99	73·36	73·74	74·12	74·50	74·88	75·26
46	75·65	76·04	76·43	76·82	77·21	77·60	78·00	78·40	78·80	79·20
47	79·60	80·00	80·41	80·82	81·23	81·64	82·05	82·46	82·87	83·29
48	83·71	84·13	84·56	84·99	85·42	85·85	86·28	86·71	87·14	87·58
49	88·02	88·46	88·90	89·34	89·79	90·24	90·69	91·14	91·59	92·05

TABLE 3.—VAPOUR PRESSURE OF WATER FROM 0° TO 100° (continued).

Temp. degrees	Tenths of a Degree									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
50	92.51	92.97	93.43	93.89	94.36	94.82	95.29	95.77	96.24	96.72
51	97.20	97.68	98.16	98.64	99.13	99.62	100.11	100.60	101.10	101.59
52	102.09	102.59	103.10	103.60	104.11	104.62	105.13	105.64	106.16	106.68
53	107.20	107.72	108.24	108.76	109.29	109.82	110.35	110.89	111.43	111.97
54	112.51	113.05	113.59	114.14	114.69	115.24	115.80	116.36	116.92	117.48
55	118.04	118.60	119.16	119.73	120.31	120.89	121.47	122.05	122.63	123.21
56	123.80	124.40	124.99	125.58	126.18	126.78	127.38	127.99	128.60	129.21
57	129.82	130.44	131.06	131.68	132.30	132.92	133.55	134.18	134.81	135.45
58	136.08	136.72	137.36	138.01	138.66	139.31	139.96	140.62	141.28	141.94
59	142.60	143.27	143.94	144.61	145.28	145.96	146.64	147.32	148.00	148.69
60	149.38	150.07	150.77	151.47	152.17	152.87	153.58	154.29	155.00	155.71
61	156.43	157.15	157.87	158.59	159.32	160.06	160.80	161.58	162.28	163.02
62	163.77	164.52	165.27	166.02	166.78	167.54	168.30	169.07	169.84	170.61
63	171.38	172.16	172.94	173.73	174.52	175.31	176.10	176.90	177.70	178.50
64	179.31	180.11	180.92	181.74	182.56	183.38	184.20	185.03	185.86	186.70
65	187.54	188.38	189.22	190.06	190.91	191.77	192.63	193.49	194.35	195.22
66	196.09	196.96	197.84	198.72	199.60	200.48	201.37	202.26	203.16	204.06
67	204.96	205.87	206.78	207.69	208.61	209.53	210.45	211.37	212.30	213.23
68	214.17	215.11	216.06	217.01	217.96	218.91	219.87	220.83	221.79	222.76
69	223.73	224.71	225.69	226.67	227.66	228.65	229.65	230.65	231.65	232.65
70	233.7	234.7	235.7	236.7	237.8	238.8	239.8	240.9	241.9	242.9
71	243.9	245.0	246.0	247.1	248.1	249.2	250.3	251.4	252.4	253.5
72	254.6	255.7	256.8	257.9	259.0	260.1	261.2	262.3	263.5	264.6
73	265.7	266.8	268.0	269.1	270.3	271.4	272.6	273.7	274.9	276.0
74	277.2	278.4	279.5	280.7	281.9	283.1	284.3	285.5	286.7	287.9
75	289.1	290.3	291.5	292.8	294.0	295.2	296.5	297.7	298.9	300.2
76	301.4	302.7	303.9	305.2	306.5	307.7	309.0	310.3	311.6	312.9
77	314.1	315.4	316.7	318.0	319.3	320.7	322.0	323.3	324.7	326.0
78	327.2	328.7	330.0	331.4	332.7	334.1	335.5	336.8	338.2	339.6
79	341.0	342.4	343.8	345.2	346.6	348.0	349.4	350.8	352.2	353.7
80	355.1	356.5	358.0	359.4	360.9	362.4	363.8	365.3	366.8	368.3
81	369.7	371.2	372.7	374.2	375.7	377.3	379.8	380.3	381.8	383.4
82	384.9	386.4	388.0	389.5	391.1	392.7	394.2	395.8	397.4	399.0
83	400.6	402.2	403.8	405.4	407.0	408.6	410.3	411.9	413.5	415.2
84	416.8	418.4	420.1	421.7	423.4	425.1	426.8	428.5	430.2	431.9
85	433.6	435.3	437.0	438.7	440.5	442.2	443.9	445.7	447.4	449.2
86	450.9	452.6	454.4	456.2	458.0	459.7	461.5	463.3	465.1	466.9
87	468.7	470.5	472.3	474.1	476.0	477.8	479.7	481.5	483.4	485.2
88	487.1	489.0	490.9	492.7	494.6	496.5	498.4	500.3	502.3	504.2
89	506.1	508.0	510.0	511.9	513.9	515.9	517.8	519.8	521.8	522.8
90	525.76	527.76	529.77	531.78	533.80	535.82	537.86	539.90	541.95	544.00
91	546.05	548.11	550.18	552.26	554.35	556.44	558.53	560.64	562.75	564.87
92	566.99	569.12	571.23	573.40	575.55	577.71	579.87	582.04	584.22	586.41
93	588.60	590.80	593.00	595.21	597.43	599.66	601.89	604.13	606.38	608.64
94	610.90	613.17	615.44	617.72	620.01	622.31	624.61	626.92	629.24	631.57
95	633.90	636.24	638.59	640.94	643.30	645.67	648.05	650.43	652.82	655.22
96	657.62	660.03	662.45	664.88	667.31	669.75	672.20	674.66	677.12	679.59
97	682.07	684.55	687.04	689.54	692.05	694.57	697.10	699.63	702.17	704.71
98	707.27	709.83	712.40	714.98	717.56	720.15	722.75	725.36	727.98	730.61
99	733.24	735.88	738.53	741.18	743.85	746.52	749.20	751.89	754.58	757.29
100	760.00	762.72	765.45	768.19	770.93	773.68	776.44	779.22	782.00	784.78
101	787.57	790.37	793.18	796.00	798.82	801.66	804.50	807.35	810.21	813.08

Schoel and Heuse, Ann. Physik. 1910, [iv.] 31, 715; Holborn and Henning, *ibid.* 1906, [iv.] 26, 833. Confirmed at 25° by the dynamic method by Derby, Daniels and Guttsche J. Amer. Chem. Soc. 1914, 36, 793; and from 25°-80° by direct weighing by Krauskopf, J. Phys. Chem. 1910, 14, 489.

TABLE 4.
VAPOUR PRESSURE OF WATER FROM 100° TO 370°.
In millimetres of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.
(*Landolt-Börnstein: Physikalische-Chemische Tabellen.*)

Temp. T _{max} °C.	Units °C.									
	0	1	2	3	4	5	6	7	8	9
100	760.0	767.6	815.9	845.1	875.1	906.1	937.9	970.6	1,004.4	1,038.9
110	1,074.6	1,111.2	1,148.8	1,187.5	1,227.3	1,268.0	1,310.0	1,353.0	1,397.3	1,442.7
120	1,486.2	1,536.9	1,590.1	1,636.4	1,687.9	1,741.0	1,795.2	1,850.9	1,907.7	1,966.4
130	2,026.3	2,087.6	2,150.6	2,214.8	2,280.9	2,347.4	2,415.5	2,486.3	2,560.8	2,638.0
140	2,710.7	2,788.4	2,867.7	2,949.1	3,032.0	3,116.9	3,203.7	3,292.5	3,383.1	3,475.9
150	3,570.7	3,661.4	3,763.3	3,867.1	3,970	4,076	4,184	4,293	4,405	4,520
160	4,636	4,755	4,877	5,001	5,128	5,257	5,388	5,522	5,659	5,799
170	5,942	6,066	6,234	6,394	6,539	6,695	6,854	7,016	7,181	7,350
180	7,521	7,695	7,873	8,054	8,238	8,425	8,617	8,811	9,008	9,209
190	9,414	9,622	9,833	10,049	10,267	10,490	10,717	10,946	11,181	11,419
200	11,661	11,907	12,157	12,410	12,668	12,931	13,199	13,470	13,745	14,025
210	17,395	17,735	18,081	18,421	18,770	19,129	19,497	19,862	20,223	20,600
220	20,982	21,369	21,761	22,158	22,562	22,972	23,387	23,807	24,234	24,666
230	25,105	25,548	25,999	26,454	26,917	27,387	27,861	28,341	28,829	29,323
240	29,823	30,329	30,843	31,363	31,891	32,424	32,964	33,512	34,066	34,636
250	35,195	35,769	36,351	36,940	37,537	38,141	38,751	39,370	39,995	40,626
260	41,270	41,919	42,575	43,239	43,911	44,591	45,279	45,975	46,680	47,393
270	48,115	48,845	49,582	50,329	51,085	51,850	52,624	53,405	54,200	55,002
280	55,812	56,630	57,460	58,302	59,151	60,007	60,877	61,756	62,642	63,542
290	64,450	65,730	66,290	67,230	68,170	69,130	70,090	71,070	72,060	73,060
300	74,050	75,060	76,100	77,140	78,190	79,260	80,320	81,400	82,490	83,600
310	84,710	85,840	86,980	88,140	89,300	90,470	91,660	92,860	94,080	95,310
320	97,560	98,780	99,950	101,100	102,300	103,500	104,730	105,960	107,200	108,450
330	109,640	110,900	112,160	113,450	114,750	116,050	117,360	118,680	120,000	121,340
340	122,680	124,040	125,400	126,780	128,160	129,560	130,970	132,390	133,820	135,260
350	136,710	138,160	139,620	141,090	142,570	144,060	145,560	147,070	148,590	150,120
360	151,650	153,180	154,720	156,270	157,830	159,400	160,980	162,570	164,170	165,780
370	167,750	169,360	170,980	172,610	174,250	175,900	177,560	179,230	180,910	182,600

Holborn and Henning, Ann. Physik. 1908, [iv.] 26, 833; Holborn and Baumann, *ibid.* 1910, v. 31, 945; Crafts, J. Chim. Phys. 1915, 13, 105.

TABLE 5.

BOILING-POINT OF WATER AT VARIOUS BAROMETRIC PRESSURES.

Barometric pressure in mm. of mercury at 0°C. at sea-level in latitude 45°. Temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

Press. mm.	Tenths of a millimeter									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
720	98.494°	497	501	505	509	513	517	520	524	528
721	532	536	540	544	547	551	555	559	563	567
722	571	574	578	582	586	590	593	597	601	605
723	609	613	617	620	624	628	632	636	640	644
724	648	652	655	659	663	667	671	675	678	682
725	98.686°	689	693	697	701	705	709	712	716	720
726	724	728	732	735	739	743	747	751	755	758
727	762	766	770	774	777	781	785	789	793	797
728	801	804	808	812	816	819	823	827	831	835
729	839	843	846	850	854	858	861	865	869	873
730	98.877°	880	884	888	892	896	899	903	907	911
731	915	918	922	926	930	934	937	941	945	949
732	953	956	960	964	968	972	975	979	983	987
733	991	994	998	*002	*006	*010	*013	*017	*021	*025
734	99.029°	032	036	040	044	048	051	055	059	063
735	99.067°	070	074	078	082	085	089	093	097	101
736	105	109	112	116	119	123	127	131	135	138
737	142	146	150	153	157	161	165	169	172	176
738	180	184	187	191	195	199	203	206	210	214
739	218	221	225	229	233	236	240	244	248	252
740	99.255°	259	263	267	270	274	278	282	285	289
741	293	297	300	304	308	312	316	319	323	327
742	331	334	338	342	346	349	353	357	361	364
743	368	372	376	379	383	387	391	394	398	402
744	406	409	413	417	421	424	428	432	436	439
745	99.443°	447	451	454	458	462	466	469	473	477
746	481	484	488	492	495	499	503	507	510	514
747	518	522	525	529	533	537	540	544	548	551
748	555	559	563	566	570	574	578	581	585	589
749	593	596	600	604	607	611	615	619	622	626
750	99.630°	633	637	641	645	648	652	656	659	663
751	667	671	674	678	682	686	689	693	694	700
752	704	708	712	715	719	723	726	730	734	738
753	741	745	749	752	756	760	764	767	771	775
754	778	782	786	790	793	797	801	804	808	812
755	99.815°	819	823	827	830	834	838	841	845	849
756	852	856	860	863	867	871	875	878	882	886
757	889	893	897	900	904	908	911	915	919	923
758	926	930	934	937	941	945	948	952	956	959
759	963	967	970	974	978	982	985	989	993	996

TABLE 5.—BOILING-POINT OF WATER AT VARIOUS BAROMETRIC PRESSURES (*continued*).

Press. mm.	Tenths of a millimetre									
	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
760	100·000°	004	007	011	015	018	022	026	019	033
761	037	040	044	048	052	055	059	063	066	070
762	073	077	081	085	088	092	096	099	103	107
763	110	114	118	121	125	129	132	136	140	143
764	147	151	154	158	162	165	169	173	176	180
765	100·184°	187	191	195	198	202	206	209	213	216
766	220	224	227	231	235	238	242	246	249	253
767	257	260	264	268	271	275	279	283	286	290
768	293	297	300	304	308	311	315	319	322	326
769	330	333	337	341	344	348	352	355	359	363
770	100·366°	370	373	377	381	384	388	392	395	399
771	402	406	410	414	417	421	424	428	432	435
772	439	442	446	450	453	457	461	464	468	472
773	475	479	483	486	490	493	497	501	504	508
774	511	515	519	522	526	530	533	537	540	544
775	100·547°	551	555	559	562	566	569	573	577	580
776	584	588	591	595	598	602	606	609	613	616
777	620	624	627	631	634	638	642	645	649	653
778	656	660	663	667	671	674	678	681	685	689
779	692	696	699	703	707	710	714	718	721	725
780	100·728	732	735	739	743	746	750	753	757	761
781	764	768	772	775	779	782	786	789	793	797
782	800	804	807	811	815	818	822	825	829	833
783	836	840	843	847	851	854	858	861	865	869
784	872	876	879	883	886	890	894	897	901	904
785	100·908°	912	915	919	922	926	929	933	937	940
786	944	947	951	954	958	962	965	969	972	976
787	980	984	988	991	995	998	*002	*006	*009	*013
788	101·016°	020	023	027	030	034	037	040	044	047
789	051	054	058	062	065	069	072	076	079	083
790	101·087°	090	094	097	101	104	108	112	115	119
791	122	126	129	133	136	140	144	147	151	154
792	158	161	165	168	172	176	179	183	186	190
793	194	197	201	204	208	211	215	218	222	225
794	229	232	236	239	243	246	250	254	257	261
795	101·265°	269	272	276	279	283	287	290	294	297
796	300	303	307	310	314	317	321	324	328	332
797	335	339	342	346	349	353	356	360	363	367
798	371	375	378	382	385	388	392	395	399	402
799	406	409	413	416	420	423	427	430	434	437
800	101·441°	—	—	—	—	—	—	—	—	—

Holborn and Henning, Ann. Physik. 1908, [iv.] 26, 833.

TABLE 6.
MELTING-POINT OF ICE AT HIGH PRESSURE.
(Landolt-Börnstein: *Physikalische-Chemische Tabellen*.)

Solid phases: triple points	Pressure kgm./cm ²	Melting-point	Reference
	0	0.0°	
	336	-2.5	1
	500	-4.1	3
	615	-5.0	1
	675	-5.53	2
	859	-7.46	2
	890	-7.5	1
	1,000	-8.7	3
	1,099	-9.75	2
Ice I. (AB)	1,141	-10.42	2
	1,155	-10.0	1
	1,353	-12.74	2
	1,410	-12.5	1
	1,500	-14.0	3
	1,597	-15.66	2
	1,625	-15.0	1
	1,835	-17.5	1
	2,000	-20.3	3
	2,042	-20.0	1
	2,200	-22.1	1
Ice I.; Ice III. (B)	2,115	-22.0	3
	2,200	-22.0	1
Ice III. (BC)	2,115	-22.0	3
	2,510	-20.0	3
Ice III.; Ice V. (C)	2,910	-18.5	3
	3,530	-17.0	3
Ice V. (CD)	3,140	-20.0	3
	3,800	-15.0	3
	4,510	-10.0	3
	5,540	-5.0	3
Ice V.; Ice VI. (D)	6,360	0.0	3
	6,380	+0.16	3
	4,500	-18.0	3
	4,790	-15.0	3
	5,280	-10.0	3
	5,810	-5.0	3
Ice VI. (DH)	6,360	0.0	3
	6,500	+1.1	3
	7,000	+5.0	3
	7,640	+10.0	3
	8,000	+12.6	3
	8,310	+15.0	3
	9,000	+20.0	3
	10,590	+30.0	3
	12,390	+40.0	3
	14,430	+50.0	3
	16,690	+60.0	3
	17,840	+64.3	3
	19,670	+72.15	3
	20,670	+76.35	3

1. Tammann, Ann. Physik. 1900, [iv.] 2, 6.
2. Tammann, Zeitsch. physikal. Chem. 1910, 72, 609.
3. Bridgman, Proc. Roy. Acad. 1912, 47, 441.

TABLE 7.
INTER-RELATIONS OF THE STABLE FORMS OF ICE.

Solid phases: triple points	Pressure kgm./cm. ²	Transition points	Reference
Ice I.; Ice III. (BG)	2,103	-20.0°	3
	2,156	-30.8	3
	2,178	-40.0	3
	2,160	-50.0	3
	2,117	-60.0	3
Ice I.; Ice II. Ice III. (G)	2,220	-80.0	1
	2,170	-34.7	3
	2,240	-37.0	1
Ice I.; Ice II. (KG)	2,164	-35.0	3
	2,072	-45.0	
	1,980	-55.0	
	1,886	-65.0	
	1,794	-75.0	
Ice II.; Ice III. (FG)	2,230	-34.0	3
	2,530	31.0	
	2,910	-28.0	
	3,370	-25.0	

THE RELATION OF VOLUME AND TEMPERATURE AT MODERATE PRESSURES FOR STEAM, WATER, AND ICE.

It is convenient next to consider the relation of the volume of unit mass of water to tem-

perature at ordinary or moderate pressures, and the available data are presented in a further series of tables. Table 8 shows the specific volume in c.c. per gram of saturated water vapour corresponding to each degree of temperature from 0°-180°; the specific volume of

TABLE 8.
SPECIFIC VOLUME OF SATURATED WATER VAPOUR.

In cubic centimetres per gram, at temperatures on the constant volume gas-thermometer (Reichsanstalt) scale.

Tempera- ture. Tens of degrees	Degrees									
	0	1	2	3	4	5	6	7	8	9
0°	205,000	191,400	178,700	167,100	156,300	146,300	137,000	128,300	120,300	112,800
10	105,900	99,400	93,390	87,770	82,650	77,660	73,090	68,850	64,870	61,150
20	57,660	54,400	51,350	48,500	45,820	43,310	40,950	38,740	36,660	34,710
30	32,880	31,160	29,540	28,010	26,570	25,230	23,950	22,750	21,620	20,550
40	19,540	18,590	17,690	16,840	16,040	15,280	14,560	13,880	13,240	12,630
50	12,050	11,500	10,980	10,490	10,030	9,585	9,165	8,766	8,388	8,028
60	7,686	7,360	7,049	6,753	6,472	6,205	5,951	5,710	5,480	5,261
70	5,050	4,850	4,669	4,477	4,303	4,136	3,978	3,826	3,681	3,542
80	3,410	3,284	3,163	3,046	2,935	2,828	2,727	2,629	2,536	2,447
90	2,361	2,279	2,200	2,124	2,051	1,981	1,914	1,850	1,788	1,728
100	1,671.0	1,617.0	1,564.0	1,513.0	1,465.0	1,418.0	1,373.0	1,329.0	1,287.0	1,247.0
110	1,209.0	1,172.0	1,136.0	1,101.0	1,068.0	1,036.0	1,005.0	974.4	945.5	917.5
120	890.7	864.0	839.7	815.5	792.0	769.4	747.5	726.5	706.1	686.4
130	667.3	648.8	631.0	613.8	597.1	581.1	565.5	550.3	535.6	521.4
140	507.7	494.4	481.6	469.1	457.1	445.4	434.0	423.0	412.4	402.1
150	391.1	382.4	372.9	363.8	355.0	346.4	338.0	329.9	321.9	314.3
160	306.8	299.6	292.6	285.9	279.3	272.8	266.6	260.6	254.7	248.9
170	243.3	237.9	232.6	227.5	222.4	217.5	212.8	208.2	203.7	199.3
180	195.1	—	—	—	—	—	—	—	—	—

Calculated by Holborn, Scheel and Henning (Wärmetabellen, 1919) from the results of Holborn and Henning (Ann. Physik. 1908, [iv.] 28, 833) and Henning (ibid. 1908, [iv.] 21, 849; 1909, [iv.] 29, 441). See also J. Southern, Phil. Mag. 1903, 17, 120.

superheated steam is similarly given at 10° intervals of temperature and for pressures from 1-19 kgm./cm.² in Table 9.

The specific volume is given for super-cooled water from -13° to 0° in Table 10, and for stable water from 0°-35° by tenths of a

degree in Table 12, from 30°-100° by degrees in Table 14, and, under pressure of the saturated vapour for ten-degree intervals, from 100°-320° in Table 15. For convenience, the same data in terms of specific gravity are given also in Tables 10, 11, 13 and 15.

TABLE 9.

SPECIFIC VOLUME OF SUPERHEATED STEAM.

Cubic centimetres per gram (M. Jakob, Zeits. Ver. Ing. 1912, 56, 1980).

Temperature	Pressure in kilograms per square centimetre.									
	1	3	5	7	9	11	13	15	17	19
Saturation temperature.	1728.1	618.2	382.6	278.5	219.5	181.3	154.6	134.6	119.3	107.1
110	1781.6	—	—	—	—	—	—	—	—	—
120	1830.2	—	—	—	—	—	—	—	—	—
130	1878.9	—	—	—	—	—	—	—	—	—
140	1927.3	630.5	—	—	—	—	—	—	—	—
150	1975.5	647.6	—	—	—	—	—	—	—	—
160	2023.7	664.6	392.3	—	—	—	—	—	—	—
170	2071.6	681.4	403.0	283.3	—	—	—	—	—	—
180	2119.6	698.1	413.6	291.3	223.2	—	—	—	—	—
190	2167.4	714.6	423.9	299.2	229.6	185.2	—	—	—	—
200	2215.2	731.1	434.2	306.8	235.9	190.6	159.1	135.9	—	—
220	2310.7	763.9	454.4	321.7	247.9	200.9	168.3	144.3	125.9	111.3
240	2406.0	796.4	474.4	336.4	259.7	210.8	177.0	152.0	133.0	118.0
260	2501.1	828.8	494.2	350.9	271.2	220.5	185.3	159.5	139.7	124.2
280	2596.0	861.1	514.0	365.3	282.6	230.0	193.5	166.8	146.3	130.2
300	2690.9	893.2	533.7	379.5	293.9	239.3	201.6	173.9	152.7	135.9
350	2927.0	973.3	582.4	414.7	321.7	262.4	221.4	191.3	166.3	150.1
400	3164.3	1052.9	630.6	449.6	349.1	285.0	240.7	210.9	183.4	163.7
450	3400.6	1132.3	678.6	484.2	376.2	307.4	259.7	224.8	198.1	177.1
500	3636.4	1211.3	726.2	518.4	402.9	329.4	278.5	241.2	212.6	190.1
550	3872.2	1290.2	773.8	556.8	429.5	351.2	297.1	257.3	226.9	202.9

TABLE 10.

SPECIFIC GRAVITY AND SPECIFIC VOLUME OF WATER BELOW 0°.

Temperature	Specific gravity (1)	Specific volume	
		(1)	(2)
-13	—	—	1.00308
-12	—	—	1.00271
-11	—	—	1.00237
-10	0.99815	1.00186	1.00207
-9	0.99843	1.00157	1.00175
-8	0.99869	1.00131	1.00150
-7	0.99892	1.00108	1.00128
-6	0.99912	1.00088	1.00105
-5	0.99930	1.00070	1.00082
-4	0.99945	1.00055	1.00062
-3	0.99958	1.00042	1.00045
-2	0.99970	1.00031	1.00033
-1	0.99979	1.00021	1.00023
0	0.99987	1.00013	1.00013

1. Weidner, Pogg. Ann. 1866, 129, 300; Rosetti, Ann. Chim. 1869, [iv.] 17, 329.
2. Mohler, Phys. Review, 1912, 35, 236.

TABLE 11.

DENSITY OF WATER IN GRAMS PER CUBIC CENTIMETER.

At temperatures from 0° to 35° on the constant volume gas-thermometer (Reichsanstalt) scale.

(Landolt-Börnstein: *Physikalische-Chemische Tabellen.*)

Degrees.	Tenths of a degree									
	0'0	0'1	0'2	0'3	0'4	0'5	0'6	0'7	0'8	0'9
0	0.999,868	874	881	887	893	899	905	911	916	922
1	927	932	936	941	945	950	954	957	961	965
2	968	971	974	977	980	982	985	987	989	991
3	992	994	995	996	997	998	999	999	000*	000*
4	1.000,000	000	000	099*	999*	998*	997*	996*	995*	993*
5	0.999,992	990	989	986	984	982	979	977	974	971
6	968	965	962	958	954	951	947	943	938	934
7	929	925	920	915	910	904	899	893	888	882
8	876	870	864	857	851	844	837	830	823	816
9	808	801	793	785	778	769	761	753	744	736
10	727	718	709	700	691	681	672	662	652	642
11	632	622	612	601	591	580	569	558	547	536
12	525	513	502	490	478	466	454	442	429	417
13	404	391	379	366	353	339	326	312	299	285
14	271	257	243	229	215	200	186	171	156	141
15	126	111	096	081	065	050	034	018	002	986*
16	0.998,970	953	937	920	904	887	870	853	836	819
17	801	784	766	749	731	713	695	677	659	640
18	622	603	585	566	547	528	509	490	471	451
19	432	412	392	372	352	332	312	292	272	251
20	230	210	189	168	147	126	105	083	062	040
21	019	997*	975*	953*	931*	909*	887*	864*	842*	819*
22	0.997,797	774	751	728	705	682	659	635	612	588
23	565	541	517	493	469	445	421	396	372	347
24	323	298	273	248	223	198	173	147	122	096
25	071	045	019	994*	968*	941*	915*	889*	863*	836*
26	0.996,810	783	756	730	703	676	648	621	594	567
27	539	512	484	456	428	400	372	344	316	288
28	259	231	202	174	145	116	087	058	029	000
29	0.995,971	941	912	882	853	823	793	763	733	703
30	673	643	613	582	552	521	491	460	429	398
31	367	336	305	273	242	211	179	148	116	084
32	052	020	988*	956*	924*	892*	859*	827*	794*	762*
33	0.994,729	696	663	630	597	564	531	498	464	431
34	398	364	330	296	263	229	195	161	126	092
35	058	023	989*	954*	920*	885*	850*	815*	780*	745*

Thiesen, Scheel and Diessehorst, *Wiss. Abh. Phys.-Tech. Reichsanstalt*, 1900, 3, 68; Chappuis, *Trav. Bur. Int.* 1904, 13.

TABLE 12.

SPECIFIC VOLUME OF WATER IN CUBIC CENTIMETRES PER GRAM.

At temperatures from 0° to 35° on the constant volume gas-thermometer (Reichsanstalt) scale.

Degrees.	Tenths of a Degree									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	1.000,132	126	119	113	107	101	095	089	084	079
1	073	069	064	059	055	051	047	043	039	035
2	032	029	026	023	020	018	016	013	011	009
3	008	006	005	004	003	002	001	001	000	000
4	000	000	000	001	001	002	003	004	005	007
5	008	010	012	014	016	018	021	023	026	029
6	032	035	039	042	046	050	054	058	062	066
7	071	075	080	085	090	096	101	107	112	118
8	124	130	137	143	149	156	163	170	177	184
9	192	199	207	215	223	231	239	247	256	264
10	273	282	291	300	309	319	328	338	348	358
11	368	378	388	399	409	420	431	442	453	464
12	476	487	499	511	522	534	547	559	571	584
13	596	609	622	635	648	661	675	688	702	715
14	729	743	757	772	786	800	815	830	844	859
15	874	890	905	920	936	951	967	983	999	015*
16	1.001,031	048	064	081	098	114	131	148	165	183
17	200	218	235	253	271	289	307	325	343	361
18	380	399	417	436	455	474	493	513	532	551
19	571	591	610	630	650	671	691	711	732	752
20	773	794	815	836	857	878	899	921	942	964
21	985	007*	029*	051*	073*	096*	118*	140*	163*	186*
22	1.002,208	231	254	277	300	324	347	370	394	418
23	441	465	489	513	538	562	586	611	635	660
24	685	710	735	760	785	810	835	861	886	912
25	938	964	990	016*	042*	068*	094*	121*	147*	174*
26	1.003,201	227	254	281	308	336	363	390	418	445
27	473	501	529	556	585	613	641	769	608	726
28	755	783	812	841	870	899	928	957	987	016*
29	1.004,046	075	105	135	165	194	225	255	285	315
30	346	376	407	437	468	499	530	561	592	623
31	655	686	717	749	781	812	844	876	908	940
32	972	005*	037*	070*	102*	135*	167*	200*	233*	266*
33	0.005,299	332	365	399	432	465	499	533	566	600
34	634	668	702	736	771	805	839	874	908	943
35	978	013*	047*	082*	118*	153*	188*	223*	259*	294*

Thiesen, Scheel and Diessehorst, Wiss. Abh. Phys.-Tech. Reichsanstalt, 1900, 3, 69; Chappuis, Trav. Bur. Int., 1904, 13.

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TABLE 13.
DENSITY OF WATER FROM 30° TO 100°.

Tens of Degrees	Degrees									
	0	1	2	3	4	5	6	7	8	9
30	0.99567	537	505	473	440	406	371	336	299	262
40	224	186	147	107	066	024	*982	*940	*896	*852
50	0.98807	762	715	669	621	573	525	475	425	375
60	324	272	220	167	113	059	005	*950	*894	*838
70	0.97781	723	666	607	548	489	429	368	307	245
80	183	121	057	*994	*930	*865	*800	*734	*668	*601
90	0.96534	467	399	330	261	192	122	051	*981	*909
100	0.95838	765	693	—	—	—	—	—	—	—

TABLE 14.
SPECIFIC VOLUME OF WATER FROM 30° TO 100°.

Tens of Degrees.	Degrees									
	0	1	2	3	4	5	6	7	8	9
30	1.00435	466	497	530	563	598	633	669	706	743
40	782	821	861	901	943	985	*028	*072	*116	*162
50	1.01207	254	301	349	398	448	498	548	600	652
60	705	758	813	867	923	979	*036	*093	*151	*210
70	1.02270	330	390	452	514	576	639	703	768	833
80	899	965	*032	*099	*168	*237	*306	*376	*447	*518
90	1.03590	663	736	810	884	959	*035	*111	*188	*265
100	1.04343	422	501	—	—	—	—	—	—	—

Thiessen, Wiss. Abh. Phys.-Tech. Reichsanstalt, 1904, 4, 1.

TABLE 15.
DENSITY AND SPECIFIC VOLUME OF WATER FROM 100° TO 320°.

Temperature.	Density	Specific Volume
100°	0.9585	1.0433
110	0.9510	1.0515
120	0.9434	1.0601
130	0.9352	1.0693
140	0.9264	1.0794
150	0.9173	1.0902
160	0.9075	1.1019
170	0.8973	1.1145
180	0.8866	1.1279
190	0.8750	1.1429
200	0.8628	1.1590
210	0.850	1.177
220	0.837	1.195
230	0.823	1.215
240	0.809	1.236
250	0.794	1.259
260	0.779	1.283
270	0.765	1.308
280	0.75	1.34
290	0.72	1.38
300	0.70	1.42
310	0.68	1.46
320	0.66	1.51

Mean values by Ramsay and Young, Phil. Trans. 1893, 183, 168; Waterston, Phil. Mag. 1863, [iv.] 22, 116; and Hrn, Ann. Chim. 1866, [iv.] 10, 32.

TABLE 16.

DENSITY AND EXPANSIBILITY OF ICE.

Date	Au- thority	Method of experiment	Kind of ice	Natural ice		Artificial ice	
				Density	α	Density	α
1845	1	Weighing in liquid	Natural .	0.9179	0.0001125	—	—
1845	2	Direct measurement of linear coefficient .	Artificial .	—	—	—	0.0001593
1845	3	Dilatometric .	Not stated .	—	[0.0001050]	—	[0.0001050]
1852	4	Dilatometric .	Artificial .	—	—	0.91567	0.0001595
1862	5	Neutrals equilibrium in liquid (chloroform and petroleum)	Artificial .	—	—	0.9177	—
1870	6	Dilatometric .	Artificial .	—	—	0.91674	—
		Dilatometric .	Artificial .	—	—	0.91619	—
		Dilatometric .	Artificial .	—	—	0.91603	—
		Dilatometric .	Artificial .	—	—	0.91603	—
1899	7	Weighing in liquid (refined petroleum)	Natural (icles)	0.91795	—	—	—
			Natural (new pond ice)	0.91792	—	—	—
			Natural (pond ice, 1 year old)	0.91623	—	—	—
		Volume by displace- ment	Natural (new pond ice)	0.91760	—	—	—
		Direct measurement of linear coefficient .	Artificial .	—	—	—	0.0001620
1901	8	Weighing in water	Natural (old and new)	0.91661	—	—	—
1902	9	Direct weighing of buoyancy in mercury	Artificial .	—	—	0.9160	0.000152
Means, neglecting results of No. 3				0.9174	0.0001125	0.9165	0.000153

1. Brunner, Pogg. Ann. 1845, 64, 116.

2. Struve, Pogg. Ann. 1845, 66, 298.

3. Marchand, J. prakt. Chem. 1845, 35, 254.

4. Plücker and Geissler, Pogg. Ann. 1852, 86, 265.

5. Dufour, Compt. rend. 1862, 34, 1080.

6. Bunsen, Pogg. Ann. 1870, 141, 1.

7. Nichols, Phys. Review, 1899, 8, 21.

8. Barnes, Phys. Zeit. 1901, 3, 81; Barnes and Cooke, Trans. Roy. Soc. Canada, 1902, 8, (iii.), 143.

9. Vincent, Proc. Roy. Soc., 1902, 69, 422.

A large number of formulae, for the most part entirely empirical, have been proposed to express the variation of volume of water with temperature, and these are collected, e.g. in Landolt-Börnstein Tabellen, 1921, p. 1231.

As examples the following may be given for water from 0°–40° and from 17°–100° respectively, due to Thiesen, Scheel and Dieckelhorst (Wiss. Abh. Phys.-Tech. Reichsanstalt, 1900, 3, 1) and Thiesen (Wiss. Abh. Phys.-Tech. Reichsanstalt, 1903, 4, 1). If s = the density,

$$1 - s = \frac{(t - 3.28)^2}{503570} \times \frac{t + 283}{t + 67.26} \quad (\text{from } 0^\circ - 40^\circ)$$

$$1 - s = \frac{(t - 3.982)^2}{466700} \times \frac{t + 273}{t + 67} \times \frac{350 - t}{365 - t} \quad (\text{from } 17^\circ - 100^\circ)$$

These volume changes may also be considered in terms of the coefficient of cubical expansion α ,

which varies with temperature in the general manner indicated below:

Temp.	20°	40°	50°	100°	140°	180°	200°
$\alpha \times 10^6$	110	217	305	452	584	722	788

(See Meyer, Nernst's Festschrift, Halle a. S., 1912, 278; Hirn, Ann. Chim. 1866, [iv.] 10, 32; Tammann and Zepernik, Zeitsch. physikal. Chem. 1895, 16, 659.)

Despite many investigations our knowledge of the density and expansion of ice is not entirely satisfactory. Table 16 gives an indication of the methods adopted, the kinds of ice used, and the final results obtained in the chief researches on the subject; the papers by Barnes and Cooke and by Vincent, cited in the Table, contain critical reviews of earlier work and should be consulted for more detailed information.

Upon examination it is at once apparent

that these data differ among themselves by amounts much greater than any experimental error to which the actual determination of density can conceivably be subject.

With isolated exceptions the values for natural ice approximate to 0.918, whilst those for artificial ice are near 0.916. The mean values in the Table are respectively less than and greater than these figures, because they each include exceptional data which appear from their magnitude to belong to the other classification. Nichols first drew attention to this apparently systematic difference, and his experiments seem to show firstly, that it is real, and secondly, that the density of natural ice decreases with lapse of time until it approaches that of artificial ice. The experiments of Barnes and Cooke, made with natural ice from the St. Lawrence river, which had been in storage for various periods up to three years, confirm the correctness of the lower value for old natural ice, but it seems probable that none of their samples of ice were as recently formed as those which other observers had found of high density, and their conclusion that age has no effect on the density of ice is open to doubt.

Cooke (Trans. Roy. Soc. Canada, 1902, 8 [iii.] 127), in a discussion of these and earlier results, advances the view that the differences arise from stresses produced in the mass of ice by certain modes of freezing, but it is evident that Nichols' results with icicles discount this hypothesis. Vincent, measuring directly the upward pull exerted by a mass of water or ice completely immersed in mercury, confirmed generally the lower value for artificial ice, but obtained very definite evidence that the same specimen of water can, on different occasions, freeze into specimens of ice having distinctly different densities.

Further investigation is clearly needed on this point, and in the meantime the density of ice may perhaps best be taken at the mean value of 0.917.

Leduc has attempted to show that the observed differences may be due to variation in the content of dissolved air, but this explanation seems inadequate, especially in view of Vincent's results; he finds ice prepared by repeatedly freezing *in vacuo* water previously boiled to expel gases has a density of 0.9176 (Compt. rend. 1906, 142, 149).

The difference between the density at 0° of water, 0.99987, and ice, 0.917, nearly 13 p.c.,

is a measure of the great expansion which takes place when water is frozen. Many important practical consequences of this expansion are well known. Freezing water produces disruptive effects in the cells of plant and animal tissues and in pipes and containers of all sorts, and these effects, occurring in the crevices of rocks, stones and buildings, and of the soil, cause progressive superficial disintegration. When water is cooled by contact with cold air, ice is formed, and because of its lower density remains, on the surface; the temperature of the bulk of water does not fall below 4°C., the temperature of maximum density, at which cooling by convection ceases. When water in process of cooling is continuously mixed, as in running streams, and free radiation occurs from the bed-rock to a clear atmosphere through shallow water, the temperature of the bed-rock and the water in contact with it may fall below 0°, when the so-called 'ground,' 'anchor' or 'frazil' ice is formed at the bottom.

Freezing of Water in Capillary Systems.—Much of the water of soils and inorganic gels fails to freeze, even at temperatures as low as -78°, because it is physically adsorbed, chemically combined, or in solid solution. E. A. Fisher (J. Physical Chem. 1924, 28, 360) points out that water present in very fine capillary tubes or pores must be under considerable tension, and so the density may not necessarily be the same as that of water in bulk, but probably less. Hence the expansion on freezing will probably be less, and since the amount of water which fails to freeze is determined by dilatometric measurements, false conclusions may thus be drawn (Chem. Soc. Abstr. 1924, 126, ii, 391).

Temperature of Maximum Density.—The data given in Tables 11 and 12 show the well-known fact that water attains a maximum density at about 4°C. Precise investigation has fixed the temperature as 3.98° at atmospheric pressure (Chappuis, Wied. Ann. 1897, 63, 202; Thiesen, Scheel and Diesselhorst, Wiss. Abh. Phys.-Tech. Reichsanstalt, 1900, 3, 68; de Coppet, Ann. Chim. 1903, [vii.] 28, 145).

At higher pressures the temperature of maximum density of water falls progressively in the manner shown in Table 17, and expressed in the following formula (Lussana, Nuovo Cim. 1910, [v.] 19, 182)

$$t_m = 4.10^{\circ} - 0.0225(p-1)$$

TABLE 17.

VARIATION OF THE TEMPERATURE OF MAXIMUM DENSITY OF WATER WITH PRESSURE.

Pressure.	Temperature of Maximum Density.	
1 atmo.	4.08°	Grassi, Ann. Chim. 1851, [iii.] 31, 437.
1.75 "	4.0	
2.85 "	3.9	
4.06 "	3.8	
5.5 "	3.7	
6.9 "	3.6	
8.6 "	3.5	
10.5 "	3.4	
41.6 "	3.3	Amagat, Compt. rend. 1903, 116, 946.
93.3 "	2.0	
144.6 "	0.6	

For this reason in specifying water at its temperature of maximum density as the standard of density, it is necessary to stipulate that the pressure must be normal. It is also lowered by the presence of dissolved salts. For a given salt, the lowering is proportional to the concentration of the solute (Law of Despretz, *Ann. Chim.* 1839, [ii.] 70, 49; 1840, [ii.] 73, 296), but it is not connected with the depression of the freezing-point and is not a colligative property (Rosetti, *Ann. Chim.* 1867, [iv.] 10, 461; 1869, [iv.] 17, 370). The molecular lowering of the temperature of maximum density by salts of monovalent ions (e.g. H^+ , Li^+ , Na^+ , K^+ and NH_4^+ with Cl^- , Br^- , I^- and NO_3^-) does exhibit a regularity in that it can be calculated from the molecular lowering of HCl (the lowest) by adding two numbers, characteristic respectively of the particular base and acid present (Wright, *J. Chem. Soc.* 1919, 115, 119): weak acids, and the salts of divalent acid and basic radicles, show no such regularity (de Coppet, *Ann. Chim.* 1894, [vii.] 3, 246, 268; *Compt. rend.* 1897, 125, 533; 1899, 128, 1559; 1900, 131, 178; 1901, 132, 1218; 1902, 134, 1208).

THE RELATION OF VOLUME AND PRESSURE FOR WATER AND ICE.

The effect of large variations of pressure upon the volume of water or ice is usually expressed in terms of the compressibility coefficient β where

$$\beta = \frac{1}{V_1} \times \frac{V_1 - V_2}{p_2 - p_1}$$

where V_1 = the volume at an initial pressure p_1 ,

and V_2 the volume at a higher pressure p_2 , at the same temperature; β is evidently the fraction by which the original volume is reduced for unit increase of pressure.

Table 18 gives the values of $\beta \times 10^6$ for water according to Amagat for pressures from 1-3000 atmospheres and temperatures from 0°-200°C. Table 19 gives the results, more accurately, but relating to a much smaller range of temperature and pressure, obtained by Richards and Stull and by Tyrer, and, for comparison, those of Bridgman at 0° and 22°.

The same data can, of course, be expressed in terms of specific volume, and Table 20 gives this quantity for water over a range of pressure from 0-12,000 kgm./cm.^2 and from -20° to +80°C.

Normal liquids show a compressibility which decreases with rise of pressure and increases with rise of temperature. These data show that the compressibility of water is thus affected by rise of pressure, but that increase of temperature up to about 50° lowers the compressibility; at higher temperatures the compressibility of water increases with rise of temperature like that of other liquids. The significance of this fact in relation to current hypotheses of the constitution of water is discussed elsewhere. The relation of the coefficient of expansion of water to pressure and temperature is given in Table 21. Experiments upon the isopiestic expansion of water at higher temperatures and pressures show that the thermal expansibility increases with temperature to a maximum value, which is the less the greater the pressure (Watson, *Proc. Roy. Soc. Edin.* 1911, 31, 456).

TABLE 18.
COEFFICIENT OF COMPRESSIBILITY β FOR WATER.
(Tabulated data are $\beta \times 10^6$).

Temp.	0°	5°	10°	15°	20°	30°	40°	50°	60°	70°	80°	100°	200°
Press. At.													
1-100	51.1	49.3	48.3	47.3	46.8	46.0	44.9	44.9	45.5	46.2	—	47.8	—
100-200	49.2	47.5	46.1	45.1	44.2	43.6	42.9	42.5	42.7	43.9	—	46.8	80.7
200-300	48.0	46.2	45.3	44.3	43.4	42.2	41.4	41.3	41.5	42.5	43.6	45.9	76.9
300-400	46.6	44.9	44.1	43.3	42.4	41.3	40.7	40.2	40.6	41.1	42.2	44.6	73.1
400-500	45.5	44.4	43.0	42.2	41.5	40.6	40.4	39.9	39.4	39.8	40.8	43.4	68.2
500-600	43.8	43.0	41.8	41.1	40.4	39.2	39.0	39.0	38.8	39.1	39.9	41.6	66.0
600-700	42.9	40.9	40.5	39.8	39.4	38.7	38.2	37.7	38.3	38.0	38.7	40.7	62.7
700-800	41.8	40.7	39.8	39.0	38.8	37.5	37.4	37.1	36.9	37.4	37.8	38.9	61.3
800-900	40.6	39.3	38.9	38.0	37.3	36.8	36.2	36.2	36.3	36.6	36.8	38.2	58.9
900-1000	—	—	—	36.8	36.5	36.0	35.3	35.3	36.0	35.1	36.2	37.1	56.5

Temp.	0°	5°	10°	15°	20°	Temperature	0°	5°	10°	15°	20°	50°
Press. At.						Press. atmo.						
1-25	52.5	51.2	50.0	49.5	49.1	1-500	47.5	45.8	44.7	43.8	43.4	61.4
25-50	51.6	49.0	49.2	48.0	47.6	500-1000	41.6	40.0	39.5	39.1	38.0	36.6
50-75	50.9	48.5	47.3	46.5	45.6	1000-1500	35.8	35.5	34.8	34.4	33.8	32.5
75-100	50.2	48.1	47.0	45.7	45.3	1500-2000	32.4	31.8	31.3	31.2	30.9	30.0
100-125	49.4	47.7	46.6	45.4	44.9	2000-2500	29.2	28.0	28.9	28.0	27.8	27.5
125-150	49.1	47.5	46.3	45.4	44.6	2500-3000	26.1	26.4	25.8	26.1	25.7	25.4
150-175	49.1	47.5	46.3	45.1	44.2							
175-200	48.8	47.2	46.0	44.7	43.8							

Amagat, *Ann. Chim.* 1893, [vi.] 29, 68, 505.

TABLE 19:
VARIATION OF THE COEFFICIENT OF COMPRESSIBILITY β FOR
WATER WITH PRESSURE.

Temperature	Pressure range: atmo.	$\beta \times 10^6$	Reference
20°	0—98.7	45.8	1
"	98.7—197.4	44.8	
"	197.4—296	42.4	
"	296—395	41.7	
"	395—494	39.9	
0°	1—2	50.28	2
10°	" "	47.80	
20°	" "	45.90	
60°	" "	44.82	
100°	" "	48.18	
0°	0—484	46.2	3
"	1450—1935	31.2	
"	2900—3390	24.4	
"	4350—4840	20.6	
"	6290—6760	14.2	
22°	0—970	39.6	
"	2900—3870	23.8	
"	5800—6760	16.3	
"	9680—10,620	9.6	

1. Richards and Stull, J. Amer. Chem. Soc. 1904, 26, 399.
2. Tyrer, J. Chem. Soc. 1913, 103, 1675.
3. Bridgman, Proc. Amer. Acad. 1912, 47, 347, 439.

TABLE 20.
SPECIFIC VOLUME OF WATER, C.C. PER GRAM, OVER A RANGE OF TEMPERATURE AND PRESSURE.

Pressure, kgm./cm. ²	Temperature										
	-20°	-10°	0°	+10°	20°	30	40°	50°	60°	70°	80°
0	—	1.0018	1.0001	1.0002	1.0017	1.0042	1.0077	1.0119	1.0169	1.0225	1.0288
1,000	—	0.9599	0.9579	0.9603	0.9631	0.9664	0.9701	0.9744	0.9792	0.9843	0.9897
2,000	0.9229	0.9244	0.9261	0.9294	0.9328	0.9365	0.9404	0.9446	0.9490	0.9538	0.9586
3,000	0.8964	0.8985	0.9016	0.9051	0.9088	0.9106	0.9165	0.9206	0.9248	0.9293	0.9338
4,000	—	0.8775	0.8808	0.8844	0.8881	0.8898	0.8957	0.8997	0.9038	0.9081	0.9124
5,000	—	0.8600	0.8633	0.8667	0.8703	0.8720	0.8779	0.8819	0.8859	0.8900	0.8941
6,000	—	—	0.8481	0.8510	0.8546	0.8565	0.8624	0.8663	0.8703	0.8743	0.8782
7,000	—	—	—	0.8371	0.8405	0.8426	0.8486	0.8525	0.8565	0.8603	0.8641
8,000	—	—	—	—	0.8276	0.8301	0.8361	0.8400	0.8439	0.8478	0.8514
9,000	—	—	—	—	0.8161	0.8209	0.8250	0.8289	0.8328	0.8365	0.8402
10,000	—	—	—	—	—	0.8190	0.8150	0.8189	0.8227	0.8265	0.8301
11,000	—	—	—	—	—	—	0.8057	0.8096	0.8134	0.8171	0.8207
12,000	—	—	—	—	—	—	0.7967	0.8006	0.8044	0.8081	0.8116

P. W. Bridgman, Proc. Amer. Acad. 1912, 48, 338.

Increase of pressure does not shift the temperature of minimum compressibility, but at high pressures this minimum disappears (Bridgman, Zettech. anorg. Chem. 1912, 77, 377).

Small as is the compressibility of water it has important practical effects and uses. It has been calculated that were water incompressible the mean sea-level would be 116 feet higher than it actually is, whereby about 4 p.c. of existing

land would be submerged (Tait, Proc. Roy. Soc. Edin. 1884, 12, 46; 1892, 20, 63, 141). Compression waves in water are transmitted with high velocity and are applied in the Constantinesco 'wave-power' system to attain the economical transmission of power, e.g. from a central motor to drilling machines or the like in mines, with an efficiency comparable with that of electrical transmission and with the

TABLE 21.

WATER—COEFFICIENT OF THERMAL EXPANSION AT HIGH PRESSURES.

Temperature	Coefficient of cubical expansion at		
	1 atmo.	500 atmo.	3000 atmo.
0°-10°	0.000012	0.000156	0.000383
0°-30°	0.000138	0.000229	0.000415
0°-50°	0.000238	0.000295	0.000413

Amagat, Compt. rend. 1887, 105, 1120.

convenience and safety characteristic of compressed air.

The compressibility of ice at -7.03° for a range of pressure from 100-500 megabars is 0.0000120 (Richards and Speyers, J. Amer. Chem. Soc. 1914, 36, 491), or about one quarter that of water at 0° ; it does not decrease greatly with increase of pressure. The much higher value calculated by Bridgman (0.000036) probably indicates that the temperature coefficient of increase of compressibility for ice is abnormally high.

In considering the remaining physical properties of water it is convenient to take them in a systematic order for all forms of water, under the main groups, mechanical, thermal, optical and magnetic, and electrical.

MECHANICAL PROPERTIES.

Crystal Form.—Ice crystals, as exemplified by snow, can assume a great variety of forms which are commonly characterised by extreme openness of structure and consequent lightness; they are readily formed by the condensation of water vapour below 0° as hoar frost. Liquid water, if free from dissolved air, freezes to clear transparent ice which may give indications of structure by transmitted light or on melting, but has usually no external crystalline form. Solid, well-defined crystals of ice are extremely rare.

Though liquid water, if perfectly pure and free from dust, can be cooled to about -15° without solidification (Thomson, Trans. Roy. Soc. Edin. 1849, 18, 575; Sorby, Phil. Mag. 1859, [iv.] 18, 105), ice always melts at a definite and fixed temperature at atmospheric pressure,

and its melting-point is therefore used to define the zero point of thermometric scales. The melting-point is lowered by increase of pressure, and this has been adduced in explanation of the phenomenon of *regelation* or welding of separate pieces of ice, and is illustrated by the well-known experiment in which a weighted loop of wire cuts through, but does not sever, a block of ice.

Ice separating from under-cooled water forms hexagonal crystal skeletons or spherulites, according to the degree of under-cooling, and is obtained in feathery forms from very dilute solutions; but inoculation of under-cooled pure water with these forms produces identical forms of ice (Hartmann, Zeitsch. anorg. Chem. 1914, 88, 128).

The crystalline form of ice is hexagonal-bipyramidal with the axial ratio $a:c$ approximately 1:1.6 (Nordenskiöld, Oefv. Akad. Förh. Stockholm, 1860, 17, 439; Rinne, Ber. Sachs. Ges. Wiss. 917, 69, 57). Its X-ray spectrum has been investigated (St. John, Proc. Nat. Acad. Sci. 1918, 4, 193; Dennison, Phys. Rev. 1921, 17, 20), and the results are interpreted by Bragg (Proc. Physical Soc. 1922, 34, 98) on the assumption that the molecules are separated into positive and negative ions arranged in a hexagonal lattice in such a manner that each oxygen atom is situated at the centre of gravity of four neighbouring oxygen atoms, from each of which it is separated by a hydrogen ion situated midway between. The extremely open character of the structure is in accordance with the low density of ice.

The velocity of crystallisation of water in long tubes, 12 mm. external and 7 mm. internal diameter, increases with the degree of under-cooling as follows:—

Temp.	-2°	-3.61°	-4.67°	-5.86°	-6.18°	-7.10°	-8.19°	-9.07°
Velocity cm./min.	31.6	48.4	71.4	107.1	114.7	266.7	415.2	684.0

(Walton and Judd, J. Phys. Chem. 1914, 18, 722, which see for a useful summary of earlier work), but at any given temperature is retarded by the presence of dissolved acids, salts, dyes, &c. The retardation is not a colligative property of the solute, but appears to depend upon the extent to which the solute is hydrated in solution (Walton and Brann, J. Amer. Chem. Soc. 1916, 38, 317; Brann, *ibid.* 1918, 40, 1188).

Colloidal ice has been obtained by cooling

solutions of water in ether or chloroform, in some cases with the use of fatty acids or rubber as protective colloids (v. Weimarn and Ostwald, Zeitsch. Chem. Ind. Kolloide, 1910, 9, 181; J. Russ. Phys. Chem. Soc. 1910, 42, 226).

Elasticity.—A mass of ice yields steadily to pressure, e.g. a bar of glacier ice supported at the ends and loaded in the middle is slowly deflected, and ice compressed in a cylinder flows steadily, and the flow once started can be maintained by relatively small pressures (How,

Ann. Physik, 1902, [iv.] 8, 405). Curiously, the bar of ice when relieved from its load slowly recovers its original form. It has been shown that a bar of ice cut from a single crystal with its length perpendicular to the optic axis is brittle and does not yield to tension or pressure (McConnel, Proc. Roy. Soc. 1891, 49, A. 323), and the behaviour of ordinary ice is therefore

probably attributable to slipping of crystal layers of finite thickness.

The conflicting results of earlier investigators are thus explained, and it is necessary only to record the determinations of modulus of elasticity E and bending moment B in grm. cms. made by Hess (L.c.) upon bars of ice cut from single crystals as tabulated below:

Elasticity of Ice.

Load in gm. on beam 1.2 cm. \times 2.5 cm. \times 4-16 cm.	Length parallel to crystal axis			Width parallel to crystal axis			Thickness parallel to crystal axis		
$E \times 10^{-10} =$	2000	5000	8000	1000	2000	3000	1000	1500	2000
$B =$	0.54	0.70	0.75	3.5	2.9	4.0	1.6	2.0	2.0
	1350	3400	4000	1500	3000	4450	1600	2350	3100

The recovery of bent ice on removal of stress is much greater than similar effects in other substances, and has not been adequately explained.

The rate of plastic flow of ice is small at low temperatures, but increases rapidly near the melting-point (Tammann, Ann. Physik, 1902, [iv.] 7, 198; Slatowratsky and Tammann, Zeitsch. physikal. Chem. 1905, 53, 341), and a similar variation characterises the hardness of ice. On Mohs' scale the hardness is about 1.5, but as measured by the penetration of a steel rod into a block of ice it is considerably greater at temperatures from -37° to -12° than at about -7° , and at the melting-point ice becomes relatively quite soft (Andrews, Proc. Roy. Soc. 1898, 40, A. 544).

Frictional resistance to motion on the surface of ice is clearly related to the above phenomena; it is greater for small pressures than for large, the respective values of the coefficient of friction being 0.36 and 0.17 (Morphy, Phil. Mag. 1913, [vi.] 25, 133).

Liquid water appears to have, like some other liquids, tensile strength. If a glass tube containing only water and its vapour and nearly filled with the former be warmed until the liquid thus expanded just fills the tube, and then allowed to cool, the water continues to fill the tube even when its volume is thereby greater by about $\frac{1}{100}$ th than that corresponding to its temperature. It is hence calculated that the tensile strength of water is some 700-900 lbs./sq. in. (Berthelot, Ann. Chim. 1850, [iii.] 30, 232; see also Budgett, Proc. Roy. Soc. 1912, 86, A. 25). The rupture of a stream of water flowing through a constriction in a pipe is probably a true tensile rupture, especially as the tensile strength, deduced from the velocity at which rupture occurs, diminishes with rise

of temperature and becomes zero at about 250° (Skinner and Entwistle, Proc. Roy. Soc. 1915, 91, A. 481; Skinner and Burfitt, Proc. Physical Soc. 1919, 31, 131), in accordance with Larmor's calculation from van der Waal's equation that the tensile strength of water could subsist only up to about 265° (Larmor, Proc. London Math. Soc. 1916, [ii.] 15, 191).

The compressibility of water has already been discussed in relation to the attendant volume change, but it must here be noted that it connotes a *bulk elasticity* which is related in the usual manner to the velocity of sound in the medium. Experimental determinations of the velocity have given the following results: At 8.1° , 1435 metres/sec. (Colladen and Sturm, Ann. Chim. 1827, [ii.] 36, 113, 225; Pogg. Ann. 1828, 12, 39, 161); at 3.9° , 1399 m./sec.; at 13.7° , 1437 m./sec.; at 25.2° , 1457 m./sec. (Martini, Wied. Beibl. 1888, 12, 566; Nuovo Cimento, 1909, [v.] 18, 441).

The velocity of sound in water vapour is 401 m./sec. at 0° (Masson, Compt. rend. 1857, 44, 464; Phil. Mag. 1857, [iv.] 13, 533), and about 410 m./sec. at 100° (Jäger, Wied. Ann. 1889, 36, 165).

Viscosity.—The viscosity of water vapour has been determined at about the ordinary temperature by several observers with substantially concordant results as follows:—

At 0° , $\eta = 90.4 \times 10^{-6}$ C.G.S. units; at 16.7° , $\eta = 96.7 \times 10^{-6}$ (Puluj, Sitzungsber. Akad. Wiss. Wien. 1878, 78 (2), 279); at 18.8° , $\eta = 97.5 \times 10^{-6}$ (Kundt and Warburg, Pogg. Ann. 1875, 155, 337, 525); at 28.9° , $\eta = 100.6 \times 10^{-6}$ (H. Vogel, Ann. der Physik, 1914, 43, 1235).

For undercooled water below 0° the most probable values of the viscosity are those given in Table 22; for water from 0° – 100° substantially

TABLE 22.
VISCOSITY OF WATER UNDER-COOLED BELOW 0° .

Temperature	Viscosity η	Temperature	Viscosity η
20.0°	0.01003	-2.10	0.01930
15.0	0.01139	-4.70	0.02121
10.0	0.01307	-6.20	0.02250
5.0	0.01523	-7.23	0.02341
0.00	0.01798	-8.48	0.02458
		-9.30	0.02549

White and Twining, Amer. Chem. J. 1913, 50, 380.

concordant determinations are recorded by a number of observers, and the more important are given in Table 23. The viscosity progressively diminishes with rise of temperature both as these data show and above 100° (becoming 0.00223 at 124° and 0.00181 at 158°: Hosking; Bingham and White; Table 23), but the variation does not follow any simple law and can only be expressed by empirical formulae which it is unnecessary to record.

Water under high pressures of the order of 400 atm. is less viscous than uncompressed water

at temperatures up to about 35°; at higher temperatures the viscosity of water is increased by increase of pressure, just as is that of most other liquids at all temperatures (Hauser, *Drude's Ann.* 1901, 5, 597).

The viscosity of ice, regarded as a fluid, has been estimated from the movement of glaciers to be of the order of $200-300 \times 10^{18}$ (Deeley and Parr, *Phil. Mag.* 1913, [vi.] 26, 85; 1914, [vi.] 27, 153), but measurements on blocks of ice or single crystals give widely divergent results (see e.g. McConnell, *Proc. Roy. Soc.* 1890, 48, A

TABLE 23.
VISCOSITY OF WATER, η IN C.G.S. UNITS, AND ITS VARIATION WITH TEMPERATURE,
ACCORDING TO VARIOUS OBSERVERS.

Temperature	1846 Poiseuille	1876 Sprung	1883 Slotte	1894 Thorpe & Rodger	1909 Hosking	1912 Bingham
0°	0.01716	0.01778	0.01808	0.017800	0.01792	0.01797
5	0.01615	0.01510	0.01524	0.015118	0.01522	0.01525
10	0.01309	0.01301	0.01314	0.013053	0.01305	0.01301
15	0.01146	0.01135	0.01144	0.011366	0.01142	0.01138
20	0.01008	0.01003	0.01008	0.010051	0.01006	0.01006
25	0.00897	0.00896	0.00896	0.008949	0.00892	0.008948
30	0.00803	0.00802	0.00803	0.008019	0.00800	0.007998
35	0.00721	0.00723	0.00724	0.007248	0.00724	0.007229
40	0.00653	0.00657	0.00657	0.006588	0.00657	0.006563
45	0.00595	0.00602	0.00602	0.006029	0.00600	0.005994
50	—	0.00553	0.00553	0.005537	0.00550	0.005500
55	—	—	0.00510	0.005124	0.00508	0.005081
60	—	—	0.00472	0.004752	0.00469	0.004735
65	—	—	0.00438	0.004432	0.00436	0.004369
70	—	—	0.00408	0.004144	0.00406	0.004075
75	—	—	0.00382	0.003885	0.00380	0.003806
80	—	—	0.00358	0.003655	0.00356	0.003570
85	—	—	0.00337	0.003450	0.00335	0.003348
90	—	—	0.00318	0.003260	0.00316	0.003143
95	—	—	0.00301	0.003095	0.00300	0.002993
100	—	—	0.00285	0.002945	0.00284	—

Poiseuille, *Mem. Acad. Roy. Sci. Inst. France*, 1846, 9, 433.

Sprung, *Pogg. Ann.* 1876, 159, 1.

Slotte, *Wied. Ann.* 1883, 20, 257.

Thorpe and Rodger, *Phil. Trans.* 1894, 185, A, 397.

Hosking, *Phil. Mag.* 1909, [vi.] 17, 502; 18, 260.

Bingham and White, *Zeit. phys. Chem.* 1912, 80, 670.

259). Hess found that the apparent value of the viscosity depends upon the direction of flow in relation to the original crystal axis, and varies also with time in the manner indicated by the results given in Table 24. It would appear that even a single crystal of ice may yield by slipping on cleavage surfaces, with consequent recrystallisation similar to that which is familiar in the case of metals yielding to stress.

Surface tension.—Water has a higher surface tension than any other common liquid except mercury. No data are available for its value in undercooled water; Table 25 gives the values of α^2 , the specific cohesion, and of γ , the surface tension in dynes/cm., at 1° intervals of temperature from 0°–90°; the progressive

diminution of γ with rise of temperature may be expressed by $\gamma = 76.09 (1 - 0.002028\theta)$ (Santia, *Journ. de Physique*, 1897, [iii.] 6, 183), or better, by $\gamma = \gamma_0 (1 - 0.0019017\theta - 0.0000249\theta^2)$ (Forch, *Ann. Physik*, 1905, 17, 744; see also Reinhold, *Ber.* 1913, 15, 903). Whilst the relative values of the surface tension at different temperatures are well represented by Table 25, the absolute values may be in error; in very careful measurements of the capillary rise (Richards and Coombs, *J. Amer. Chem. Soc.* 1915, 37, 1656; Richards and Carver, *ibid.* 1921, 43, 827) and of the 'drop-weight' of water (Harkins and Brown, *J. Amer. Chem. Soc.* 1919, 41, 499) a number of sources of error incidental to both methods have been discovered and eliminated, and the final results

TABLE 23A.

VISCOSITY OF WATER, γ IN C.G.S. UNITS IN THE NEIGHBOURHOOD OF ITS POINT OF MAXIMUM DENSITY.

Thorpe and Rodger (*loc. cit.*) have determined by the tube method the Viscosity of Water at various Temperatures in the vicinity of its point of maximum density, with the results seen in the annexed table.

Mean temp.	γ		Difference.
	Observed (mean).	Calculated.	
0.37	-01757	-01757	-00000
1.13	-01710	-01712	+00002
1.88	-01670	-01671	+00001
2.41	-01640	-01641	+00001
3.09	-01608	-01605	-00003
3.84	-01568	-01566	-00002
4.47	-01535	-01535	-00000
5.19	-01500	-01500	-00000
5.94	-01464	-01465	+00001
6.67	-01433	-01433	-00000
7.41	-01401	-01401	-00000
8.01	-01377	-01375	-00002

[Note on Table 23a: The viscosity of water at different temperatures has also been determined by the rotating cylinder method by Leroux (Ann. Physique, 1925, [x.] 4, 163), the water being contained between two concentric cylinders, of which the outer is rotated at known velocity and the resulting twisting moment on the inner cylinder measured.

Moritz (Pogg. Ann. 70, 1847), from observations made by the method of Coulomb (oscillating disc), inferred that water had a maximum viscosity in the neighbourhood of 4° . Other observers, and more especially Poiseuille and Sprung, using the tube method, were unable to detect any peculiarity in the rate of change of viscosity at temperatures at about the point of maximum density. The observations of Thorpe and Rodger lend no support to the conclusions of Moritz. It must be borne in mind, however, that the anomalous change in the density of water amounts only to about 1 part in 10,000; hence, since the accuracy attained in these special observations of viscosity probably does not exceed 1 in 5,000, it may be doubted whether any anomalous change in viscosity of the same order of magnitude as that observed in the case of the density would be detected by any of our present experimental methods.]

TABLE 24.

VISCOSITY OF ICE, $\gamma \times 10^{10}$ C.G.S. UNITS, FOR VARIOUS ORIENTATIONS, PRESSURES AND TIMES.

Relation of beam to axis of crystal	Length parallel to axis			Width parallel to axis			Thickness parallel to axis		
	2000	5000	6000	1000	2000	3000	1000	1500	2000
Load: grams.									
Duration of test.									
15 seconds .	6.5	10.5	0.55	3.7	2.4	11.0	7.5	10.0	8.0
60 " .	17.5	11.5	3.6	8.0	6.0	9.0	7.5	11.0	7.0
120 " .	10.0	13.5	3.7	12.0	10.0	—	7.5	9.0	11.0
300 " .	11.0	16.6	3.5	21.0	17.6	—	8.0	12.0	12.0

H. Hess, Ann. Physik. 1902, [iv.] 8, 405.

show respectively $\gamma_{100} = 72.75$ and $\gamma_{100} = 72.800$ respectively. Richards and Carver (*loc. cit.*) have proved experimentally, by a very ingenious optical method, that the surface of water is actually tangential to a properly wetted glass surface, and thus that the ordinary formula connecting surface tension and capillary rise holds precisely. Minute traces of dust or impurities have a considerable effect on the

surface tension, and precise measurements can only be made in a totally enclosed apparatus; Harkins and Brown have found that the capillary rise is affected by 'steaming' the tubes beforehand with the vapour of the liquid under investigation.

Absorbed or dissolved gases affect the surface tension; Richards and Carver find $\gamma_{100} = 72.73$ in air as compared with 72.75 in *vacuo*; dis-

TABLE 25.

SURFACE TENSION OF WATER.

Expressed in terms of the Specific Cohesion c^2 in mm^2 and Surface Tension, (γ), dynes per cm., from 0° to 40° in dry air and from 40° to 80° in air saturated with water vapour.

Temperature	c^2 mm^2	γ dynes/cm.	Temperature	c^2 mm^2	γ dynes/cm.
0°	15.406	75.49	40°	14.295	69.54
1	15.375	75.34	41	14.26	69.3
2	15.344	75.20	42	14.23	69.2
3	15.314	75.05	43	14.20	69.0
4	15.283	74.90	44	14.17	68.8
5	15.251	74.75	45	14.14	68.6
6	15.221	74.60	46	14.11	68.5
7	15.192	74.45	47	14.08	68.3
8	15.163	74.30	48	14.05	68.1
9	15.134	74.15	49	14.02	68.0
10	15.105	74.01	50	13.99	67.8
11	15.076	73.86	51	13.96	67.6
12	15.045	73.70	52	13.93	67.4
13	15.017	73.56	53	13.90	67.3
14	14.989	73.41	54	13.87	67.1
15	14.959	73.26	55	13.84	66.9
16	14.933	73.11	56	13.81	66.7
17	14.904	72.96	57	13.78	66.6
18	14.878	72.82	58	13.75	66.4
19	14.849	72.66	59	13.73	66.2
20	14.821	72.53	60	13.70	66.0
21	14.795	72.37	61	13.66	65.8
22	14.768	72.22	62	13.63	65.6
23	14.741	72.08	63	13.60	65.5
24	14.714	71.93	64	13.57	65.3
25	14.686	71.78	65	13.54	65.1
26	14.659	71.63	66	13.51	64.9
27	14.633	71.48	67	13.47	64.7
28	14.607	71.33	68	13.44	64.5
29	14.581	71.18	69	13.41	64.4
30	14.556	71.03	70	13.39	64.2
31	14.527	70.88	71	13.35	64.0
32	14.504	70.74	72	13.31	63.8
33	14.476	70.58	73	13.28	63.6
34	14.447	70.44	74	13.26	63.4
35	14.424	70.29	75	13.24	63.3
36	14.398	70.14	76	13.21	63.1
37	14.373	69.99	77	13.17	62.9
38	14.348	69.85	78	13.14	62.7
39	14.323	69.70	79	13.11	62.5
			80	13.08	62.3

Volkman, Wied. Ann. 1890, 11, 177; 1882, 17, 353; 1895, 56, 457 (0° - 40°).
Brunner, Pogg. Ann. 1847, 70, 481 (40° - 80°).

solved CO_2 , CO , N_2O , H_2S , H_2O , and N_2 similarly cause a small lowering of the surface tension (Quinke, Pogg. Ann. 1870, 139, 1, 89; 1877, 160, 337; Volkman, Wied. Ann. 1880, 11, 177; 1882, 17, 353; 1894, 53, 653; 1895, 56, 457; 1896, 66, 220; Forch, Wied. Ann. 1899, 68, 301; Ann. Physik, 1905, [iv.] 17, 750; Bhatnagar, J. physical. Chem. 1920, 24, 716).

By measurement of the amplitude of the wave produced when a stream of water emerges under pressure from capillary of elliptical cross-section, evidence has been obtained that the surface tension in a freshly formed surface of

water is about 0.5 dyne/cm. less than in old surfaces (Meyer and Stocker, Zeitsch. Elektrochem. 1916, 22, 5; Stocker, Zeitsch. physikal. Chem. 1920, 94, 149).

From the cooling effect of adiabatic expansion of water, the internal pressure has been calculated to be 2150 atmospheres (Parsons and Cook, Proc. Roy. Soc. 1911, A. 85, 332).

The surface tension in the interface between water and several organic liquids is given in Table 26; it is always less, and usually much less, than in pure water.

The coefficient of diffusion of water vapour

at 760 mm. pressure into air (I), carbon dioxide (II), and hydrogen (III) in cm.²/sec. is given in Table 27.

Molecular data have been calculated as follows for water vapour at 0°:

Mean molecular velocity, 55,650 cm./sec.

Mean free path, at 760 mm. pressure, 4.04×10^{-8} cm.

Molecular diameter, about 4.0×10^{-8} .

The number of molecules per gram-molecule of liquid water is estimated to be 8.5×10^{23} (Sand, Trans. Faraday Soc. 1919, 15, 84).

TABLE 26.

SURFACE TENSION, DYNES/CM., IN THE INTERFACE BETWEEN WATER AND SOME ORGANIC LIQUIDS.

Organic liquid	Ref.	0°	10°	20°	30°	40°	50°	60°
Benzene . . .	1	—	35.56	34.96	34.34	33.84	—	—
Benzine . . .	2	—	—	48.3	—	—	—	—
Carbon disulphide . . .	3	—	—	38.8	—	—	—	—
Carbon tetrachloride . . .	1	46.97	45.97	45.05	44.04	43.04	—	—
Chloroform . . .	3	—	—	25.8	—	—	—	—
Ethyl capronate . . .	1	21.03	21.42	21.29	21.15	21.02	—	—
Ethylene dibromide . . .	1	—	38.28	37.20	36.08	35.03	—	—
Heptaldehyde . . .	1	10.78	12.51	13.74	14.41	14.82	14.50	12.13
Heptene . . .	1	—	—	28.11	—	—	—	—
Heptylic acid . . .	1	8.34	7.93	7.54	7.13	7.00	—	—
Hexane . . .	1	—	51.25	—	50.66	50.48	—	—
Octane . . .	1	—	51.01	50.81	—	49.58	—	—
n-Octyl-alcohol . . .	1	7.75	—	—	8.97	9.32	—	—
Sec-octyl alcohol . . .	1	8.44	8.80	9.24	9.65	10.04	—	—
Olive oil . . .	3	—	—	18.2	—	—	—	—
Petroleum . . .	2	—	—	48.3	—	—	—	—

1. Harking and Cheng, J. Amer. Chem. Soc. 1921, 43, 35.

2. A. Pockels, Wied. Ann. 1899, 67, 668.

3. Quincke, Pogg. Ann. 1870, 139, 1.

TABLE 27.

COEFFICIENT OF DIFFUSION OF WATER VAPOUR.

Into air (I), carbon dioxide (II), and hydrogen (III), in cm.²/sec. at 760 mm. pressure.

Temperature	I.	II.	III.
0°	0.198	0.132	0.687
49.5°	0.283	0.181	1.000
92.4°	0.345	0.238	1.179

Winkelmann, Wied. Ann. 1884, 22, 1, 152; 1884, 23, 203; 1885, 26, 105; 1888, 33, 445; 1889, 36, 92; Ann. Physik. 1901, 6, 104; 1902, 8, 388.

THERMAL PROPERTIES.

Conductivity.—The principal data for the thermal conductivity of liquid water are given in Table 28; the considerable variation among them is a measure of the difficulty of making a precise measurement of the conductivity, owing to the effects of convection and radiation, but it is clear that it is very small as compared with that of metals, yet greater than that of other non-metallic liquids (e.g. alcohol 0.00055; benzene 0.00033). The conductivity shows a linear increase with temperature and may be represented by conductivity = $0.001325(1 + 0.002984t)$ Cal./cm. sec. degree (Jakob, *l.c.*).

The thermal conductivity of solid ice is about four times that of water, the most probable of the recorded values being 0.0057 (Neumann,

Ann. Chim. 1862, [iii.] 66, 183; Phil. Mag. 1863, [iv.] 25, 63), 0.0052 (Straneo, Atti R. Accad. Lincei, 1897, [v.] 6, (2), 262), and 0.0052 at 0°; 0.0058 at -57°, 0.0052 at -117° (Lees, Phil. Trans. 1898, 191, A, 399; Proc. Roy. Soc. 1905, 74, 337); in all cases gm. calories transmitted per sec. per sq. cm. through a thickness of 1 cm. for 1° temperature drop.

As a matter of common experience the thermal conductivity of snow is much less than that of ice, but it varies considerably with the nature and density of the snow, and attempts to measure it have given widely diverse results. Approximately it is of the order of $\frac{1}{10}$ th to $\frac{1}{15}$ th that of ice (Andrews, Proc. Roy. Soc. 1881, 40, 544; Abels, Rep. Meteorol. Acad. Petrograd, 1892, 16, 53; Hjelström, Oef. Akad. Stockholm, 1889, 46, 869; Jansson, *ibid.* 1901, 58, 297; Okada, J. Meteorol. Soc. Japan, 1905, 241).

TABLE 28.
CONDUCTIVITY FOR HEAT OF LIQUID WATER.

In calories per cm. per second per degree difference of temperature.

Temperature	Conductivity	Reference
4.1°	0.00129	1
7.8°	0.001347	2
11.0°	0.00149	3
12.0°	0.00136	4
20.0°	0.00143	5
23.7°	0.00143	6
24.5°	0.00136	3
28°	0.00150	7
40.8°	0.00155	8
41.4°	0.001492	2
72.4°	0.001610	2

1. Wachsmuth, Wied. Ann. 1893, 48, 158.
2. Jakob, Ann. Physik 1920, [iv.] 63, 537.
3. Lees, Phil. Trans. 1898, 191, 399.
4. H. F. Weber, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1885, 809.
5. Milner and Chattock, Nature, 1898, 58, 532.
6. Weber, Wied. Ann. 1880, 10, 103, 304, 472.
7. Jäger, Sitzungsber. Akad. Wiss. Wien, 1890, 99 [2. a.], 245.
8. Lundquist, Mon. Sci. 1871, 500.

Change of State.—The general relation of the state of aggregation to temperature has been discussed, but reference should be made to the undercooling of the liquid and vapour and the superheating of the liquid.

In the absence of nuclei, water vapour may be cooled much below its saturation temperature without deposition of visible water. Solid nuclei, such as particles of dust, spores, &c., may, and in ordinary air do, cause the condensation of liquid water immediately the saturation temperature is reached. Even less tangible nuclei will suffice. O. T. R. Wilson's simple and ingenious method of rendering the track of α -particles in a gas susceptible to visual observation or photographic record depends upon the fact that gaseous ions (produced by collision between the α -particle and molecules) will act as nuclei for the condensation of super-saturated water vapour.

Similarly, pure water in *vacuo*, in fine capillary tubes, or covered with petroleum, may be cooled some 15° below zero without solidification; even when slightly undercooled, water may be caused to crystallize by mechanical shock or agitation in the absence of nuclei (S. W. Young, J. Amer. Chem. Soc. 1911, 33, 148; Young and Croas, *ibid.* 1911, 33, 1375; Young and van Sicken, *ibid.* 1913, 35, 1067; Hartley and Thomas, J. Chem. Soc. 1906, 89, 1013). There is thus for water no evidence of the so-called 'metastable,' as distinct from 'stable,' condition in which nuclei are essential to crystallisation.

Liquid water is readily superheated; it is indeed difficult to boil water without slight local superheating, and very frequently the superheating is so considerable that when steam bubbles originate they increase in size with explosive violence, producing 'bumping.' In fresh distilled water minute bubbles of dissolved

air expelled on heating serve as nuclei for steam bubbles and minimise the bumping, and the same effect is frequently attained artificially by introducing air-filled porous solids, e.g. broken pottery, or a fine stream of air into the liquid. Without special precautions air-free water can be heated to 130° (see e.g. Donny, Ann. Chim. 1844, [iii.] 16, 167; Gernez, *ibid.* 1875, [v.] 4, 335; Krebe, Pogg. Ann. 1868, 133, 673; 1869, 136, 144; 1869, 138, 489), and if it is suspended in a mixture of olive oil and linseed oil of its own density it may be heated to 178° without boiling (Dufour, Ann. Chim. 1863, [iii.] 68, 370).

Latent Heat.—Heat is absorbed and rendered 'latent' both in the fusion of ice and in the evaporation of ice or water.

Table 29 gives the values of the heat of evaporation of water (frequently and more conveniently called the latent heat of steam) determined by a number of independent investigators at various temperatures from 0°–180°. The value at 100° is an important constant, and for this the most probable round value is 539.0 15° gm. cal. per gram.

Table 30 similarly gives data for the latent heat of fusion of ice, which usefully can be, but commonly is not, called the latent heat of water. Bunsen's value is undoubtedly erroneous, but if corrected for the difference in density between old and new ice (g.s.) becomes 79.67 in good agreement with more recent determinations. The rounded value 79.7 may be used with confidence for most purposes.

There is, of course, a direct relation between the latent heat of steam or water and the effect of dissolved substances upon the boiling-point and freezing-point.

The molecular elevation of the boiling-point is 0.52° (Beckmann, *Zeitsch. physikal. Chem.* 1891, 8, 223; 1906, 63, 177), and the molecular

depression of the freezing-point is 1.66° (Raoult, *physikal. Chem.* 1906, 63, 441; Zetsch, *Electrochem.* 1920, 26, 238; Dickinson and Osborne, *Proc. Roy. Soc.* 1910, A, 83, 459; Roth, *Zetsch.* *physikal. Chem.* 1906, 63, 441; Zetsch, *Electrochem.* 1920, 26, 238; Dickinson and Osborne, *J. Franklin Inst.* 1915, 179, 499).

TABLE 29.

LATENT HEAT OF STEAM—HEAT OF EVAPORATION OF WATER.
(According to various observers.)

Temperature	Heat of evaporation 15° gm. cal./gm.	Reference	Temperature	Heat of evaporation 15° gm. cal./gm.	Reference
0°	594.8	1	80°	551.6	4
15°	590.9	2	99-90°	538.9	5
20°	585.3	2	100°	540.5	2
25°	581.9	3	100°	539.1	4
30°	578.7	3	100°	538.3	6
30°	579.8	4	100°	539.0	7
40°	574.0	2	100°	538.9	8
40°	574.5	4	120°	525.8	4
40-2°	572.6	3	140°	511.4	4
40-8°	566.5	3	160°	497.0	4
60°	563.4	4	180°	482.7	4

1. Dieterici, *Wied. Ann.* 1889, 37, 504; *Ann. Physik* 1905, 16, 912.
2. A. W. Smith, *Phys. Review*, 1903, 16, 383; 17, 193; 1907, 25, 145; 1911, 33, 173.
3. Griffiths, *Phil. Trans.* 1895, 186, A, 261.
4. Henning, *Ann. Physik*, 1906, [iv.] 21, 489; 1909, [iv.] 29, 441; 1919, [iv.] 58, 759.
5. Joly, *Phil. Trans.* 1905, 186, A, 322.
6. Richards and Mathews, *J. Amer. Chem. Soc.* 1911, 33, 863.
7. Mathews, *J. Phys. Chem.* 1917, 21, 536.
8. T. Carlton-Sutton, *Proc. Roy. Soc.* 1917, 93, 155.

TABLE 30.

LATENT HEAT OF FUSION OF ICE (15° gm. cal./gram.).
(According to various observers.)

Temperature	Latent heat of fusion	Reference
-6.5°	78.03	1
-5.0°	78.60	1
-2.8°	77.71	1
-0.7°	78.26	2
0°	79.25	3
"	79.06	4
"	80.03	5
"	79.24	6
"	79.69	7
"	79.61	8
"	79.2	9
"	79.67	10
"	79.63	11
"	79.74	12

1. Pettersen, *Oefversigt af Kongl. Vetenskaps. Akad. Förhandlingar*, Stockholm, 1878, 35, No. 2, 57.
2. Zakrzewski, *Bull. Acad. Cracow*, 1892, 153.
3. Person, *Ann. Chim.* 1847, [iii.] 21, 333; 1848, [iii.] 24, 136, 264; 1849, [iii.] 27, 252.
4. Regnault, *Ann. Chim.* 1843, [iii.] 8, 27; 1849, [iii.] 26, 278.
5. Bunsen, *Pogg. Ann.*, 1870, 141, 31.
6. Desormes, *Compt. rend.* 1843, 18, 981.
7. A. W. Smith, *Phys. Review*, 1903, 16, 383; 17, 193.
8. Bogojawinski, *Chem. Zentr.* 1905, ii, 945.
9. Leduc, *Compt. rend.* 1906, 142, 46.
10. Roth, *Zetsch. physikal. Chem.* 1906, 63, 441.
11. Dickinson, Harper and Osborne, Bureau of Standards, U.S.A., *Bull.* 1914, 16, 338; *J. Franklin Inst.* 1915, 179, 453.
12. Dickinson and Osborne, Bureau of Standards, U.S.A., *Bull.* 1915, 12, 46.

Specific Heat.—The specific heat of steam at the temperature and pressure of saturation and at higher temperatures or lower pressures (when it is unsaturated or 'superheated') is of great theoretical and practical importance in connection with the generation of steam and its use in all types of prime movers. Table 31 gives the values at temperatures from 80°-550° and under pressures from 0.5 to 30 atmospheres. The specific heat of saturated steam increases

with temperature and pressure; that of unsaturated steam at constant pressures less than about 9 atmospheres decreases to a minimum value and then increases progressively with temperature; the minimum of specific heat occurs at temperatures which increase with pressure, and may occur at pressures above 9 atmospheres at higher temperatures than have yet been subject to experiment.

The specific heat of steam at or near

TABLE 31.

SPECIFIC HEAT OF UNSATURATED ("SUPERHEATED") STEAM AT THE TEMPERATURE t° AND UNDER THE CONSTANT PRESSURE p KG./SQUARE CM.

(t_s indicates the saturation temperature under the corresponding pressure.)

t°	$p=0.5$	1	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
$t_s=80.3^{\circ}$	99.1°	119.6°	142.9°	158.1°	169.6°	179.1°	187.1°	194.1°	200.4°	206.1°	211.4°	216.2°	220.8°	225.0°	229.0°	232.8°	
80	0.479	0.486	0.499	0.525	0.551	0.578	0.605	0.633	0.663	0.694	0.726	0.759	0.794	0.829	0.865	0.902	0.940
110°	0.470	0.481	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
120°	0.468	0.477	0.498	—	—	—	—	—	—	—	—	—	—	—	—	—	—
130°	0.467	0.475	0.494	—	—	—	—	—	—	—	—	—	—	—	—	—	—
140°	0.466	0.473	0.489	—	—	—	—	—	—	—	—	—	—	—	—	—	—
150°	0.465	0.472	0.486	0.519	—	—	—	—	—	—	—	—	—	—	—	—	—
160°	0.465	0.471	0.483	0.512	0.549	—	—	—	—	—	—	—	—	—	—	—	—
170°	0.465	0.470	0.481	0.507	0.538	—	—	—	—	—	—	—	—	—	—	—	—
180°	0.466	0.469	0.479	0.502	0.528	0.561	0.602	—	—	—	—	—	—	—	—	—	—
190°	0.466	0.469	0.478	0.498	0.522	0.549	0.583	0.625	—	—	—	—	—	—	—	—	—
200°	0.466	0.469	0.478	0.495	0.515	0.539	0.567	0.601	0.643	—	—	—	—	—	—	—	—
210°	0.467	0.470	0.477	0.493	0.510	0.531	0.555	0.584	0.616	0.657	0.705	—	—	—	—	—	—
220°	0.467	0.470	0.477	0.491	0.506	0.524	0.545	0.569	0.595	0.627	0.664	0.709	—	—	—	—	—
230°	0.468	0.471	0.477	0.489	0.504	0.519	0.537	0.557	0.579	0.604	0.633	0.667	0.706	0.757	0.816	0.890	—
240°	0.469	0.472	0.477	0.488	0.501	0.515	0.530	0.548	0.566	0.588	0.611	0.638	0.669	0.704	0.743	0.794	0.862
250°	0.470	0.473	0.477	0.488	0.499	0.512	0.525	0.540	0.556	0.573	0.594	0.614	0.639	0.665	0.694	0.731	0.770
260°	0.471	0.474	0.478	0.487	0.498	0.508	0.521	0.534	0.548	0.563	0.579	0.597	0.617	0.638	0.661	0.687	0.715
270°	0.472	0.474	0.478	0.487	0.497	0.507	0.518	0.529	0.541	0.555	0.568	0.583	0.599	0.616	0.635	0.658	0.676
280°	0.473	0.475	0.479	0.487	0.496	0.505	0.515	0.525	0.536	0.547	0.559	0.571	0.585	0.599	0.614	0.630	0.647
290°	0.474	0.476	0.480	0.487	0.495	0.504	0.513	0.523	0.531	0.541	0.552	0.562	0.574	0.586	0.598	0.611	0.625
300°	0.475	0.477	0.481	0.488	0.495	0.503	0.511	0.519	0.527	0.536	0.545	0.555	0.564	0.574	0.585	0.596	0.607
310°	0.477	0.478	0.482	0.488	0.495	0.502	0.510	0.518	0.525	0.533	0.540	0.548	0.557	0.566	0.575	0.584	0.593
320°	0.478	0.480	0.483	0.489	0.496	0.502	0.509	0.516	0.523	0.530	0.536	0.543	0.550	0.558	0.566	0.574	0.582
330°	0.479	0.482	0.484	0.490	0.496	0.502	0.508	0.515	0.520	0.527	0.533	0.539	0.545	0.552	0.559	0.566	0.573
340°	0.481	0.483	0.485	0.491	0.496	0.502	0.507	0.513	0.519	0.525	0.530	0.536	0.541	0.547	0.553	0.559	0.565
350°	0.482	0.484	0.486	0.492	0.497	0.502	0.507	0.512	0.517	0.523	0.528	0.533	0.537	0.543	0.548	0.554	0.559
360°	0.483	0.485	0.487	0.492	0.497	0.502	0.507	0.511	0.516	0.521	0.526	0.530	—	—	—	—	—
370°	0.485	0.486	0.488	0.493	0.498	0.503	0.507	0.511	0.516	0.520	0.524	0.528	—	—	—	—	—
380°	0.486	0.488	0.490	0.494	0.498	0.503	0.507	0.511	0.515	0.519	0.523	0.527	—	—	—	—	—
390°	0.487	0.489	0.491	0.495	0.499	0.503	—	—	—	—	—	—	—	—	—	—	—
400°	0.489	0.490	0.492	0.496	0.500	0.504	—	—	—	—	—	—	—	—	—	—	—
410°	0.490	0.492	0.494	0.497	0.501	0.505	—	—	—	—	—	—	—	—	—	—	—
420°	0.492	0.494	0.496	0.498	0.502	0.506	—	—	—	—	—	—	—	—	—	—	—
430°	0.494	0.495	0.497	0.500	0.504	0.507	—	—	—	—	—	—	—	—	—	—	—
440°	0.496	0.497	0.499	0.501	0.505	0.508	—	—	—	—	—	—	—	—	—	—	—
450°	0.498	0.498	0.500	0.503	0.506	0.509	—	—	—	—	—	—	—	—	—	—	—
460°	0.499	0.500	0.501	0.505	0.507	0.510	—	—	—	—	—	—	—	—	—	—	—
470°	0.501	0.502	0.503	0.506	0.508	0.512	—	—	—	—	—	—	—	—	—	—	—
480°	0.503	0.504	0.505	0.507	0.509	0.513	—	—	—	—	—	—	—	—	—	—	—
490°	0.505	0.505	0.506	0.509	0.511	0.514	—	—	—	—	—	—	—	—	—	—	—
500°	0.506	0.506	0.506	0.510	0.512	0.515	—	—	—	—	—	—	—	—	—	—	—
510°	0.507	0.508	0.510	0.512	0.513	0.516	—	—	—	—	—	—	—	—	—	—	—
520°	0.509	0.509	0.511	0.513	0.515	0.517	—	—	—	—	—	—	—	—	—	—	—
530°	0.510	0.511	0.513	0.515	0.516	0.518	—	—	—	—	—	—	—	—	—	—	—
540°	0.512	0.513	0.515	0.517	0.518	0.520	—	—	—	—	—	—	—	—	—	—	—
550°	0.514	0.515	0.516	0.518	0.520	0.522	—	—	—	—	—	—	—	—	—	—	—

Knoblauch and Balach, *Zetisch. Ver. Ing.* 1922, 66, 418; based on previous work by Knoblauch et al.

atmospheric pressure has been measured at still higher temperatures; up to 1400° it is represented by $C_{p,0} = 0.4669 - 0.0.168 \times 10^{-4} t^2$ or $C_{p,0} = 0.4644 + 0.006925 \times 10^{-6} t^3$ (Holborn and Henning, *Ann. Physik*, 1907, [iv.] 23, 808; see also *Ann. Physik*, 1905, [iv.] 78, 739; *Wiss. Abh. Phys.-Tech. Reichsanstalt*, 1905, 4, 131; and Lorenz, *Phys. Zeit.* 1904, 5, 383). The ratio of the specific heats at constant pressure and constant volume is about 1.3 at 103°

1.330 at 110°, 1.313 at 120°, and 1.312 at 130° (Tretz, Bonn, 1903).

The heat capacity of water, usually at 15°, is used as a standard, and its variation with temperature is therefore of great practical importance and has been the subject of many precise investigations. Some of the more important results are given in Table 28 (see also, *inter alia*, Lédin, *Mitt. naturw. Ges. Winterthur*, 1906; *Dissemin. Ann. der Physik*,

1906, [iv.] 16, 593; Barnes, Phil. Trans. 1902, A. 199, 149; Barnes and Cooke, Phys. Review, 1902, 15, 65; Cotty, Ann. Chim. 1911, [viii.] 24, 333.

With rise of temperature from 0°C. the specific heat decreases rapidly to a minimum value and then increases more slowly at a rate which itself increases but slightly with temperature; the measurements of Callendar and of Jaeger and Steinwehr agree in placing the minimum of specific heat at about 35°.

Numerous formulae have been proposed to express the variation of the specific heat of water with temperature, but they have no physical basis; as an example, the formula $C_p = 1.00733 - 0.0007416t + 0.000016845t^2 - 0.000,000,09552t^3$

where $C_{100} = 1$, agrees well from 0°–100° with the best experimental values (Narbutt, Zeitsch. Physik. Chem. 1918, 19, 513).

Below 0° the specific heat of undercooled

water increases very rapidly with fall of temperature, attaining the value 1.0155 at –5° (Barnes, l.c.).

The specific heat of water at 0° is decreased by 0.0061025 if the pressure is increased by one atmosphere.

The specific heat of ice is less well known; it is about half that of water at 0° and becomes quite small at low temperatures. A number of determinations are given in Table 33. It appears to increase very rapidly just below the melting-point (A. W. Smith, Phys. Review, 1903, 17, 193), probably owing to physical inhomogeneity.

Entropy.—The entropy of ice at 0°, calculated from absolute zero, is found to be 9.96 per gram molecule; adding 5.26 the entropy of fusion of ice at 0°, and 1.58 that due to heating water from 0° to 25°, the entropy of water at 25° is 16.8 per gram molecule (Lewis and Gibson, J. Amer. Chem. Soc. 1917, 39, 2575).

TABLE 32.
SPECIFIC HEAT OF WATER.

Temperature	Regnault Air-thermometer	Bousfield: Hydrogen- thermometer	Callendar Kelvin scale	Jaeger and v. Steinwehr Kelvin scale
0°	0.9992	1.0070	1.0093	(1.005)
5°	0.9994	1.0039	1.0047	1.0030
10°	0.9997	1.0016	1.0019	1.0013
15°	1.0000	1.0000	1.0000	1.0000
20°	1.0004	0.9991	0.9980	0.9990
25°	1.0008	0.9989	0.9980	0.9983
30°	1.0012	0.9990	0.9975	0.9979
35°	1.0017	0.9997	0.9973	0.9979
40°	1.0022	1.0006	0.9973	0.9981
45°	1.0028	1.0018	0.9975	0.9987
50°	1.0034	1.0031	0.9978	0.9996
55°	1.0041	1.0045	0.9982	—
60°	1.0048	1.0058	0.9987	—
65°	1.0056	1.0070	0.9993	—
70°	1.0064	1.0080	1.0000	—
75°	1.0072	1.0088	1.0008	—
80°	1.0081	1.0091	1.0017	—
85°	1.0091	—	1.0026	—
90°	1.0101	—	1.0036	—
95°	1.0111	—	1.0046	—
100°	1.0122	—	1.0057	—
120°	1.0160	—	1.0108	—
140°	1.0224	—	1.0167	—
160°	1.0286	—	1.0234	—
180°	1.0355	—	1.0309	—
200°	—	—	1.0392	—

Regnault, Mém. de l'Acad. 1847, 21, 729; Pogg. Ann. 1850, 79, 241.

W. R. and W. E. Bousfield, Phil. Trans. 1911, 211, A. 199.

Callendar, Proc. Roy. Soc. 1912, 86, A. 254; Phil. Trans. 1912, 212, A. 1.

Jaeger and v. Steinwehr, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1915, 434; Ann. Physik. 1915, 44, 206.

WATER.

TABLE 33.
SPECIFIC HEAT OF ICE.
(According to various observers.)

Temperature	Specific heat	Reference
-250.6°	0.0303	1
-235°	0.086	1
-252° to -188°	0.146	2
-185.9°	0.189	1
-188° to -78°	0.285	2
-189.5° to -81.7°	0.266	3
-100°	0.325	4
-188° to 0°	0.337	5
-185° to 0°	0.345	6
-50°	0.409	4
-78.4° to 0°	0.424	5
-40° to 0°	0.431	7
-76.9° to -2.9°	0.433	3
-78° to 18°	0.463	2
0°	0.505	7

1. Pollitzer, Zeitsch. Elektrochem. 1913, 19, 513.
2. Dewar, Proc. Roy. Soc. 1905, A, 76, 325.
3. Nernst, Koref and Lindemann, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1910, 247.
4. Nernst, *ibid.* 1910, 262.
5. Jackson, J. Amer. Chem. Soc. 1912, 34, 1470.
6. Nordmeyer and Bernoulli, Ber. 1907, 5, 175.
7. Dickinson and Osborne, Bureau of Standards, U.S.A., Bull., 1915, 12, 49.

OPTICAL PROPERTIES.

Crystalline luminescence.—It has been reported that if water be rapidly frozen, bright flashes of luminescence are observed (Trautz, Zeitsch. physikal. Chem. 1905, 53, 9).

Colour: absorption of light.—There is much evidence, irrelevant here, that the bright blue colour often observed in water, notably in that of china-clay settling pits, reservoirs for large scale water-softening, and some lakes, e.g. Lake Geneva, is due to the scattering of light by

TABLE 34.
WATER VAPOUR—ABSORPTION BANDS IN THE INFRA-RED.
Maxima in μ ($=10^{-3}$ mm. $=10^4$ Å).

0.944*	(4.56)	9.30	19.70
1.128	(4.70)	9.50	20.5
1.157	4.98	9.74*	21.6
1.367	5.04	9.98	22.9
1.411	5.18	10.30*	24.1
1.480	5.24	10.66	27.1
1.843		10.80	29.4
1.870	6.42	10.94*	31.0*
1.904	6.49	11.24	33.1
1.985		11.47	
(2.010)	6.56	11.66*	
	6.61	11.89	
2.698		12.42*	
2.948	7.44	12.82	
2.997	7.58	13.34*	
3.028	7.75	13.62	
3.070	7.88	14.32*	
3.112	8.04	14.98	
3.194*	8.17	15.62*	
3.245	8.23	16.00	
3.295	8.36	(16.80)	
3.340	8.42	17.33*	
3.402	8.51	18.37	
3.463	8.73	19.22	
	8.99		

Hettner, Ann. Physik. 1916, 55, 495.

minute suspended particles. But glacier ice and the water produced therefrom, which are undoubtedly very pure, show by transmitted light a distinct greenish-blue colour (H. Davy, *Collected Works*, 1840, 9, 199; Bunsen, *Pogg. Ann.* 1851, 83, 187; Rayleigh, *Nature*, 1910, 83, 48).

Pure distilled water in a tube several metres long and blackened internally is quite definitely greenish-blue by transmitted light.

As ozone is deep blue, liquid oxygen pale slightly greenish-blue, and hydrogen peroxide, methyl alcohol, ethyl alcohol and similar simple hydroxyl compounds are bluish-green, this colour is probably an intrinsic property of pure water. In smaller thicknesses water appears colourless.

The absorption spectrum of water in the visible region accords with its observed colour. In the red from $660\text{--}040\mu$ the absorption coefficient is about 0.3, in the orange at approximately 600μ it is about 0.15, whence it falls rapidly to about 580μ , and is less than 0.05 throughout the regions of the spectrum from yellow to violet (von Aufsess, *Die Farbe der Seen*, München, 1903). The absorption in the ultra-violet has been studied by Kreusler (*Ann. der Physik*, 1901, [iv.] 6, 412).

Water is opaque to infra-red radiation over a wide range of wave-length. The most recent measurements are given in Table 34 (*see also* Bode, *Ann. Physik*, 1909, [iv.] 30, 326; von Bahr, *Ber.* 1913, 15, 731; and, for the fine structure, Sleator, *Astrophys. J.* 1918, 48, 125; Wichmann, *Physikal. Zeitsch.* 1921, 22, 535; *Ann. Physik* 1922, [iv.] 66, 501).

Water vapour is more transparent than liquid water to infra-red radiation. The opacity of the atmosphere to such radiation is mainly due to its content of water vapour, and does not extend to wave-lengths shorter than about 11μ ; the absorption by an equivalent layer, say 2 cm., of liquid water is complete down to 1.2μ . The difference gave rise to prolonged controversy between Magnus and Tyndall before its nature was established (Magnus, *Pogg. Ann.* 1861, 112, 497; 114, 635; 1863, 118, 575; 1864, 121, 186; 1866, 127, 613; 1867, 130, 207; Tyndall, *Proc. Roy. Soc.* 1860, 10, 37; 1861, 11, 558; 1879, 30, 10; 1881, 31, 307, 478; 1883, 35, 21; *Phil. Mag.* 1861, [iv.] 22, 377; 1862, [iv.] 23, 252; 1863, [iv.] 26, 44; 1866, [iv.] 32, 118; 1867, [iv.] 33, 425).

Water also absorbs X-rays (for details, *see* Hewlett, *Phys. Review*, 1921, 17, 284; Richtmyer, *ibid.* 1921, 18, 13).

Refractive Index.—Table 35 gives the refractive index of water for light of various wave-lengths and at temperatures from $0^{\circ}\text{--}80^{\circ}$; these values are substantially confirmed by more recent and very precise determinations, which give, for the iron line E ($\lambda=6270.11$)

$$n_D^{15^{\circ}} = 1.3356359$$

and, for sodium light, the following values referred to air and *in vacuo*:

Temperature .	20°	25°	30°
n_D in air .	1.33299	1.33248	1.33190
n_D in vacuo .	1.33335	1.33284	1.33225

TABLE 35.

REFRACTIVE INDEX OF WATER.

Against air at the same temperature; and its rate of increase with temperature for the temperature ranges and spectral lines specified.

Light		n_0°	$(n_0^{\circ}-n_{10}^{\circ}) \times 10^4$	n_{10}°	$(n_{10}^{\circ}-n_{20}^{\circ}) \times 10^4$	n_{20}°	$(n_{20}^{\circ}-n_{30}^{\circ}) \times 10^4$	n_{30}°	$(n_{30}^{\circ}-n_{40}^{\circ}) \times 10^4$	n_{40}°
Element	λ , Å									
Cd .	2144.5	1.40500	103	1.40397	253	1.40144	382	1.39762	454	1.39308
Cd .	2194.7	1.39987	104	1.39883	252	1.39631	390	1.39241	453	1.38788
Cd .	2265.1	1.39360	103	1.39257	256	1.39001	377	1.38624	455	1.38100
Cd .	2312.9	1.38982	104	1.38878	253	1.38625	378	1.38247	452	1.37795
Au .	2428.1	1.38210	107	1.38103	254	1.37849	374	1.37475	451	1.37024
Cd .	2573.2	1.37447	103	1.37344	251	1.37093	374	1.36719	450	1.36309
Au .	2768.1	1.37007	103	1.36904	248	1.36656	371	1.36285	448	1.35837
Cd .	2748.7	1.36739	102	1.36637	250	1.36387	368	1.36019	446	1.35573
Al .	3082.3	1.35768	97	1.35671	247	1.35424	365	1.35059	441	1.34618
Cd .	3403.6	1.35139	95	1.35044	244	1.34800	364	1.34436	437	1.33999
Cd .	3511.9	1.34834	96	1.34738	241	1.34497	361	1.34136	434	1.33703
Al .	3944.1	1.34457	91	1.34366	242	1.34124	359	1.33765	431	1.33334
Cd .	4415.9	1.34071	90	1.33981	240	1.33741	356	1.33385	429	1.32956
Cd .	4678.3	1.33908	88	1.33815	238	1.33577	352	1.33225	428	1.32797
Cd .	4800.1	1.33834	84	1.33750	234	1.33518	353	1.33163	429	1.32734
Cd .	5328.5	1.33582	83	1.33499	233	1.33266	350	1.32916	423	1.32493
Na .	5893.1	1.33381	81	1.33300	231	1.33069	351	1.32718	418	1.32060

Flatow, *Ann. Physik*, 1909, [iv.] 12, 85: the values given by Flatow are in substantial agreement with the determinations of other observers cited, e.g. Landolt-Börnstein, *Tabellen*, 1923, p. 436.

(Gifford, Proc. Roy. Soc. 1906, A, 78, 406; Baxter, Burgess and Daudt, J. Amer. Chem. Soc. 1911, 33, 893).

* The dispersion equivalent $n_D - n_A$ and the dispersive power $(n_D - n_A)/(n_D - 1)$ are given as follows:

Temperature	0°	10°	20°	30°	40°	50°	60°	70°
Dispersion equivalent	0.0147	148	148	145	148	147	144	141
Dispersive power	0.0429	439	445	438	449	448	441	435

(Gladstone and Dale, Phil. Trans. 1858, 148, 887; 1863, 153, 323).

Measurements with electrical waves, $\lambda = 3.5$ – 4.5 cm., show that the refractive index of water increases with the wave-length and that water exhibits anomalous dispersion (Marxkyng, Bull. Acad. Sci. Cracow, 1911, 123).

Ice exhibits double refraction and is optically positive. The refractive indices for sodium light are for the ordinary ray 1.3091 and for the extraordinary ray 1.3104 (Pulfrich, Wied. Ann. 1888, 34, 336; cf. the values 1.3083 and 1.3133 respectively of Meyer, *ibid.* 1887, 31, 322).

Scattering of Light.—It has been shown that pure water, free from ultra-microscopic suspended particles, scatters light, and that the scattered light is polarised, but the interpretation of the phenomenon is as yet incomplete or lacking (see Einstein, Ann. Physik. 1910, 33, 1275; Cabannes, J. Phys. Chem. 1920, [vi.] 1, 129; Martin, J. Phys. Chem. 1920, 24, 248; 1922, 26, 75; 1923, 27, 558; Rayleigh, Proc. Roy. Soc. 1920, 97 A, 435; Raman, *ibid.* 1922, 102, A, 151; Phil. Mag. 1923, 45, 625).

MAGNETIC AND ELECTRICAL PROPERTIES.

Coefficient of magnetisation.—The coefficient of magnetisation for water referred to unit mass has been determined by several observers to be about -0.72×10^{-4} C.G.S. units at 20° (de Haas

T°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Ω	0.9998	1.0001	1.0008	1.0018	1.0029	1.0041	1.0053	1.0065	1.0074

Electrical conductivity.—Pure water is a very poor conductor of electricity. The purest water ever obtained (see Purification) had a specific conductivity 0.043×10^{-8} reciprocal ohm (mho) at 18°.

It is calculated that the conductivity of

and Drapier, Ann. Physik, 1913, [iv.] 42, 673; Weiss and Piccard, Compt. rend. 1912, 155, 1234; Piccard, Arch. Sci. phys. nat. 1913, [iv.] 35, 458; see also Gray and Birse, J. Chem. Soc. 1914, 105, 2707; Hayes, Phys. Rev. 1914 (2), 3, 295). This coefficient has a temperature coefficient of about $+0.00012$ at 20°.

Ice is said to be diamagnetic (Brunner, Pogg. Ann. 1850, 79, 173).

Magneto-optic Rotation.—The rotation of the plane of polarisation of light by a given thickness of water in a given magnetic field depends upon the wave-length of light and upon the temperature. The specific rotation (for 1 cm. of liquid in unit magnetic field) for the D line at 18° is $\omega_{18}^D = 0.01309$ minutes of arc (Agerer, Sitzungsber. Akad. Wiss. Wien. 1905, 114, 830), and its variation with temperature is given between 3° and 98° by $\omega_t^D = 0.01311(1 - 0.0305t + 0.0305t^2)$ (Rodger and Watson, Zeitsch. physikal. Chem. 1896, 19, 357).

The molecular magnetic rotation of water at 4°C. is taken as the standard, unity, for fixing that of other liquids, their molecular magnetic rotation being then given by

$$\Omega = \frac{\omega \times \text{mol. weight}}{18}$$

Thus the variation of the molecular magnetic rotation of water is of practical importance and is illustrated by the following data (Rodger and Watson):—

TABLE 36.
DIELECTRIC CONSTANT OF WATER, ϵ .

Temperature	λ cm.	ϵ	Reference
—	∞	76	1
—	∞	80	2
18°	∞	81.1	3
17°	50	81.0	4
17°	40	80.7	4
17°	30	80.4	4
0	75	88.2	5

1. Cohn and Arons, Wied. Ann. 1886, 28, 454; 1888, 33, 13, 31.
2. Smale, Wied. Ann. 1897, 57, 315.
3. Turner, Zeitsch. physikal. Chem. 1900, 35, 385.
4. Rukop, Diss. Grieswald, 1911.
5. Drude, Wied. Ann. 1896, 59, 17.

it varies very rapidly with temperature (see Noyes, Kato and Roeman, *J. Amer. Chem. Soc.* 1900, 32, 154).

Ice is quite a good insulator; its specific resistance is 4865 megohms at 0° and 33,540 megohms at -17° . Thus, a cable, the insulation of which is defective through moisture, will frequently show a good insulation test when exposed to severe frost.

Dielectric capacity.—The dielectric constant for steam at 145° and 760 mm. is $\epsilon=1.00705$, and its variation with temperature is expressed by $\epsilon_t = \epsilon_{t_1} - \alpha(t_t - t_1)$ where $\alpha = 1.4 \times 10^{-4}$ and $t_1 = 145^\circ$ (Bäcker, *Zeitsch. physikal. Chem.* 1901, 36, 305).

Table 36 gives a series of values of ϵ for water for different wave-lengths. The dielectric constant varies with pressure from 7–200 atmospheres by about 0.0046 p.c. per atmosphere (Falckenberg, *Ann. Physik.* 1920, [vi.] 61, 145).

The dielectric constant for ice for $\lambda=5000$ cm. at -18° is 3.1 (Abegg, *Wied. Ann.* 1898, 65, 229) and for $\lambda=75$ cm. at -190° is 1.78–1.88 (Behn and Kiebitz, *Boltzmann's Festschrift*, Leipzig, 1904, 610).

The ionising potential for water vapour is calculated to be 8.64 volts (Compton, *Phys. Review*, 1916, (2), 8, 412).

THE CHEMICAL PROPERTIES OF WATER.

Molecular constitution.—It was formerly supposed that the relatively high density of water vapour in the neighbourhood of the boiling-point and at lower temperatures connoted the presence in it of molecules more complex than H_2O (see e.g. Bose, *Zeitsch. Elektrochem.* 1908, 14, 269; Oddo, *Gazz. chim. ital.* 1915, 45, i. 319; 395), but if the experimental values are corrected for the deviation of water vapour from the ideal gas-laws and recalculated by the Clausius-Clapeyron equation the results afford no evidence whatever for any deviation from the simple formula H_2O , and this must, therefore, be assumed to represent correctly the molecular state of water vapour (Kendall, *J. Amer. Chem. Soc.* 1920, 42, 2477; Menzies, *ibid.* 1921, 43, 851).

On the other hand, experiments with a modified Wilson's expansion apparatus, interpreted in accordance with Lenard's theory, indicate the presence of about 1.9×10^{-11} p.c. of uncharged nuclei of relatively large dimensions which are most probably polymerised molecules of the type $(H_2O)_n$ or $(H_2O)_x$ (Andrén, *Ann. Physik.* 1917, [iv.] 52, 1).

With regard to liquid water, there is a great body of evidence pointing to the presence of complex molecules. It is now fairly generally held that the abnormality of water as compared with other liquids in so many physical properties is due to polymerisation. This explanation was first advanced by Whiting (*A New Theory of Cohesion Applied to the Thermodynamics of Liquids and Solids*, Harvard University, Cambridge, Mass. 1884, p. 70), who pointed out that water at 0° may contain 25–33 p.c., and at 100° 17–28 p.c. of dissolved ice, and that the observed expansion of 4 p.c. by volume in this interval is the resultant of a normal expansion of some 8–10 p.c. by volume and a contraction due to the melting of the

dissolved ice. Eight years later, Röntgen (*Wied. Ann.* 1892, [5] 45, 91) independently suggested that water consists of 'ice molecules' and 'water molecules,' the former being more complex but less dense than the latter.

Later, Sutherland elaborated the hypothesis still further and, possibly influenced by Traube's theory that normal liquids consist of 'liquidogenic' and 'gasogenic' molecules, supposed water to consist of single, double and triple molecules, to which he gave the names *hydrol* (H_2O), *dihydrol* (H_4O_2), and *trihydrol* (H_6O_3).

In liquid water we then have the equilibria: $2H_2O \rightleftharpoons 3H_4O \rightleftharpoons 6H_6O$. Steam is hydrol; ice is supposed to consist chiefly or wholly of trihydrol. Because of the lower density of ice it seems probable that trihydrol is less dense than dihydrol; and our present knowledge of the crystal structure of ice (*q.v.*) accords well with the view. Whiting's theory, originally propounded simply to explain the anomalous expansion of water, has been applied successively to the other physical properties of water, and has been found to accord so well with the observed facts that its substantial truth seems clear (see e.g. Walden, Guye, Bonsfield and Lowry, Sutherland and Nernst, *Trans. Faraday Soc.* 1910, 6, 71–123). It is of interest to consider some examples.

The melting of ice is attended by considerable absorption of heat and decrease of volume; *ex hypothesi* then, these phenomena characterise the conversion of trihydrol to dihydrol. Therefore, in accordance with Le Chatelier's theorem, either rise of temperature or increase of pressure will tend to dissociate trihydrol and so reduce the proportion present in water. If the volume change of water on heating is the resultant of (a) contraction due to depolymerisation of trihydrol and (b) the normal expansion of dihydrol, the preponderance of (a) up to 4° (owing to the relatively higher proportion of trihydrol then present) can explain the observed net contraction between 0° and 4° . Similarly, the diminution of the proportion of trihydrol by pressure explains the lowering of the temperature of maximum density by increase of pressure.

The minimum of compressibility of water about 50° is best accounted for by Bonsfield and Lowry's extension of the hypothesis (*Trans. Faraday Soc.* 1910, 6, 85); they assume that monohydrol, like trihydrol, is less dense than dihydrol, and constitutes an important proportion of water above 50° . The increased proportion of a less dense and therefore more compressible constituent both above and below that temperature then accords with the observed greater compressibility (see also Richards and Palitzsch, *J. Amer. Chem. Soc.* 1919, 41, 63, for a discussion of this matter, and Pagliani, *Gazz. chim. ital.* 1920, 50, i. 186).

Similarly convincing explanations have been elaborated for the observed variations with temperature and pressure of the viscosity (Pagliani, *l.c.*), specific heat (Nernst, *J. Chem. Soc.* 1910, A. ii. 844), index of refraction (Chénaveau, *Compt. rend.* 1913, 156, 1972), magnetisation (Piccard, *ibid.* 1912, 155, 1497), dielectric constant (Falckenberg, *Ann. Physik.* 1920, [iv.] 61, 145), &c.

Measurements of the molecular weight of water by the cryoscopic and ebullioscopic

methods in supposedly neutral solvents give no evidence of association, but in fact water does react (*sic* *infra*) with such solvents in a manner which renders the method untrustworthy. More reliable conclusions may be drawn from measurements upon dilute solutions in such definitely reactive solvents as phosphorus oxychloride or nitrogen tetroxide, and these give concordant values for the molecular weight approximating closely to 36, indicating the formula H_2O_n (Oddo, *Gazz. chim. ital.* 1916, 46, i. 172; see also Bruni and Amadori, *Gazz. chim. ital.* 1910, 40, ii. 1). Attempts to calculate the complexity of ice molecules in solution from the variation of expansibility, compressibility and specific heat on the assumption that ice (H_2O_n) in solution in water retains its normal density lead to values for n around 12 (Duclaux, *Compt. rend.* 1911, 152, 1387), but this assumption is probably incorrect.

Many attempts have been made by extrapolation to calculate the properties of pure monohydrol and dihydrol, but in the present state of knowledge these are premature (see e.g. Sutherland, *J. Chem. Soc.* 1910, A. ii. 843; Oddo, *Gazz. chim. ital.* 1916, 46, i. 188).

Observations upon the formation and liquefaction of ice crystals (Skworzoff, *J. Chem. Soc.* 1911, A. ii. 970) and the phenomena of scattering of light by water suggest the presence in water of molecules of definite structure, which is intelligible on the assumption that water is actually not a simple liquid, but, at low temperatures, a solution of ice molecules in water (dihydrol). From this standpoint, the freezing-point of water is simply to be regarded as the temperature at which the concentration of trihydrol, increasing with fall of temperature, becomes equal to the solubility of trihydrol in water which, it is assumed, decreases with fall of temperature. Regelation of ice under slight pressure may conceivably occur through local

liquefaction of the ice and its resolidification on release of pressure. But neither pressure nor capillary action (alleged by Thomson, *Proc. Roy. Soc.* 1857, 3, 455; 1859, 9, 198; 1862, 11, 473; *Phil. Mag.* 1862, [iv.] 23, 407; 24, 395) are necessary, because regelation can occur under water without pressure (Faraday, *Proc. Roy. Soc.* 1860, 10, 440). On the ice solution hypothesis it is easy to understand how two blocks of ice under water may grow together by a process of solution and recrystallisation.

In addition to the evidence indicated very briefly above there is a mass of experimental work on solution which can best be explained on the foregoing hypothesis.

It is, perhaps, important to observe that if this hypothesis of the constitution of water be correct, the melting of ice, the expansion of water (at least at low temperatures), the generation of steam, &c., commonly regarded as types of simple physical change, are in fact changes of precisely the same kind as, say, the dissociation of nitrogen tetroxide or phosphorus pentachloride or the polymerisation of aldehydes, cyanogen chloride, &c., the essentially chemical character of which is never questioned. It is unnecessary to elaborate the obvious conclusion as to the validity of the distinction so frequently drawn between chemical and physical change.

CHEMICAL REACTIONS.

Dissociation and synthesis.—Water is a fairly stable compound, and is dissociated only to a small extent at about 3000°, the temperature of the oxyhydrogen flame.

In the oxyacetylene flame, which is considerably hotter, steam is largely dissociated, and the wide applicability of this flame to the welding of metals is in fact due to the consequent presence in it of free hydrogen. The following table shows the percentage dissociation of water vapour at high temperatures:—

Temperature	1124°	1207°	1290°	1432°	1510°	1590°	1695°	1984°	2370°	2488°	2561°	2656°
P.c. dissociated	0.008	0.019	0.034	0.102	0.182	0.354	0.518	1.79	4.3	6.6	9.6	11.1

The data from 1984° upwards, obtained by an explosion method, are less trustworthy than those at lower temperatures, but probably represent well enough the general trend of the reaction (Löwenstein, *Zeitsch. physikal. Chem.* 1906, 54, 715; Langmuir, *J. Amer. Chem. Soc.* 1906, 18, 1357; v. Wartenburg, *Zeitsch. physikal. Chem.* 1906, 56, 513; Bjerrum, *ibid.* 1912, 79, 513; but see Holt, *Phil. Mag.* 1907, [vi.] 13, 630).

In agreement with these facts, gaseous hydrogen and oxygen readily combine to form water when heated, when exposed to the electric spark or to a silent electric discharge, when subjected to the radiations of radioactive elements, or when exposed to ultra-violet light.

There is no evidence, though the assumption has frequently been made, that oxygen and hydrogen combine at all at ordinary temperatures in the dark, though they do so very slowly in sunlight (Baker, *Proc. Chem. Soc.* 1902, 13, 40). Isothermal increase of pressure to 56 atmospheres has no effect in promoting union (de la Roche, *Schweigger's Journ.* 1811, 1, 172; see also Degen, *Pogg. Ann.* 1836, 28, 644).

At 100° no combination can be detected in 218 days, but at 300° the formation of water is just appreciable in 65 days (Meyer and Raun, *Ber.* 1895, 28, 2904). At 400° the velocity of reaction is such that the formation of water may be recognised within a week (Bons, *J. Chem. Soc.* 1902, 81, 535; 1904, 85, 694), and thereafter the velocity of the reaction increases rapidly with temperature until at about 510°–560° explosive combination occurs. The precise value of the ignition temperature depends on the composition of the explosive mixture (being lowest, 507°, when the ratio $H_2 : O_2 = 1 : 4$) and falls with increase of pressure (Dixon and Coward, *J. Chem. Soc.* 1909, 95, 514; Dixon, *ibid.* 1910, 97, 661), but depends also upon the method of experiment and the material of the containing vessels. A small proportion of water vapour is essential to combination by normal combustion (Baker) or through the catalytic action of platinum (French, *Chem. News*, 1900, 81, 292); oxygen and hydrogen dried with phosphorus pentoxide do not react on platinum black, and only combine slowly in contact with a platinum wire at about 800°; but the explosion flame, once started, is similar in both cases and

gained gases (Dixon and Bradshaw, Proc. Roy. Soc. 1907, A, 79, 224).

Ignition of detonating gas by an electric spark is frequently a purely thermal effect, but this cannot be true of the slow combination brought about by the silent discharge (Berthelot, Ann. Chim. 1879, [v.] 17, 142; Deherain and Maquenne, Compt. rend. 1881, 93, 895, 963, 1021; Mixer, Amer. Journ. Sci. 1898, [iv.] 4, 51; Kirby, Phil. Mag. 1904, [vi.] 7, 223). A general examination of the effects indicates that the cathode column is the region of greatest chemical activity (Kirby, Phil. Mag. 1907, [vi.] 13, 269), and it seems probable that reaction proceeds by the ionisation of both gases, though short wave-length radiations akin to ultra-violet light may contribute to the effect.

Kernbaum has found (Compt. rend. 1910, 151, 319) that H_2O_2 and H_2 are produced by the silent discharge in oxygen and hydrogen mixtures, and concludes that the action of the discharge is analogous to that of ultra-violet light.

Ultra-violet light causes combination of hydrogen and oxygen and decomposes water, the reaction in either case tending to the same point of equilibrium which, for example, at 150° is that corresponding to thermal equilibrium at 1250° (Coehn, Ber. 1910, 43, 880; Coehn and Grote, Nernst's Festschrift, 1912, 136; Andréeff, J. Russ. Phys. Chem. Soc. 1911, 43, 1342). Water in a quartz vessel is decomposed thus even by sunlight (Kernbaum, Compt. rend. 1909, 149, 273; Bull. Acad. Sci. Cracow, 1911, A, 583).

The action of ultra-violet light in decomposing water is chiefly due to the radiation of very short wave-length ($\lambda=1900$), and is best observed, therefore, by the use of low-tension or new high-tension quartz mercury vapour lamps, which emit radiation relatively rich in rays of short wave-length (Tian, J. Chem. Soc. 1915, A, ii, 828; Obolowsky, Ann. Physik, 1912, [iv.] 39, 961).

In this decomposition pure hydrogen is at first the only gaseous product; later oxygen also is produced and accumulates until the composition of the mixture is that of detonating gas. This is best explained on the assumption that the primary action is an auto-oxidation producing hydrogen and hydrogen peroxide, $2H_2O \rightarrow H_2 + H_2O_2$, oxygen being formed by a secondary decomposition of the latter,



which can result from the action of moderately short wave-length radiation (λ 2500-3000) (Tian, Compt. rend. 1911, 152, 1012). In support of this theory, there is evidence that hydrogen peroxide formed from water-vapour in air by the action of ultra-violet rays in sunlight forms active nuclei for the condensation of moisture (Bleber, Ann. Physik, 1912, [iv.] 39, 1313). Contrary to suggestions which have been made, it would seem that the amount of hydrogen peroxide produced by ultra-violet light is much too small to account for the bactericidal action of the latter (see Courmont, Nogier and Roehaiz, Compt. rend. 1910, 150, 1453).

The fact that changes of potential occur at polished inert electrodes immersed in solutions of photo-sensitive colouring matters and exposed

to light may be explained on the assumption of a photochemical decomposition of the water by visible light; but there is no other evidence in support of this hypothesis (Baur and Rebmans, Helv. Chim. Acta. 1921, 4, 256).

The synthesis and decomposition of water by α -radiation is well established (Davis and Edwards, J. Soc. Chem. Ind. 1905, 24, 266; Pickel, Zeitsch. anorg. Chem. 1904, 38, 307; Lind, J. Amer. Chem. Soc. 1919, 41, 531, 551; Duane and Scheurer, Compt. rend. 1913, 156, 466). In a given spherical or cylindrical vessel the velocity of reaction depends only on the quantity of emanation present and the gas pressure, but the velocity diminishes with increase in the volume of the vessel and depends upon the hydrogen:oxygen ratio. There is reason to suppose that combination is preceded by collision-ionisation of both gases, but the mechanism of reaction is not well understood.

Catalytic action in the synthesis of water was first observed by Davy (Phil. Trans. 1817; 97, 45, 77) in the case of platinum, and has been the subject of so many investigations that its adequate discussion here would be impossible, and properly belongs to the general consideration of catalytic action.

The energy change involved in these reactions is expressed by the heat of formation of water for which the chief data are given below.



$x=68,310$. Ice calorimeter; const. pressure, $t=0^\circ$ (Schuller and Wartha, Wied. Ann. 1877, 2, 381).

68,390. Burning at const. pressure, $t=18^\circ$ in 15° calories (Thomsen, Thermochem. Untersuch. 2, 45).

68,400. Burnt in bomb; calc. to const. pressure at $t=17^\circ$ in 15° cal. (Mixer, Silliman's J. 1903, (4), 16, 214).

68,380. Mean result of critical recalculation of foregoing, at 18° and const. pressure, in 15° cal. (Roth, Zeitsch. f. Elektrochem. 1920, 26, 1, 288).

Water is decomposed by the passage of an electric current, but owing to its very low conductivity the extent of the decomposition is very small with pure water. In practice, the electrolytic decomposition of water so-called, is effected by the electrolysis of aqueous solutions of electrolytes, and according to the ionic hypothesis the production of one at least of the constituent gases at the electrodes is due to a secondary action of the discharged ions.

It has long been known that the passage of an electrical discharge through steam produces both decomposition and a sorting of the products apparently akin to electrolysis (Perrot, Compt. rend. 1858, 46, 180; 47, 359; Ann. Chim. 1861, [iii.] 61, 161; J. J. Thomson, Recent Researches in Electricity and Magnetism, Cambridge, 1893, 559). But both oxygen and hydrogen may appear at either or both electrodes according to the size and form of the discharge vessel, and it seems probable that the separation observed is due to effects of diffusion and gaseous flow and not to true electrolysis (Chapman and Liddbury, J. Chem. Soc. 1902, 81, 130; Holt and Hopkins, Phil. Mag. 1906, [vi.] 16, 92).

Oxidizing and reducing action.—It is well known

knowledge that water acts on many metals, usually forming a basic oxide and hydrogen. The alkali and alkaline earth metals react with cold water; glucinum (beryllium), magnesium, and many rare-earth metals react with water below its boiling-point; zinc, cadmium, tin, iron, cobalt, nickel, and chromium decompose steam at a red heat, and some other metals, e.g. copper and lead, react only at a white heat. Mercury, silver, gold, platinum, iridium, &c., do not react at all with water.

Whilst this is broadly true for ordinary distilled water and ordinary metals, some qualification is necessary.

The very detailed and critical study which has been made of the interaction of water and air upon iron shows clearly how greatly such actions are influenced by minute traces of impurity in either water or metal, and it has been proved that water has no action on magnesium below 100° if free from air (Roberts and Brown, *J. Amer. Chem. Soc.* 1903, 25, 801), and acts extremely slowly at ordinary temperatures with sodium amalgam if free from traces of hydrogen peroxide (Baker and Parker, *J. Chem. Soc.* 1913, 103, 2060). Therefore caution must be used in regarding the observed reactions with metals, especially at low temperatures, as those of pure water. It is known that in the wet oxidation of some metals, e.g. zinc, hydrogen peroxide is produced and appears to take part in the reaction (*see e.g. Smith, J. Chem. Soc.* 1906, 89, 479).

Water can also oxidise many non-metals. Silicon is attacked by water in glass vessels at 100°, but the action is probably due to dissolved alkali (Moissan and Siemens, *J. Chem. Soc.* 1904, A. ii. 398) and occurs with pure water only at a higher temperature. Reaction of steam with carbon begins at about 850° (Farup, *Zeitsch. anorg. Chem.* 1906, 50, 276), and at higher temperatures proceeds according to the equations $C + H_2O \rightarrow CO + H_2$; $C + 2H_2O \rightarrow CO_2 + 2H_2$, with a reversible secondary reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ (*see Gautier, Compt. rend.* 1906, 142, 1352). It is of great importance in the manufacture of producer-gas and water-gas (*q.v.*). Boron at a red heat similarly yields with steam boric oxide and hydrogen. At 2000° even nitrogen is oxidised by steam with the production of nitric oxide and hydrogen, $N_2 + 2H_2O \rightleftharpoons 2NO + H_2$, the mixture at equilibrium containing about 0.5 p.c. by volume of NO (Tower, *J. Amer. Chem. Soc.* 1905, 27, 1209).

Some of the lower oxides of metals, e.g. MnO, UO_2 , CrO , or compounds derived therefrom, e.g. potassium cobaltocyanide $K_3Co(CN)_6$, and molybdenous chloride Mo_2Cl_4 , are oxidised by water with liberation of hydrogen.

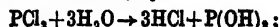
Thus the oxidising action of water is pronounced at high temperatures and occurs at low temperatures with powerful reducing agents.

Towards some non-metals, notably the halogens, water acts as a reducing agent, forming the non-metallic hydride and free oxygen. This action occurs with sulphur and phosphorus, but the oxygen simultaneously forms the non-metallic oxide. Thus with sulphur above 100° the reaction is represented by the equation $2H_2O + 3S \rightleftharpoons 2H_2S + SO_2$, though, of course,

equilibrium is reached at low concentrations of H_2S and SO_2 .

Hydrolysis.—Under this heading are included many of the most important and characteristic reactions of water.

The typical case is the hydrolysis of non-metallic chlorides, e.g. PCl_3 , PCl_5 , BCl_3 , $SiCl_4$, &c., to form hydrogen chloride and the hydroxy acid of the non-metal, e.g.



$BCl_3 + 3H_2O \rightarrow 3HCl + B(OH)_3$. Similar reactions occur with the corresponding bromides and iodides, and their irreversible character constitutes an important distinguishing characteristic of non-metallic elements. The one outstanding exception to this rule is the case of the halides of carbon, e.g. CCl_4 , $CBBr_4$, $C_2H_4Br_2$, &c., which are not hydrolysed by water to any appreciable extent at ordinary temperatures.

A similar, but reversible hydrolysis occurs to a greater or less extent with many metallic halides. The chlorides of bismuth and antimony are extensively hydrolysed in cold dilute aqueous solution, insoluble oxychlorides being precipitated: $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$; $SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$, and the higher chlorides of lead, tin, titanium, &c., $PbCl_4$, $SnCl_4$, $TiCl_4$, are hydrolysed with the formation of the corresponding hydroxides, which in some cases remain in solution. Many other metallic salts, e.g. $MgCl_2$, $ZnCl_2$, $CuSO_4$, &c., are appreciably hydrolysed in their aqueous solutions, which thereby acquire an acid reaction. It is indeed only in the case of relatively few salts, those of strong bases such as the alkalis, with strong acids such as the halogen hydrides, nitric acid, sulphuric acid, perchloric acid, &c., that hydrolysis in solution is inappreciable. Just as the hydrolysis of the salts of weak bases with strong acids, e.g. $Al_2(SO_4)_3$, gives acid solutions, so that of salts of strong bases with weak acids, e.g. Na_2CO_3 , Na_2S , &c., causes their solution to have an alkaline reaction. It is frequently assumed that the neutral character of a solution of, say, potassium chloride, indicates an absence of hydrolysis, but this is by no means necessarily so. The neutrality of such a solution is quite compatible with extensive hydrolysis to yield equivalent amounts of acidic and basic solutes of the same type which, by the preponderance of one or other sort, give the basic or acidic character to solutions in which hydrolysis obviously occurs. This point is of importance to the theory of solutions (Vol. vi. p. 286).

The hydrolytic action of water increases with temperature, so that at a red-heat most metallic salts are completely hydrolysed by steam, e.g. $MgCl_2 + H_2O \rightarrow MgO + 2HCl$ (Moldenhauer, *Zeitsch. anorg. Chem.* 1906, 51, 369), and many, e.g. $NaCl$, which show no sign of hydrolysis in the cold, are partly decomposed.

Many binary compounds of metals with non-metals are readily and completely hydrolysed by water at ordinary temperatures, to produce the metallic hydroxide and the non-metallic hydride. The sulphides, selenides, nitrides, phosphides, and silicides of magnesium, glucinum, and aluminium are thus decomposed, and the hydrolysis of aluminium phosphide

or silicide is a convenient method for the preparation of phosphine or silicon hydride. Hydrolysis of the carbides is of special interest; some, e.g. aluminium or glucinum carbide, yield pure methane; others give various mixtures of hydrocarbons and hydrogen. The hydrolysis of calcium carbide to produce acetylene is the basis of a great industry, and that of nitrides, e.g. AlN , to produce ammonia has been employed in some processes for the fixation of atmospheric nitrogen.

Some binary compounds of non-metals, e.g. boron nitride, and the sulphides and selenides of boron and silicon, are similarly hydrolysable.

Hydrolysis of many metallic hydrides, e.g. LiH , CaH_2 , &c., yields the metallic hydroxide and hydrogen.

In organic chemistry innumerable hydrolytic reactions of importance are known, e.g. of organo-metallic compounds $\text{Zn}(\text{CH}_3)_2$, halides, esters, cyanides, etc.

Addition.—The direct addition reactions of water with basic and acidic oxides to form bases and acids occupy an intermediate position between hydrolytic action of the foregoing type and the so-called simple hydration discussed below.

Anhydrides of strong acids and bases, e.g. SO_3 , P_2O_5 , N_2O_5 , or Na_2O , CaO , Li_2O , &c., combine very readily with water; those of weaker acids and bases, e.g. B_2O_3 , SiO_2 , or ZnO , MgO , &c., react slowly or at higher temperatures. Data for the heat of hydration of typical basic oxides are given in Table 37.

TABLE 37.

HEATS OF HYDRATION OF OXIDES.

Typical examples of the heat of hydration of basic oxides, hydroxides and peroxides are given in the following table: the values given are in 15° gram-calories.

Heats of hydration	15° gram-calories	Reference
$\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH}$	14,400	1
$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$	35,440	1
	35,620	4
$\text{K}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{KOH}$	42,100	1
$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$	15,100	1
	15,540	4
$\text{SrO} + \text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2$	17,100	1
	17,700	4
$\text{BaO} + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2$	17,600	1
	22,260	4
$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$	5,400	1
$\text{ZnO} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2$	-2,750	4
$\text{Ti}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{TiOH}$	3,230	4
$\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{NaOH} \cdot \text{H}_2\text{O}$	3,250	1
$\text{KOH} + \text{H}_2\text{O} \rightarrow \text{KOH} \cdot \text{H}_2\text{O}$	8,900	1
$\text{KOH} + 2\text{H}_2\text{O} \rightarrow \text{KOH} \cdot 2\text{H}_2\text{O}$	15,400	1
$\text{Sr}(\text{OH})_2 + 8\text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	26,280	4
	24,700	1
$\text{Ba}(\text{OH})_2 + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$	3,580	4, 2
$\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	27,470	4
" " " " " "	24,400	1
$\text{SrO}_2 + 9\text{H}_2\text{O} \rightarrow \text{SrO}_2 \cdot 9\text{H}_2\text{O}$	20,480	3
$\text{BaO}_2 + \text{H}_2\text{O} \rightarrow \text{BaO}_2 \cdot \text{H}_2\text{O}$	2,800	1
$\text{BaO}_2 + 10\text{H}_2\text{O} \rightarrow \text{BaO}_2 \cdot 10\text{H}_2\text{O}$	18,200	3

1. Berthelot, *Thermochimie*, II. 1897.
2. de Forcrand, *Compt. rend.* 1888, 103, 60.
3. de Forcrand, *Compt. rend.* 1901, 130, 1017.
4. Thomsen, *Thermochem. Untersuch.* III. 1883.

This type of hydration leads to a profound change in the properties of the compound, and it is generally held that the water loses its character as such and enters into the constitution of the product in the form of hydroxyl groups. Such addition, therefore, resembles hydrolysis, save that one product only results.

Hydration.—The union of water with substances to form hydrates, as distinct from hydroxides, is characterised by the slightness of its effect upon the physical and chemical

properties of the original substance. This is especially well seen where a compound forms a series of hydrates, e.g. FeCl_3 , Na_2CO_3 , CuSO_4 , as these differ from each other only slightly in colour, solubility, &c., and not at all in chemical properties.

It is the practice to confine the term hydrate to compounds in which water is present in fixed and simple molecular proportions; this, however, is an arbitrary rule. We have practically no evidence as to the manner in which

water of hydration (water of crystallisation) is held in the molecule. We know simply that water is evolved from hydrates, usually at comparatively low temperatures, that it is not directly and necessarily concerned in the most characteristic reactions of the hydrated substance, and that it can frequently be replaced molecule for molecule by other solvents, e.g. ether or alcohol, with a minimal change in the character of the hydrate.

The ease with which water is expelled from hydrates is illustrated by its liberation by simple grinding (Gillette, Chem. News, 1911, 104, 313), and in one recorded case by the action of light (McKee and Berkheiser, Amer. Chem. J. 1908, 40, 303). It has been suggested that hydrates may retain some water in solid solution (Richards, J. Amer. Chem. Soc. 1911, 33, 888).

Water of crystallisation has many of the properties of free water. It acts like free water upon calcium carbide (Masson, J. Chem. Soc. 1910, 97, 851) and upon some metals, e.g. magnesium (Michailenko and Mushinsky, J. Russ. Phys. Chem. Soc. 1912, 44, 181). It exhibits the same infra-red absorption bands as water (Schaefer and Scherbert, Ann. Physik. 1916, [iv], 50, 339).

Water can pass through solid plates of crystalline hydrates (Baker and Adams, J. Chem. Soc. 1911, 99, 597) by a process apparently resembling its diffusion through solutions.

Hydrated salts are curiously akin to the solutions from which they form. Where the colour of an anhydrous salt differs from that of its solution, e.g. CuSO_4 , CoCl_2 , CuBr_2 , CuCl_2 , &c., the colour of the crystalline hydrate is usually that of the solution. Hydrates exhibit a definite vapour tension of water; hence, on the kinetic theory, water molecules must pass freely in and out of the crystal space lattice as they do in and out of a solution. If the pressure of water vapour above the hydrate is less than its vapour tension, the hydrate loses water and *effloresces*. Conversely, it absorbs water and may *deliquesce*.

When a salt, capable of forming several hydrates (typically $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which can yield $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and CuSO_4) is in equilibrium with its vapour in a closed space, and water is slowly but continually removed, the pressure of aqueous vapour over the hydrate remains constant until the whole is converted to the next lower hydrate, when the vapour pressure *suddenly* drops to that characteristic of the second hydrate and maintains that

TABLE 38.
VAPOUR PRESSURES OF HYDRATED SALTS.

Equilibrium	p.	Reference
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{aq. vap.}$	18.2 mm.	1
	19.22 "	2
	19.20 "	3
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + \text{aq. vap.}$	18.0 "	1
	19.13 "	2
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} + \text{aq. vap.}$	12.4 "	1
	14.51 "	2
$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 + \text{aq. vap.}$	8.9 "	1
$\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{CO}_3 + \text{aq. vap.}$	1.1 "	1
$\text{Ca(OH)}_2 \rightleftharpoons \text{CaO} + \text{aq. vap.}$	0.8 "	1
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{aq. vap.}$	4.8 "	1
	5.26 "	4
	5.8 "	2
$\text{BaCl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{BaCl}_2 + \text{aq. vap.}$	2.5 "	1
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + \text{aq. vap.}$	7.0 "	1
	7.68 "	4
	7.80 "	2
	7.77 "	5
$\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O} + \text{aq. vap.}$	4.7 "	1
$\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{aq. vap.}$	0.8 "	1

1. Foote and Scholes, J. Amer. Chem. Soc. 1911, 33, 1309.
2. Wilson, J. Amer. Chem. Soc. 1921, 43, 704.
3. Baxter and Lansing, J. Amer. Chem. Soc. 1920, 42, 412.
4. Partington, J. Chem. Soc. 1911, 99, 466.
5. Menzies, J. Amer. Chem. Soc. 1920, 42, 1951.

value until conversion to the third hydrate is complete. This step by step transformation, readily interpreted in terms of the phase-rule, affords a means of detecting the existence of hydrates.

If during dehydration the vapour pressure be plotted against the percentage of water in the residual solid, the existence of a hydrate will be evidenced by a flat 'platform' on the curve; a continuous curve indicates the absence of definite hydrates.

Care must be exercised in applying this method, because there is frequently a delay, or period of induction, in the rise of the vapour pressure to the value characteristic of the temperature (Cumming, *Trans. Chem. Soc.* 1910, 97, 593; Partington, *ibid.* 1911, 99, 466; Ephraim and Millmann, *Ber.* 1917, 50, 539; Ephraim and Wagner, *Ber.* 1917, 50, 1068).

Indeed, Faraday showed (*Pogg. Ann.* 1834, 33, 186) that whereas hydrated sodium carbonate, sodium hydrogen phosphate, and sodium sulphate readily effloresce in air, perfect crystals of these salts may be kept in air for years without change. Inoculation with the lower hydrate at once causes the vapour pressure to assume its normal value. The period of induction in dehydration receives a rational explanation if we consider that the minute particles of the second phase formed at first by dehydration have, like small drops of water, an abnormally high vapour pressure (Rae, *J. Chem. Soc.* 1916, 109, 1229; see Pavlov, *J. Russ. Phys. Chem. Soc.* 1909, 41, 679).

Table 37 contains data for the thermal effect of several typical hydration reactions. Table 38 gives the equilibrium pressure of water vapour, in mm. of mercury, at 25° over a few of the more important crystalline hydrated salts, when in equilibrium with a lower hydrate or the anhydrous salt.

Solution and ionisation.—Water is, *par excellence*, the solvent. It has been argued that all substances are soluble in water, but this is not proven. Most salts and compounds usually classed as insoluble, e.g. silver chloride, glass, silica, are well known to have a small, but definite, solubility in water. The great majority of solids and liquids, and all known gases, are distinctly soluble, and some very soluble, in it.

There is much reason to believe that the solvent power of water and its pre-eminence as an ionising solvent are both due to chemical action between solvent and solute of the kind considered under hydrolysis and hydration.

An overwhelming mass of real evidence exists that substances dissolved in water are intimately associated, one had better say combined, with water or 'solvated' (see, for a list of references, Dhar, *Zeitsch. Elektrochem.* 1914, 20, 67; and for a critical review of earlier work, Washburn, *Hydrates in Solution*, Tech. Quart. 1908, 21, 360; as examples of more recent evidence, see e.g. Schaeffer, Paulus and M. C. Jones, *Phys. Zeitsch.* 1914, 15, 447; Philip and Bramley, *J. Chem. Soc.* 1915, 107, 371, 1637; Kornfeld, *Monatsh.* 1915, 36, 865; Purser, *Trans. Faraday Soc.* 1917, 13, 123; Smith, Landa and Bouman, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, 23, 969), and some

chemists have preferred to interpret all solution phenomena in terms of such compounds, even going so far as to regard the solute of the solvent as being combined with the solute (Kahlenberg, *Trans. Faraday Soc.* 1905, 1, 42).

On the other hand, much work adduced as evidence for solvation is unconvincing and contradictory. Kendall has remarked: "In the system $H_2SO_4-H_2O$, for instance, as many as 102 different hydrates have been 'discovered,' ranging in composition from $36H_2SO_4 \cdot H_2O$ to $H_2SO_4 \cdot 4950H_2O$. Few of these have been encountered twice by independent investigators, the opportunity for originality being almost unlimited." Thus many chemists have supported the original view of Ostwald and van't Hoff, which regards the solvent simply as a dispersive medium, enabling the solute to behave as if alone and in a gaseous state (see *Brit. Association Report*, 1890, 60, 311-338).

But the 'solvate' theory, rejecting the conception of ionisation altogether (see e.g. Armstrong and Worley, *Proc. Roy. Soc.* 1912, 87 A, 604), fails to explain in any satisfactory manner the mechanism of conduction in electrolytes, whilst the strict ionic theory equally fails to explain why and how ionic dissociation occurs.

It has been generally recognised by those who admit the existence of ions, that the ions in solution are hydrated (see Arrhenius, *Theories of Solutions*, pp. 184-195), and it has been pointed out that the rival 'solvate' and 'ionic' theories are in reality not irreconcilable but supplementary (Walker, *Brit. Association Report*, 1911, 81, 356).

There is, in fact, an intimate and general connection between ionisation and compound formation in solutions, and Kendall and Boege have strongly advocated the hypothesis that ionisation is preceded by, and is a consequence of, the formation of such compounds (Kendall and Boege, *J. Amer. Chem. Soc.* 1917, 39, 2323; this paper contains a detailed discussion of the hypothesis and numerous references to the literature, and should be consulted; the same idea had been indicated by others, to whom reference is made in the above paper, and was formulated with some precision by Bogorodski, *J. Russ. Phys. Chem. Soc.* 1914, 46, 1716).

Experiments with tetraethyl-ammonium iodide in a large number of solvents have shown that conductivity of solutions is fundamentally related to the dielectric constant and to the state of unsaturation of the simple molecules of the solvent (Walden, *Zeitsch. physikal. Chem.* 1903, 46, 103; 1906, 54, 129; H. C. Jones, *Amer. Chem. J.* 1901, 25, 232). These properties, as might be anticipated from their general parallelism, have a causal relationship (Thomson, *Phil. Mag.* 1914, [vi.] 27, 757; Lewis, *J. Amer. Chem. Soc.* 1913, 35, 1443; 1916, 38, 762).

Unsaturation implies the presence in the molecule of electrons which are free to move under the influence of an electric field. The simple water molecule (H_2O) contains two doublets, as in the formula $H^+ \cdots O^- \cdots H^+$; and the six free electrons of the oxygen atom will move into such positions as enable them to exert a maximum attractive force upon the

positive parts of these doublets, so that an unequal distribution of electric charges will result. By proximity of two such molecules this unequal distribution is accentuated and may lead to the formation of associated molecules, possessing a still larger electrostatic moment, in which the constraints are correspondingly weakened. Further association can occur with enhancement of these effects.

Great attractive forces are exerted by such associated molecules upon any solute RX ; these forces are cumulative as the molecules come into closer proximity, and can evidently lead to the formation of complexes of the type $R(H_2O)_n-X$, in which the constraints upon the electrons are still further weakened. Such complexes are much less stable than the simple component molecules and dissociable at any point, and it is thus possible to see how hydration may cause ionisation.

The essential probability of this theory is illustrated by the case of aqueous hydrochloric acid. Both hydrogen chloride and water when pure are almost non-conductors (Kohlrausch and Heydweiller, *Zeitsch. physikal. Chem.* 1894, 14, 326; Steele, McIntosh and Archibald, *ibid.* 1906, 55, 148); both contain unsaturated atoms in the simple molecule and are in consequence associated; both have high dielectric constants. When mixed they constitute a good electrolyte.

In contrast with the older ionic hypothesis, Kendall's theory permits us to regard the ionisation and conductivity as due to both constituents of the solution. Complex molecules $(H_2O)_2(HCl)$, are formed and dissociate to yield positively and negatively charged radicals. Taking the simplest case these would be either $(Cl \cdot H_2O)^-$ and $(H \cdot H_2O)^+$ or $(HCl \cdot OH)^-$ and $(HCl \cdot H)^+$, and on inspection these two alternatives are seen to be the same thing. The complex $(H_2OCl)^-$ may be regarded either as a hydrated chloride ion or a solvated hydroxyl ion.

The following table shows the degree of dissociation of pure water at various temperatures from 0° – 50° ; α being the weight in grms. of hydrogen ion in 1 c.c. of water at the stated temperature.

Temp.	$\alpha \times 10^{10}$
0°	0.36
2°	0.40
10°	0.57
18°	0.80
28°	1.10
34°	1.45
42°	1.91
50°	2.44

(Kohlrausch and Heydweiller, *Wied. Ann.* 1894, 53, 234; *Zeitsch. physikal. Chem.* 1894, 14, 230; the numbers are in substantial agreement with the indirect measurements of Arrhenius, *Zeitsch. physikal. Chem.* 1893, 11, 323; Nernst, *ibid.* 1894, 14, 155; Lorenz and Nehl, *ibid.* 1909, 66, 748; Noyes and Kato, *ibid.* 1910, 73, 20; Dolezalek, *Zeitsch. Elektrochem.* 1899, 5, 538; Kanolt, *J. Amer. Chem. Soc.* 1907, 29, 1414; Lewis, Brighton and Sebastian, *ibid.* 1917, 39, 2260; Lunden, *J. Chem. Phys.* 1907, 5, 589; Heydweiller, *Ann. Physik.* 1909, [iv.] 23, 511).

The heat of formation of water from its ions is +14,700 gm. cal. per gm. mol. at 0° , the value at other temperatures t , being given by +14,700–50 t . This is the most probable value derived from a number of researches by different methods, as follows:

1. From the heat of neutralisation of strong acids by strong bases (Wörmann, *Ann. Physik.* 1905, [iv.] 18, 793; Heydweiller, *Ann. Physik.* 1909, [iv.] 23, 503; Thomsen, *Thermochem. Untersuch.* 1882; Müller, *Bull. Soc. chim.* 1918, [iv.] 23, 8; Müller and Bauer, *J. Chim. Phys.* 1904, 2, 457).

2. From the change of conductivity of pure water with change of temperature; calculated by van't Hoff from the data of Kohlrausch and Heydweiller.

3. From the variation with temperature of degree of hydrolysis of salts (Lunden, *J. Chem. Phys.* 1907, 5, 145, 574; 1908, 6, 6, 81; Noyes, *Carnegie Inst. Publ.* 1907, No. 63).

H. V. A. B.

Water in its Economic and Sanitary Relations, Drinking Water.

Water for Domestic Supply.

Water is absolutely indispensable to both animal and vegetable life; it is the cause of many of the most striking phenomena in nature, and is employed for countless purposes by man. Its distribution is as wide as that of the air itself whilst its amount on the earth is enormously greater. In an absolutely pure state it is never met with in nature. The impurities in natural water are derived from the materials—solid, liquid, or gaseous—with which it comes in contact, and they may be present either in suspension or in solution or in both. Inasmuch, therefore, as the interest attaching to different waters depends upon the impurities they contain, and these are dependent upon the matters with which they have been in contact, it is most convenient to classify waters according to their origin.

1. *Rain-water, snow, hail, dew, and hoar-frost.* All these forms of water are obtained by the condensation of the aqueous vapour which is invariably present in the air. The amount of aqueous vapour which can be contained in a given volume of air is solely dependent upon the temperature. If the atmosphere has become saturated with aqueous vapour at any given temperature and is cooled below that temperature, the excess of aqueous vapour will condense, according to circumstances, as rain, hail, snow, mist, dew, or hoar-frost. This condensation is promoted by the presence of dust and electrically charged particles. All these forms of water having been only in contact with the air and not with the earth are characterised by the small proportion of solid matter which they contain, although the amount found, especially in the vicinity of towns, is often considerably greater than would be anticipated, and the rain-water falling in the neighbourhood of the sea is often mixed to a considerable extent with sea-spray, which with favourable winds is carried many miles inland. In the following table are recorded the maximum, minimum, and average proportions of several ingredients in samples of rain-water collected at Rothamsted and elsewhere, expressed in parts per 100,000—

	Total solid impurity	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum	0.62	0.021	0.003	0.005	0	0	0
Maximum	8.58	0.372	0.121	0.155	0.044	1.65	1.7
Average	3.42	0.095	0.021	0.049	0.007	0.33	0.5
Rain-water collected at Land's End, Cornwall, Jan. 2, 1873	42.80	0.131	0.034	0	0.020	21.8	10.0
Rain-water collected near Hyde Park, London, Nov. 8, 1873	2.76	0.383	0.040	0.210	0.008	0.5	1.1

It is thus seen that the composition of rain-water, even in the open country, is liable to great fluctuations, and that the amount of impurity, both mineral and organic, is occasionally surprisingly large. The amount

of organic impurity in dew and hoar-frost is still greater owing to these forms of water being condensed out of the lowest and most-contaminated couches of the atmosphere. Thus—

SEVEN SAMPLES OF DEW AND HOAR-FROST, ROTHAMSTED, 1869 AND 1870.

(Results of Analysis expressed in parts per 100,000.)

	Total solids	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Chlorine	Hardness
Minimum	2.64	0.195	0.026	0.130	0	0.35	1.3
Maximum	8.00	0.450	0.196	0.280	0.050	0.80	2.5
Average	4.87	0.264	0.076	0.198	0.023	0.53	1.9

Two other impurities, not referred to above, which are generally present in the rain-water and snow of towns are sulphurous and sulphuric acids derived from the combustion of coal. Angus Smith found in the rain-water of London 3.05, of Liverpool 3.96, in that of Manchester 4.48, and in that of Glasgow 7.02 parts of sulphuric acid per 100,000, to a considerable extent in the free state. Sendtner found freshly-fallen snow in Munich to contain 0.7 part sulphuric acid (SO_3) per 100,000, on the following day 1.76 parts, after 10 days 6.22 parts, and after 16 days 9.18 parts. The presence of this free acid in the rain-water of towns is, of course, not only detrimental to vegetation, but also to sculptures and buildings in which marble or limestone are employed. The proportion of ammonia increases in the snow after lying on the ground (Wagner, *Technologie*, 306).

2. *Upland surface water* most nearly approaches in composition to that of the atmospheric waters dealt with in the last section. It is, in fact, rain-water which has undergone minimum contact with the earth, although in consequence of its solvent action even this contact is sufficient to impart to the water in many cases such proportions of dissolved matter as are never found in rain-water. The amount and nature of these ingredients depend, of course, mainly upon the kind of soil over which the water has travelled, and consequently it becomes convenient to sub-divide this class according to the geological character of the ground from which the upland surface water has been obtained.

In the tables on p. 370 are recorded the maximum, minimum, and average amounts of impurity found in the examination of a large series of samples of waters principally derived from land not under cultivation, so as to represent the characters naturally acquired by water passing over the various geological formations.

The tables (I. and II.) show that upland surface waters generally contain a considerable amount of dissolved matters only when they are derived from calcareous strata. The organic matter is subject to great variation, but in every case contains only a very small proportion of nitrogen in comparison with the carbon, indicating that the organic substances present are of vegetable origin, which is further attested by the almost entire absence of ammonia, nitrates, and nitrites, all of which, when present in amount beyond that in which they occur in rain-water, are nearly exclusively derived from the decomposition of animal matters. The chlorine is also low, the upland gathering grounds being generally beyond the reach of sea-spray and not receiving the liquid excrements of animals, which are particularly rich in chlorides, whilst from their mere surface contact with the soil they have not extracted any considerable quantities of the salts present in the latter, as is the case with spring- and well-water.

3. *Surface water derived from cultivated land*.—This includes the great body of river-waters, inasmuch as practically all streams flow through and receive accessions from land under cultivation before reaching the sea. The com-

WATER.

I.—WATERS FROM NON-CALCAREOUS STRATA.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Upland surface water from Igneous rocks. ¹										
Maximum . . .	12.70	0.582	0.071	0.004	0.029	0.073	2.10	0.4	5.7	5.9
Minimum . . .	1.52	0.074	0.013	0	0	0.014	0.35	0	0.8	0.8
Average (18 samples)	5.15	0.278	0.033	0.001	0.002	0.035	1.13	0.1	2.0	2.1
(b) Upland surface water from Metamorphic, Cambrian, Silurian, and Devonian rocks. ²										
Maximum . . .	12.48	1.059	0.076	0.008	0.043	0.110	3.35	1.8	6.9	6.9
Minimum . . .	2.14	0.042	0.001	0	0	0.002	0.52	0	0.3	0.4
Average (81 samples)	5.12	0.293	0.024	0.002	0.006	0.031	0.92	0.3	2.5	2.5
(c) Upland surface water from Yoredale and millstone grits and non-calcareous portion of the Coal Measures. ³										
Maximum . . .	15.00	1.457	0.103	0.024	0.042	0.116	1.59	3.7	8.1	8.7
Minimum . . .	4.58	0.033	0	0	0	0.012	0.65	0	0.9	0.9
Average (47 samples)	8.75	0.377	0.033	0.003	0.010	0.050	1.05	0.4	4.3	4.7
(d) Upland surface water from Lower London Tertiaries and Bagshot beds.										
Maximum . . .	13.14	0.439	0.056	0.012	0.020	0.086	2.60	0.9	5.6	5.6
Minimum . . .	5.92	0.282	0.039	0	0	0.039	1.24	0	1.8	1.8
Average (3 samples)	8.40	0.379	0.048	0.004	0.007	0.058	2.06	0.3	3.5	3.8

¹ All soft and peaty. Generally turbid, and of a yellowish or even brownish colour.² This water is also generally peaty, and often turbid and coloured. Owing to the large area of these rocks exposed they form some of the most important gathering grounds, especially in Scotland.³ Soft, but generally turbid, peaty, and of a yellow or brownish colour.II.—WATERS FROM CALCAREOUS STRATA.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Upland surface water from Silurian and Devonian rocks. ¹										
Maximum . . .	14.46	0.475	0.046	0	0.055	0.080	1.62	3.5	9.6	9.6
Minimum . . .	12.26	0.103	0.008	0	0	0.016	0.83	0	5.2	7.5
Average (3 samples, all from Scotland)	13.71	0.301	0.026	0	0.021	0.047	1.20	1.2	7.4	8.6
(b) Upland surface water from Mountain Limestone. ²										
Maximum . . .	23.40	0.812	0.097	0.002	0.042	0.097	1.59	9.3	10.6	14.6
Minimum . . .	12.45	0.218	0.023	0	0	0.024	0.92	1.7	4.3	9.8
Average (7 samples)	17.07	0.370	0.047	0.001	0.011	0.059	1.24	5.7	7.0	12.7
(c) Upland surface water from calcareous portion of Coal Measures. ³										
Maximum . . .	77.36	0.856	0.089	0.010	0.061	0.122	4.85	11.6	13.6	25.0
Minimum . . .	10.20	0.082	0.001	0	0	0.014	0.84	0	3.0	6.2
Average (26 samples)	22.79	0.346	0.037	0.003	0.016	0.056	1.52	4.0	8.3	12.3
(d) Upland surface water from Lias, New Red, and Conglomerate Sandstone.										
Maximum . . .	26.32	0.506	0.075	0.008	0.034	0.100	2.00	16.0	12.9	24.8
Minimum . . .	11.08	0.186	0.020	0	0	0.022	0.99	2.9	3.1	6.0
Average (8 samples)	18.92	0.300	0.042	0.002	0.012	0.056	1.50	7.6	6.3	14.0
(e) Upland surface water from Magnesian Limestone. ⁴										
Ripon, the Kex Beck, 8 miles from source, Jan. 27, 1874 . . .	17.84	0.172	0.036	0.001	0	0.037	1.40	6.4	8.3	14.7
(f) Upland surface water from Oolites. ⁵										
The Frome, above Woodlands Mill, Somersetshire, March 10, 1870 . . .	17.46	0.326	0.025	0.004	0.042	0.070	1.55	6.6	5.6	12.4

¹ Owing to the compact nature of the limestone in these old formations, the hardness is very moderate.² Hardness not excessive, but large amount of organic matter (peaty), rendering the waters coloured and unpalatable.³ Of very variable character; generally of only moderate hardness, but containing much peaty matter, and hence coloured and unpalatable.⁴ Slightly turbid.⁵ Slightly turbid. Owing to the porous nature of Oolite formation, surface water is very rare.

position of such waters is very varied, depending upon local circumstances, and being liable to great fluctuations at different seasons of the year. This group may be conveniently divided into two sub-groups, according as the water

is derived from calcareous or non-calcareous districts. The following results of analyses of British waters of this description are compiled from the Sixth Report of the Rivers Commission, 1874:—

SURFACE WATERS FROM CULTIVATED LAND.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
(a) Water from non-calcareous districts. ¹										
Maximum	18.10	1.124	0.112	0.056	0.258	0.393	2.80	4.6	8.0	10.1
Minimum	5.26	0.125	0 ²	0	0	0.017	0.70	0	1.8	2.1
Average (31 samples)	9.52	0.276	0.034	0.007	0.089	0.128	1.49	0.6	4.3	4.9
(b) Water from calcareous districts. ³										
Maximum	110.40	1.338	0.307	0.030	1.005	1.096	12.75	26.3	42.1	67.3
Minimum	13.22	0.069	0.009	0	0	0.033	0.54	0	2.1	7.8
Average (144 samples)	30.08	0.268	0.053	0.005	0.257	0.314	2.24	12.4	8.2	20.6

¹ Usually turbid, organic matter generally moderate in amount, but partially of animal origin.

² This result is extremely improbable, more especially as the particular water in question (a sample of the water supplied to Bury and Radcliffe, Lancashire) contained 0.229 organic carbon, 0.032 ammonia, and 0.066 nitrogen as nitrates and nitrites.

³ Generally turbid, the organic matter is much the same in amount as in the water from non-calcareous districts, but generally more nitrogenous, in consequence of calcareous soils being usually under higher cultivation than non-calcareous ones. The total combined nitrogen is also for the same reason considerably greater, and the hardness is, of course, very much higher.

In connection with the effect of cultivated land upon the water with which it comes in contact, it is instructive to note the nature of the water which drains from such land, as this throws light upon the composition of subterranean waters (from springs and wells), which will be considered below.

In the following table is recorded the composition of the water obtained from drain-pipes placed from 18 ins. to 5 ft. below a plot of land at Rothamsted which had remained both unmanured and uncropped for a period of 11-15 years:—

COMPOSITION OF WATER FROM LAND UNMANURED AND UNCROPPED FOR ELEVEN TO FIFTEEN YEARS.¹ (6th Rep. Riv. Com. p. 62.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum	63.28	0.235	0.116	0.026	4.936	4.981	3.80	7.2	11.9	16.6
Minimum	18.00	0.006	0.026	0	0.607	0.654	0.60	0.3	3.3	3.6
Average (15 samples distributed over four years)	32.06	0.154	0.053	0.006	2.195	2.253	1.65	4.1	8.5	12.6

¹ The samples varied from clear to turbid.

It will be seen that the conversion of the original nitrogenous organic matter in the soil into mineral products is a very slow process, large quantities of nitrates being still present in the drainage waters after the lapse of so many years.

It is interesting to compare with the above the composition of the water draining from a plot of land unmanured for 16-21 years, but continuously bearing an annual wheat crop during that time:—

COMPOSITION OF WATER FROM LAND UNMANURED FOR SIXTEEN TO TWENTY-ONE YEARS, BUT CONTINUOUSLY BEARING WHEAT CROPS. (6th Rep. Riv. Com. p. 80.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	48.40	0.242	0.058	0.006	2.268	—	3.80	14.1	22.4	32.7
Minimum . . .	13.80	0.099	0.010	0	0	—	0.80	8.9	3.9	13.5
Average (11 samples distributed over five years) . . .	24.96	0.170	0.034	0.002	0.645	—	1.37	10.8	8.4	19.2

As might have been anticipated, the proportions of ammonia and nitrates finding their way into the drainage water in this case were much less, and in the summer months during the growth of the crop the amount of this mineral nitrogen found in the drainage water was practically nil.

We will, in the next place, compare with the above the composition of the drainage water from land which had been manured annually with 14 tons of farmyard manure per acre over a period of 24-29 years, and bearing wheat continuously during that time:—

COMPOSITION OF DRAINAGE WATER FROM LAND MANURED WITH 14 TONS FARMYARD MANURE PER ACRE FOR TWENTY-FOUR TO TWENTY-NINE YEARS. (6th Rep. Riv. Com. p. 58.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	51.20	1.243	0.335	0.052	2.592	2.754	3.35	12.1	20.6	32.1
Minimum . . .	14.00	0.181	0.036	0	0.082	0.130	0.60	1.4	5.4	8.7
Average (13 samples over five years) . . .	25.90	0.519	0.115	0.009	0.528	0.665	1.30	6.8	8.6	15.4

Thus the difference between the drainage waters from the unmanured and manured land is not nearly so great as might have been expected, being principally confined to the larger proportion of organic matter found in the latter.

The above results may be compared with

those obtained in the analysis of a number of samples of the drainage water from sewage farms, in all of which the town sewage is, or was, applied to land, with the double object of purifying the sewage and deriving a profit out of the crops raised. Thus:—

COMPOSITION OF DRAINAGE WATER FROM SEWAGE FARMS. (6th Rep. Riv. Com. pp. 55-57.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
Maximum . . .	103.00	2.160	0.517	1.366	6.499	6.833	13.40	36.9	39.3	56.6
Minimum . . .	18.60	0.108	0.034	0.005	0	0.069	2.15	0	3.9	3.9
Average (72 samples) . . .	64.02	0.982	0.191	0.388	0.756	1.266	6.36	17.6	15.4	33.0

It will be seen that the drainage water from sewage farms is generally richer in organic and inorganic impurities than the water draining from manured or unmanured land, the passage of the water through the ground being in the latter case a much slower one, and thus allowing time for more perfect purification by soil and

plants. Occasionally, as indicated by the above minimum results, the drainage water from sewage farms is remarkably free from impurities. A much purer drainage water is often yielded in the intermittent downward filtration of sewage through suitable land.

The knowledge thus gained of the composition

SHALLOW WELL WATERS.

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Gneiss and Silurian rocks ¹ (8th Rep. Riv. Com. p. 69).										
Maximum	100.20	0.362	0.110	0.625	2.465	3.090	17.00	22.3	19.2	41.5
Minimum	6.32	0.027	0.003	0	0.033	0.040	0.90	0	3.3	3.4
From Devonian rocks ² (29 samples analysed).										
Maximum	105.20	0.794	0.172	0.630	4.197	4.261	17.00	18.3	47.8	55.7
Minimum	12.16	0.004	0.003	0	0.033	0.039	1.60	0	3.2	5.0
From Yoredale and Millstone grits ³ (20 samples analysed).										
Maximum	133.60	0.859	0.216	0.010	5.100	5.200	13.90	37.2	65.1	90.0
Minimum	5.92	0.039	0.007	0	0.006	0.013	0.65	0	2.9	2.9
From Coal Measures ⁴ (44 samples analysed).										
Maximum	220.92	1.200	0.169	0.170	10.102	10.262	29.00	28.2	112.6	140.8
Minimum	9.40	0.024	0.007	0	0	0.015	0.99	0	1.4	3.4
From Mountain Limestone and Magnesian Limestone ⁵ (9 samples analysed).										
Maximum	108.88	0.190	0.070	0.002	4.812	4.884	13.35	40.1	48.5	88.6
Minimum	45.84	0.037	0.010	0	0.527	0.549	2.40	18.3	21.8	40.7
From New Red Sandstone ⁶ (87 samples analysed).										
Maximum	240.20	2.349 ⁷	0.346 ⁷	0.620	14.717	15.333	39.00	52.0	99.6	127.1
Minimum	20.64	0.029	0.009	0	0	0.027	1.40	0	3.8	17.1
From Lias ⁸ (38 samples analysed).										
Maximum	306.85	1.792	0.298	0.152	19.858	20.123	40.50	40.1	111.0	116.9
Minimum	49.48	0.062	0.023	0	0	0.033	1.75	0	2.1	2.7
From Oolites ⁹ (25 samples analysed).										
Maximum	269.60	2.662	0.531	0.240	12.220	12.508	44.50	42.6	55.9	78.9
Minimum	31.00	0.041	0.008	0	0	0.178	1.23	10.8	3.1	23.0
From Upper and Lower Greensand and Wealden ¹⁰ (21 samples analysed).										
Maximum	381.10	0.485	0.196	0.160	6.722	6.735	82.50	35.8	44.7	80.5
Minimum	10.52	0.014	0.006	0	0	0.012	2.10	0	3.8	3.8
From Chalk ¹¹ (33 samples analysed).										
Maximum	159.16	0.772	0.340	1.700	6.345	7.779	28.50	39.7	47.1	71.5
Minimum	32.48	0.014	0.007	0	0.613	0.628	1.79	12.0	5.6	23.6
From gravel on the London Clay ¹² (49 samples analysed, 37 from London itself).										
Maximum	396.50	1.006	0.604	2.750	25.840	25.927	34.60	49.2	164.3	191.0
Minimum	31.80	0.040	0.012	0	0	0.013	1.90	0	5.7	14.3
From Bagshot beds ¹³ (8 samples analysed).										
Maximum	286.80	1.295	0.154	0.630	17.940	—	31.15	21.5	111.9	131.7
Minimum	23.18	0.078	0.027	0.001	0	0.087	2.48	5.4	5.6	13.1
From Fluvio-marine series ¹⁴ (13 samples analysed).										
Maximum	66.12	0.429	0.093	0.016	3.640	3.734	7.20	12.1	29.3	36.4
Minimum	8.16	0.063	0.010	0	0	0.010	2.40	0	4.6	4.6
From Alluvium and gravel ¹⁵ (29 samples analysed).										
Maximum	320.72	0.931	0.940	3.050	11.265	14.300	36.25	36.4	118.6	163.4
Minimum	28.58	0.015	0.010	0	0	0.074	1.70	2.7	1.9	4.6

¹ In almost all cases clear and palatable. ² Generally clear and palatable. ³ Almost all clear and palatable.⁴ In many cases clear and palatable; but in others turbid, and even very turbid.⁵ All clear or slightly turbid and palatable.⁶ Generally clear, or only slightly turbid and palatable. In a few cases saline taste.⁷ Even this water clear and palatable. ⁸ In nearly all cases clear, or slightly turbid and palatable.⁹ Varying from clear and palatable to very turbid. In some cases saline taste.¹⁰ Mostly more or less turbid. Palatable.¹¹ Clear to very turbid. Palatable, or occasionally slight saline taste.¹² Generally more or less turbid and palatable. Occasionally slight saline taste.¹³ Generally more or less turbid and palatable.¹⁴ More or less turbid and palatable.¹⁵ Generally clear or only slightly turbid and palatable. Occasionally slight saline taste.

tion of waters draining from cultivated land becomes of special value in studying the nature of the next group of waters (shallow well water).

4. *Shallow well water.*—It has been estimated that about twelve millions of the inhabitants of Great Britain are supplied with water for domestic purposes from shallow wells. This class of water is very liable to serious contamination with sewage and refuse animal matters, inasmuch as such wells are almost invariably sunk in the vicinity of human dwellings, and frequently within a few feet of the cesspool receiving their drainage. It is these waters which have most frequently caused serious outbreaks of typhoid fever. In consequence of the great practical interest attaching to these waters, their composition will be considered in connection with the principal geological formations upon which such shallow wells may be sunk.

The results recorded in the previous table serve to show the general composition of shallow well waters as met with in Great Britain. The composition of these waters varies within very wide limits, even when derived from one and the same geological formation, which is due to their being not generally an aqueous extract of a soil in its natural condition, but of ground which is often saturated with sewage and other animal refuse. In consequence of the oxidising power of soil, the organic matter of this refuse is not unfrequently almost entirely destroyed before reaching the wells, and even the ammonia, which is one of the first products of its decomposition, has often disappeared, having generally become converted into nitrates and nitrites. Of nitrates and nitrites these shallow well waters generally contain some, and often a large amount, which thus, together with the ammonia,

DEEP WELL WATERS. (6th Rep. Riv. Com. p. 89.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Devonian rocks.										
Maximum . . .	45.30	0.083	0.016	0.001	0.696	0.713	4.20	26.2	16.4	32.6
Minimum . . .	8.94	0.021	0.005	0	0.044	0.049	1.40	0.5	3.1	3.6
Average (5 samples)	29.41	0.047	0.012	0	0.400	0.412	2.96	8.9	9.4	18.3
Polluted well at Bromyard . . .	85.12	0.177	0.048	0	2.279	2.327	11.25	25.0	16.2	41.2
Polluted well at Dundee . . .	27.50	0.119	0.027	0.025	0.532	0.580	3.05	9.6	8.5	18.1
From Millstone Grit.										
Well at Bradford, Yorks . . .	55.40	0.150	0.005	0.028	0.038	0.066	3.23	6.8	7.3	14.1
Well at Glossop, Derby . . .	26.32	0.092	0.020	0.003	0.019	0.042	0.89	9.8	5.9	15.7
From Coal Measures.										
Maximum . . .	144.88	0.198	0.064	0.170	1.468	1.494	59.85	28.2	48.5	75.0
Minimum . . .	33.42	0.045	0.014	0	0	0.029	1.29	5.7	1.2	9.9
Average (9 samples)	83.10	0.119	0.034	0.044	0.207	0.278	18.05	15.1	20.6	35.7
Polluted well at Holyrood, Edinburgh . . .	92.54	0.326	0.175	0.056	0.950	1.171	7.95	27.9	8.3	36.2
From Magnesian Limestone. ¹										
Mansfield, Woodhouse . . .	54.32	0.139	0.039	0	1.188	1.227	3.20	23.4	26.0	49.4
Pontefract, Yorks . . .	84.92	0.054	0.021	0	2.673	2.694	5.55	26.5	40.8	67.3

¹ The following is a more recent analysis made by the writer of water derived from deep wells in the Magnesian Limestone:—

RESULTS OF ANALYSIS EXPRESSED IN PARTS PER 100,000.

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total Combined nitrogen	Chlorine	Hardness	Remarks
Standard and South Shields Water Supply, March 3, 1900.	45.52	0.029	0.005	Trace	0.328	0.333	3.65	35.0	(Alkalinity = 33.4 CaCO ₃ Total Hms (CaCO ₃) = 15.3 " Magnesia (MgO) = 6.3)

DEEP WELL WATERS (continued).

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From New Red Sandstone.										
Maximum	62.84	0.091	0.038	0.039	3.508	3.528	7.51	19.4	20.0	35.6
Minimum	14.20	0	0	0	0	0.009	1.30	0	4.9	5.7
Average (28 samples)	30.63	0.036	0.014	0.003	0.717	0.734	2.94	7.4	10.5	17.9
Polluted well at Lichfield	32.06	0.163	0.038	0.003	0.489	0.529	2.20	9.3	9.0	18.3
Polluted well at Liverpool	86.70	0.135	0.038	0.005	8.678	8.721	12.61	11.5	24.0	35.5
Polluted well at Oxton	27.80	0.249	0.034	0.001	0.376	0.411	3.52	5.6	8.5	14.1
From Lias.										
Well at Northampton	57.76	0.168	0.024	0.003	0	0.026	5.15	8.6	1.7	10.3
Well at Somerton, Somerset	84.20	0.124	0.030	0	0.778	0.808	3.70	35.3	14.7	50.0
Polluted well at Trowbridge, Wilts	144.34	0.236	0.057	0.002	0.550	0.609	36.70	27.4	29.7	57.1
From Oolites.										
Maximum	41.90	0.054	0.018	0.110	1.898	1.907	3.70	18.0	10.6	23.0
Minimum	26.60	0.023	0.005	0	0	0.099	1.35	8.3	3.6	18.9
Average (5 samples)	33.60	0.037	0.010	0.022	0.625	0.654	2.69	13.8	6.8	20.6
Polluted (maximum of 3 wells)	71.04	0.217	0.053	0.002	0.778	0.800	7.80	26.4	12.9	39.3
Polluted (minimum of 3 wells)	27.48	0.106	0.020	0	0	0.047	2.10	12.6	8.6	21.2
From Hastings Sand, Lower and Upper Greensand, and Wealden.										
Maximum	79.20	0.120	0.021	0.074	1.074	1.085	10.00	27.8	26.0	44.3
Minimum	28.24	0.028	0.003	0	0	0.007	1.60	1.1	1.2	3.6
Average (20 samples)	45.20	0.068	0.014	0.016	0.196	0.223	5.38	16.8	10.5	27.3
Polluted well in Lower Greensand at Sevenoaks	38.76	0.447	0.072	0	0.252	0.324	5.90	7.2	13.4	20.6
From Chalk.										
Maximum	66.34	0.131	0.064	0.029	2.277	2.319	11.10	38.6	13.8	50.0
Minimum	23.30	0	0	0	trace	0.014	1.00	10.8	2.7	19.1
Average (66 samples)	36.88	0.050	0.017	0.001	0.610	0.628	2.76	21.2	6.5	27.7
Polluted wells, maximum	216.40	0.821	0.186	0.150	3.401	3.484	106.0	36.1	34.3	51.5
Polluted wells, minimum	32.16	0.107	0.028	0	0	0.204	1.83	13.9	5.3	23.9
From Chalk beneath London Clay.										
Maximum	106.70	0.195	0.067	0.118	0.645	0.681	38.80	29.5	25.4	48.5
Minimum	33.38	0.055	0.005	0	0	0.053	2.38	0	0.9	0.9
Average (13 samples)	78.09	0.093	0.028	0.048	0.068	0.135	15.02	9.7	8.7	18.4
Polluted wells at Colchester	96.20	0.174	0.030	0.021	2.582	2.629	31.00	12.7	13.0	25.7
Polluted wells at Hounslow	82.40	0.273	0.042	0.001	0.846	0.889	9.05	26.2	8.1	34.3
From Thanet Sand and Drift.										
Maximum	61.10	0.133	0.021	0.190	0.438	0.457	9.10	23.7	12.0	34.0
Minimum	45.96	0.074	0.019	0	0	0.019	5.20	4.5	3.6	8.1
Average (4 samples)	53.84	0.113	0.020	0.072	0.116	0.202	6.32	14.4	7.6	22.9

testify to the water having previously been in contact with nitrogenous organic matter which has subsequently undergone destruction. In shallow well waters, even when the organic matter is only small in amount, it is generally highly nitrogenous, pointing to its probable animal origin, and in some exceptional cases the organic nitrogen found is actually in excess of the carbon. These waters, which are generally suspicious from the presence of mineral nitrogen, become in the highest degree dangerous when the proportion of organic matter is large.

5. *Deep well waters*.—It is convenient to distinguish for sanitary purposes between waters which are obtained from comparatively shallow wells and those which are derived from wells, say, upwards of 100 ft. in depth, and sometimes reaching to the distance of more than 1000 ft. below the surface of the earth. The presumption is that waters obtained from such a depth have undergone perfect filtration through porous strata, and consequently it is not usual to view the evidence of previous contact with animal matters afforded by the presence of mineral nitrogen with so much suspicion as in the case of the waters from the shallower wells. The great efficiency of the filtration which most of these deep well waters have undergone is attested both by their freedom from organic matter, and from every kind of suspended material, whether organic or inorganic. In consequence of the excellent water obtainable from such deep wells, they have been multiplied greatly during past years, so that at the present time not only are many towns (including a part of London) and villages supplied from this source, but also nearly all larger breweries and many private establishments. In some cases these deep wells are of the kind known as 'Artesian' (from Artois, in France, where they were probably first employed); that is to say, on reaching the water-bearing stratum the water rises to the level or even considerably above the level of the ground, due to the underground water being confined under pressure beneath an impervious stratum of clay or the like, and through the outcrop of the water-bearing stratum being at a considerably higher altitude than the point at which the boring has been made. Thus, in the London basin, 'Artesian wells' are obtained by sinking through the London clay into the chalk beneath, which has its outcrop at considerable altitudes in the chalk hills on the north and south of the Thames valley. Owing to the large abstraction from such water-bearing strata, the water of many wells which formerly rose to the surface has now to be pumped. In the majority of deep wells the water does not rise nearly to the surface, and the pumps have often to be placed at considerable depths in the shaft. It is usual to line these wells with closely-fitting iron cylinders, in order to exclude surface water, as unless this is done the deep wells may become as objectionable and dangerous as shallow ones.

The preceding tables afford a survey of the general character of the deep well waters obtained in Great Britain. In nearly all the samples of which the maximum, minimum, and average results are given, it may be taken that the wells are unpolluted by surface water, but for the sake of comparison there are appended

to most of the sections analyses of deep well waters from the same strata in which pollution by surface or imperfectly-filtered water is highly probable.

These results demonstrate the great superiority from a chemical point of view of the subterranean waters obtained at great depths to those derived from shallow wells. Indeed, these deep well waters are, as regards organic matter, amongst the purest to be found in nature, and hence, unless extremely hard, are of the best quality for drinking purposes.

Closely associated with these deep well waters is the next group of spring waters.

6. *Spring water*.—In the following table is given the composition of, presumably unpolluted, British spring waters arranged according to the geological nature of the ground from which they are derived, whilst for the sake of comparison the composition of probably polluted spring waters from the same geological source is in many cases appended.

7. *Mineral spring waters*.—Many spring waters possess marked medicinal properties in consequence of the materials they hold in solution. Until the discovery of radium it was generally supposed by chemists that the therapeutic value of such waters containing only an insignificant amount of mineral matter must be imaginary, but it is now known that some of these, such as the waters of Bath and Burton, are pronouncedly radioactive, and it is generally accepted at the present time that the old-established efficacy of these waters in the treatment of gout and rheumatism is due to their content of radioactive material (*see* Nature, 1911, 86, 157). Indeed, radium-salt is now much employed for the artificial production of radioactive water for medicinal purposes. An immense number of mineral waters are in use, and have been submitted to careful analysis; a very extensive collection of such analyses is to be found in Raspe's *Heilquellen Analysen*, Dresden, 1885.

These mineral waters are conveniently classified by Hermann Weber (Quain's Dictionary of Medicine), according to the ingredients which characterise them, into—(1) Simple thermal waters; (2) common salt or muriated saline waters; (3) alkaline waters; (4) sulphated saline waters; (5) iron or chalybeate waters; (6) sulphur waters; (7) earthy and calcareous waters.

(1) *The simple thermal waters*, whilst containing only a moderate proportion of dissolved solids, are characterised by a high temperature, from 27°–65°, and sometimes by the presence of an unusually large proportion of nitrogen, which is now known to be mixed with appreciable quantities of helium. Doubtless the medicinal reputation of most, if not all, of these waters depends on their radioactivity. The principal springs of this class are: Panticon, Leukerbad, Bormio, Gastein, Pfäfers, Johannisbad, Ragatz, Wildbad, Plombières, Burton, Bath, Looe, Teplitz, Schlangenbad, &c.

(2) *Common salt or muriated saline waters* contain sodium chloride as the principal constituent, although this also occurs often in large quantity in many of the other classes of mineral waters. These salt waters or brines are very common in almost all countries. Some of the

SPRING WATER. (6th Rep. Riv. Com. p. 107.)

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		
								Temporary	Permanent	Total
From Granite and Gneiss.										
Maximum	9.44	0.119	0.019	0.002	0.204	0.210	3.10	1.2	5.3	5.6
Minimum	1.40	0	0	0	0	0.013	0.55	0	1.2	1.2
Average (8 samples)	5.94	0.042	0.008	0.001	0.108	0.115	1.69	0.4	2.6	3.0
From Silurian Rocks.										
Maximum	27.10	0.096	0.042	0.005	0.659	0.674	3.70	6.9	9.3	15.8
Minimum	3.04	0.011	0.002	0	0	0.011	0.90	0	1.5	1.6
Average (15 samples)	12.33	0.051	0.014	0.001	0.178	0.192	1.84	1.5	5.3	6.6
From Devonian and Old Red Sandstone.										
Maximum	66.90	0.124	0.034	0.006	4.104	4.128	13.80	22.4	12.4	29.9
Minimum	5.50	0.009	0.001	0	0.013	0.028	1.30	0	1.9	2.2
Average (22 samples)	25.06	0.054	0.012	0.001	0.764	0.777	3.85	4.8	7.2	12.0
From Mountain Limestone.										
Maximum	98.50 ¹	0.286	0.023	0.006	1.022	1.036	32.00 ¹	20.9	29.5	48.5 ¹
Minimum	15.70	0.011	0	0	0	0.001	0.70	2.1	3.3	11.0
Average (13 samples)	32.06	0.087	0.010	0.001	0.224	0.235	4.63	10.9	8.9	19.8
From Yoredale and Millstone Grits.										
Maximum	40.80	0.109	0.028	0.006	0.617	0.650	3.45	21.4	11.5	26.4
Minimum	3.32	0.017	0.004	0	0	0.005	0.95	0	2.7	2.7
Average (8 samples)	17.73	0.042	0.011	0.001	0.169	0.181	1.73	6.6	5.7	12.3
From Coal Measures.										
Maximum	39.60	0.120	0.027	0.008	1.813	1.860	3.35	14.5	17.1	25.7
Minimum	6.84	0.029	0.004	0	0	0.010	0.95	0	2.3	2.6
Average (22 samples from millstone grit and coal measures)	21.91	0.050	0.014	0.001	0.393	0.408	1.85	5.2	7.9	13.1
From Magnesian Limestone.										
Pontefract, Yorks	66.52	0.058	0.038	0.002	1.686	1.726	3.40	24.9	34.8	59.7
From New Red Sandstone.										
Maximum	74.26	0.118	0.069	0.014	1.256	1.275	7.00	19.8	25.0	35.7
Minimum	12.90	0.027	0	0	0	0.006	1.30	0	4.2	8.0
Average (15 samples)	28.69	0.065	0.017	0.001	0.330	0.349	2.19	8.1	10.7	18.8
From Lias.										
Maximum	58.12	0.131	0.036	0.009	1.332	1.353	4.80	32.3	17.4	45.7
Minimum	21.22	0.024	0.006	0	0	0.035	1.35	9.1	5.3	15.1
Average (7 samples)	36.41	0.073	0.019	0.001	0.467	0.487	2.48	21.3	8.6	30.1
From Oolites.										
Maximum	52.16	0.140	0.021	0.014	1.157	1.168	3.30	30.0	13.5	38.7
Minimum	22.30	0.009	0.003	0	0	0.014	0.97	11.3	3.5	16.9
Average (35 samples)	30.33	0.043	0.011	0.001	0.402	0.414	1.55	18.2	6.2	24.5
From Lower Greensand, Hastings Sand, and Upper Greensand.										
Maximum	68.40	0.135	0.028	0.003	1.116	1.129	7.10	25.0	22.1	40.2
Minimum	4.55	0.002	0.002	0	0.034	0.045	1.10	0	0.7	0.7
Average (19 samples)	30.05	0.053	0.012	0	0.326	0.338	2.98	13.6	6.6	20.2
From Chalk.										
Maximum	39.30	0.097	0.023	0.006	0.863	0.874	7.40	25.3	8.1	33.2
Minimum	25.36	0.008	0.003	0	0	0.009	1.05	6.8	3.6	12.4
Average (30 samples)	29.84	0.044	0.010	0.001	0.382	0.392	2.45	18.1	5.8	23.6
From Fluvio Marine, Red Crag, Drift, and Gravel.										
Maximum	225.24	0.164	0.043	0.007	1.277	1.293	4.27	32.2	94.3	126.6
Minimum	24.62	0.004	0.006	0	0.004	0.034	2.10	0.7	6.1	13.6
Average (18 samples)	61.23	0.080	0.019	0.001	0.354	0.374	2.76	18.0	19.6	37.6

¹ Water supply of Western-super-Mare; these exceptionally high results doubtless due to access of sea water.

principal ones in England are: Droitwich, Nantwich, Middlewich, Woodhall, and Harrogate; Leamington and Cheltenham along with sodium sulphate. In Germany: Kissingen, Homburg, Nauheim, Kreunach, Soden, Pyrmont, Wiesbaden, Ischl, Kreuth, Baden-Baden, &c. In France: Bourbonne-les-Bains, Lamotte-les-Bains, Balaruc, Salins. In Italy: Castellamare, Ischia, Monte Catini, La Porretta. In Switzerland: Bex.

(3) *Alkaline waters* are characterised by the presence of sodium carbonate, almost always with more or less free carbon dioxide, and sometimes with a large quantity also of sodium chloride. Of the simply alkaline waters, there are—(a) *Hot*: Vichy, Neuenahr, Mont-Dore, Chaudesaigues, Nérès; (b) *Cold*: Apollinaris, Vals, Salsbrunn, Biliu, Wilhelmsquelle, Taunus, Marcollo; whilst the chief muriated alkaline waters are: (a) *Hot*: Ems, Royat, La Bourboule; and (b) *Cold*: Luhatschowitz, Selters, Gleichenberg, Rosbach, Vie-sur-Cère. Several of these, but especially La Bourboule and Mont-Dore, contain a marked proportion of arsenic.

(4) *Sulphated waters* contain either sodium or magnesium sulphate, or both, as the prominent ingredients, in some cases also associated with sodium carbonate and chloride. They are often called '*bitter waters*.' The chief simple sulphated waters are: Galthof, Pullna, Said-schutz, Sedlitz, Birmensdorf, Ivanda, Hunyadi Janos, Epsom, Aranjuez, Friedrichshall, Mergentheim; the two latter are also rich in chlorides. Weaker springs of the same kind are found at Leamington, Cheltenham, Scarborough, and at Purton Spa. Of alkaline sulphated waters there are: Carlsbad, Marienbad, Tarasp-Schuls, Franzensbad, Elster, and Bertrich.

(5) *Iron or chalybeate waters* are those in which an unusual proportion of this element is present, either in otherwise comparatively pure water or associated with other mineral matters. Thus, of comparatively pure chalybeate waters, there are those of Schwalbach, Spa, Brückenaau, Schandau, Lieberwerda, Flinsberg, Freienwalde, Reccaro, Königswarth, Liebenstein, Altwasser, Alexisbad, Muskau, Tunbridge Wells, and some of the springs at Harrogate; whilst of waters in which the iron is associated with a considerable quantity of other salts, there are those of Aratap, Orezza, Pyrmont, Driburg, Rippoldsau, Griesbach, Antogost, Petersthal, Bocklet, St. Moritz, Reinerz, Godesberg, Cudowa, Imnan, and Santa Catarina.

(6) *Sulphur waters* are those containing appreciable quantities of either sulphuretted hydrogen or the sulphides of sodium, potassium, calcium, or magnesium. Some of the more important thermal sulphur waters are those of Eaux Chaudes, Cauterets, Saint Sauveur, Barges, Bagnères-de-Luchon, Ax, Escaldes, Le Vernet, Amélie-les-Bains, Uriage, Allevard, Aix-les-Bains, Aix-la-Chapelle, Baden (Austria), Baden (Switzerland), Lavey, Schinznach, Battaglia, and Abano in the Euganean Mountains, Panticosa, Mehadia, Helouan, near Cairo; whilst of cold sulphur springs there are those of Eilen, Neundorf, Langenbrücken, Weibach, Meisberg, Reutlingen, Engheim, Challes, Stachelberg, Hemsrich, Gurnigel, some of the Harrogate springs, Llandrindod, Builth, Moffat, Strathpeffer, Lischnyarna.

(7) *Earthy and calcareous waters* are characterised by the presence of large proportions of calcium carbonate and sulphate, and magnesium carbonate. Some of the more important are found at Wildungen, Lippespringe, Weissenburg, Contrexéville, Bagnères-de-Bigorre, St. Arnaud, Crausac, whilst the table waters of Cousan, St. Galmier, and Taunus are of the same character.

8. *Sea water*.—The ocean is a great evaporating-basin, which is constantly receiving waters, more or less impure, in the shape of rivers, whilst at the same time it is constantly losing pure water in the form of vapour, the impurities remaining behind and imparting to the sea its well-known saline character. This also distinguishes all lakes which are devoid of outlet, like the Dead Sea, Caspian, Aral, Great Salt Lake Utah, &c., in which the same process of concentration by evaporation is going on. As will be seen from the table on the next page, the composition of the ocean varies considerably in different places and at different depths, whilst land-locked seas, like the Mediterranean, Black Sea, and Baltic, present even still greater differences.

Thus in the vicinity of the poles the proportion of salt is less than near the equator; similarly, land-locked seas, such as the Black Sea and Baltic, which receive large rivers are less salt; whilst the Mediterranean in most places is more salt than the great oceans. Of salt lakes the Dead Sea is far more and the Caspian far less salt than the oceans. In addition to sodium chloride, the principal substances present in sea water are the sulphates and carbonates of calcium and magnesium, and salts of potassium, whilst in very minute quantities there are found also a number of others, amongst which may be mentioned bromides, iodides and fluorides, silica, phosphoric and nitric acids, iron, silver, gold, copper, lead, arsenic, zinc, cobalt, nickel, lithium, rubidium, and caesium.

The volume of gas dissolved in sea water is, according to Hunter (Chem. Soc. Trans. 1870, 20), only from 2.2 to 3.6 vols. in 100 vols. of water.

	CO ₂	O	N
	per cent.	per cent.	per cent.
2.2 vols. consisted of	28.62	21.94	49.44
3.5 " "	48.28	17.22	34.50

A very extensive examination of the composition of sea water was made in connection with the voyage of H.M.S. *Challenger*, and the elaborate report prepared thereon by Dittmar should be consulted for detailed information on this subject. From 77 complete analyses, the following numbers for the average composition of ocean-water salts are calculated:—

Average composition of ocean-water salts, in parts per 100 of total salts (Dittmar).

Chlorine	55.232
Bromine	0.1884
Sulphuric acid (SO ₃)	6.410
Carbonic acid (CO ₂)	0.152
Lime (CaO)	1.676
Magnesia (MgO)	2.209
Potash (K ₂ O)	1.232
Soda (Na ₂ O)	41.234
(Basic oxygen equivalent to the halogens)	(—12.438)

100.000

(Results of Analysis expressed in parts per 1000.)

Sea	Point of collection of sample	Na	Cl	Mg	Ca	K	SO ₄	Br	CO ₂	Fe	Fired residue	Authors
Atlantic Ocean	0° 47' S.—33° 20' W.	11.081	19.460	0.9598	0.4597	0.7604	2.577	0.4099	—	—	35.700	
"	20° 54' N.—40° 44' W.	10.464	19.012	1.2735	0.4684	0.7252	2.446	0.3102	—	—	34.700	
"	41° 18' N.—36° 28' W.	11.719	20.840	1.1981	0.5568	0.6682	3.029	0.3878	—	—	38.400	Bibra, Annalen, 77, 90.
North Sea	Cape Horn	10.457	18.841	1.1763	0.5280	0.5916	2.878	0.3271	—	—	34.800	
"	Between Belgium and England	10.117	18.954	1.3141	0.4782	0.6811	2.563	0.2924	—	—	34.400	
Straits of Dover	Some miles from Havre	10.206	18.168	1.1582	0.3244	0.3536	2.590	(?)	—	—	32.800	Bischof, C. Géolog., 1, 99.
Mediterranean	Marseilles	10.142	17.794	1.2305	0.4093	0.0425	2.882	0.1046	0.078	traces	32.700	Figuer et Mialhe, J. Pharm. [iii.] 13, 406.
"	At 3500 metres from the coast of Cettie	10.688	21.099	3.0037	0.048	0.0041	5.716	(?)	0.142	—	40.700	Laurent, J. Pharm. 21, 93, [ii.] 92, 172.
"	The Lagoon of Venice	11.706	20.527	1.3104	0.4411	0.2643	2.943	0.434	0.0679	0.0028	37.700	Usiglio, Ann. Chim.
Pacific Ocean	3.5 metres below the surface	8.779	15.882	1.1646	0.1769	0.4356	2.682	(?)	—	—	29.100	Calamai, 1847.
"	140 metres below the surface	10.262	18.950	1.3151	0.4719	0.6038	2.786	0.3102	—	—	34.700	Bibra, l.c.
Baltic	"	10.233	19.321	1.4714	0.4752	0.6336	2.827	0.2394	—	—	35.200	Pfaff, Schweigger's Journ. 22, 271.
"	"	5.894	10.386	1.6115	0.3663	—	0.719	—	—	—	17.710	
Black Sea	Coast south of the Crimea	5.512	9.574	0.6822	0.1305	0.0975	1.2605	0.005	0.2475	0.1271	17.605	Göbel, P. Suppl. 1, 187.
Sea of Azof	Between Kertch and Mariapol	3.997	6.585	0.4010	0.0908	0.0670	0.8045	0.004	0.0695	0.0358	11.900	Ibid.
Caspian Sea	South-west of Pischnoi	1.144	2.737	0.4098	0.1916	0.1397	1.337	(?)	0.0773	0.0401	6.296	Ibid.
Dead Sea	From the surface	0.885	17.628	4.177	2.180	0.474	0.2424	0.167	traces	traces	27.078	Terrell, Compt. rend. 62, 1829. (Wurtz, Dictionnaire de Chimie.)
"	From 300 metres below the surface	14.900	174.985	41.428	17.269	4.386	0.6276	7.093	traces	traces	278.135	

To these may be added the following analysis of the water of the Irish Channel in the winter of 1870 (Thorpe and Morton, Chem. Soc. Trans. 1871, 506).

(Results of Analysis expressed in parts per 1000.)

NaCl	26.43918	MgSO ₄	2.06608	CaSO ₄	1.33168	NH ₄ Cl	0.00044	Sp.gr at 0°C.—1.02721
KCl	0.74619	MgCO ₃	Trace	CaCO ₃	0.04764	FeCO ₃	0.00503	" 15°C.—1.02494
MgCl ₂	3.15083	Mg(NO ₃) ₂	0.00207	LiCl	Trace	SiO ₂	Trace	Total—33.85946
MgBr ₂	0.07025							

The salinity of the ocean, expressed in parts of total salts per 1000 parts of sea-water, was found to vary between the following limits: Minimum (from the southern part of the Indian Ocean, south of 66° lat.), 33.01; maximum (from the middle of the North Atlantic, at about 23° lat.), 37.37.

As regards the carbon dioxide in sea water, Dittmar comes to the following conclusions: (1) Free carbonic acid in sea water is the exception; as a rule, the carbonic acid is less than the proportion corresponding to bicarbonate. (2) In surface waters the proportion of carbonic acid increases when the temperature falls, and *vice versa*. (3) Within equal ranges of temperature it seems to be lower in the surface water of the Pacific than it is in the surface water of the Atlantic Ocean.

Drinking Water. It has long been known that the palate is by no means a safe guide in the choice of drinking water, for although unpalatable waters are obviously unsuitable for drinking, palatable waters may contain materials capable of doing serious injury. It is now established beyond question that the diseases termed 'zymotic' are due to minute forms of life known as micro-organisms, and in a number of cases the specific forms responsible for such diseases have been discovered, identified, and studied. Of zymotic diseases there are two—Asiatic Cholera and Typhoid Fever—which are with certainty known to be propagated by drinking water, and in the case of these two diseases authorities are agreed as to the particular organisms to which they are due. The propagation unquestionably takes place through the excreta of persons suffering from these diseases gaining access to water which is afterwards used for drinking, whilst water contaminated with the sewage of healthy persons is generally believed to be capable of producing diarrhoea and other minor disturbances in those drinking it.

In selecting water for drinking purposes it is necessary, therefore, in the first instance, to make a careful inquiry as to the possibility of the water having been in contact with refuse animal matters, and if possible all waters open to such suspicion should be discarded. For the same reason it is of the first importance in the examination of water to discover what evidence, if any, there is of the water having been in contact with such refuse substances. In the present state of knowledge this is a difficult matter, as, although the results of chemical analysis frequently point to such contamination when on a sufficiently large scale, it is occasionally and indeed generally impossible to prove the negative. The bacteriological examination, on the other hand, is of extreme delicacy, but, inasmuch as we have at present no means of ascertaining whether the bacteria indicative of faecal contamination are derived from man or from the lower animals, the results obtained by this means, also, are often of restricted value from a hygienic point of view. It becomes, therefore, of the greater importance to make a thorough inspection of the source and to trace out the further history of the water, for unless this be done the results of the scientific examination may often receive an erroneous interpretation. As, however, it is comparatively rarely

that natural waters are to be met with which are absolutely above suspicion of any contamination with refuse animal matters, it is generally necessary to be satisfied with relative purity, and thus the examination, chemical and biological, of drinking waters becomes a matter of the highest importance and utility. The natural waters which can lay claim to the greatest degree of safety for drinking purposes are of two kinds.

1. Unpolluted surface waters (generally upland waters).

2. Naturally filtered waters (spring and deep well waters).

In the first case the waters, both by inspection and analysis, must bear no evidence of animal contamination, and this is generally only possible in the case of waters which are found at altitudes above that of human habitations. A number of our large towns are supplied with water of this kind, although the gathering-grounds do in most cases contain some houses, so that absolute freedom from sewage contamination cannot generally be guaranteed. In the table on p. 381 the chemical composition of some of these upland surface water supplies is recorded.

The majority of upland surface waters are either very soft or of only very moderate hardness, and as in many of these towns extensive manufactures are carried on, these supplies are not only valued because of their safety for drinking, but also on account of their fitness for industrial purposes. It should always be remembered, however, that these surface waters may at times receive more or less sewage contamination, and that the ova of animal parasites derived from the cattle grazing on the gathering-grounds may also be present, and that, therefore, to reduce these sources of danger to a minimum, it is highly desirable that such waters should be subjected to prolonged storage in reservoirs, followed by careful filtration through sand before delivery to the consumer.

In the second class of water its original purity is a matter of secondary consequence, the guarantee of safety resting upon the exhaustive process of filtration which the water has undergone in passing through porous strata of the earth's crust. This filtration effects, on the one hand, the more or less complete chemical purification of the water from organic substances, and, on the other hand, the mechanical removal of organised matters, such as bacteria and animal parasites. The most perfectly filtered waters of this kind are those obtained from springs and from deep wells, and, again, many of our towns are supplied with water of this kind—more especially from the Chalk, Greensand, Oolite, and New Red Sandstone formations, which constitute efficient filter beds. In the table on p. 382 is recorded the chemical composition of the water supplied to some of our towns from such sources.

Of other forms of drinking water we have river waters and shallow-well waters, upon both of which a very large portion of the population is dependent for domestic supply. Both of these classes of water are open to grave objections, and nearly all the best authenticated cases of the propagation of cholera and typhoid through drinking water have been traced to

UPLAND SURFACE WATER SUPPLIES.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		Remarks	
								Temporary	Permanent		Total
Heywood and Middleton supply, Sept., 1908	8.96	0.044	0.010	0	0.037	0.047	1.15	0.4	2.2	2.6	Almost clear.
Tarquay supply, April, 1903	6.84	0.141	0.018	Trace	0.118	0.136	1.50	0.3	2.2	2.5	Very slightly turbid.
Paisley supply, Sept., 1898	8.68	0.487	0.064	0.002	0.035	0.101	1.15	0.1	3.8	3.9	Clear.
Pontypridd supply, Nov., 1907	5.28	0.183	0.025	0	0.032	0.057	0.80	—	—	2.3	Very slightly turbid.
Cardiff supply, Dec., 1908	6.28	0.160	0.016	0	0.024	0.040	0.75	0.3	3.0	3.3	Almost clear.
Aberdeen supply, intake from River Dee, March, 1910	4.76	0.193	0.026	0	0.010	0.036	0.90	0.2	1.6	1.8	Very slightly turbid.
Aberdeen, proposed supply from River Avon, March, 1910	2.60	0.091	0.015	0	0.008	0.023	0.55	0	0.5	0.5	Very slightly turbid.
Glasgow, L. Katrine water, Nov., 1891	2.80	0.149	0.025	0	0.004	0.029	0.72	—	—	0.6	Slightly turbid.
Liverpool, Rivington Water, Average for 1903	9.82	0.153	0.025	0.002	0.005	0.032	1.52	—	—	4.1	
" Vyrnwy Water	4.67	0.211	0.027	0.002	0	0.029	0.87	—	—	1.5	
Birmingham, Elan Valley Water, Jan., 1911	6.44	0.171	0.019	0	0.016	0.035	0.90	0.2	2.5	2.7	Almost clear.
" " " June, "	4.92	0.089	0.015	Trace	0.016	0.031	0.85	0.3	2.6	2.9	Almost clear.
Dewsbury supply, Dec., 1910	7.52	0.226	0.025	0.002	0.053	0.080	1.00	0.2	2.7	2.9	Slightly turbid and opalescent.
" " " July, 1911	6.24	0.067	0.005	Trace	0.035	0.040	1.10	0.2	2.5	2.7	Slightly turbid.
Belfast, Woodburn supply, Jan., 1910	14.40	0.325	0.022	Trace	0.032	0.054	1.75	5.5	3.6	9.1	Almost clear.
" " " June, "	15.32	0.155	0.019	Trace	0.027	0.046	1.50	5.6	3.4	9.0	Almost clear.
" " " " "	13.68	0.427	0.036	0	0.026	0.062	1.20	4.4	3.5	7.9	Almost clear.
" Stonyford supply, Jan., 1910	12.16	0.265	0.031	Trace	0.016	0.047	1.15	4.2	3.4	7.6	Almost clear.
" " " June, "	9.28	0.195	0.015	0	0.041	0.056	1.25	0.2	3.4	3.6	Very slightly turbid.
" " " " "	7.00	0.171	0.018	Trace	0.027	0.045	1.25	0.5	2.2	2.7	Slightly turbid.

WATER

WATER SUPPLIES FROM DEEP WELLS AND SPRINGS.
(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness		Remarks
								Temporary	Permanent	
Portsmouth supply: from chalk springs, August, 1905	29.80	0.032	0.009	Trace	0.326	0.335	1.65	19.0	5.3	24.3
Nottingham: borehole 500 ft. deep in New Red Sandstone, Dec., 1910	19.80	0.020	0.005	0	0.020	0.025	1.25	9.6	7.8	17.4
Liverpool: Dudlow Lane well in New Red Sandstone, 1903	18.43	0.024	0.007	0	0.677	0.684	3.01	—	—	7.8
" Green Lane well " " " "	32.79	0.028	0.007	0	0.625	0.632	3.33	—	—	19.1
" Windsor well " " " "	41.20	0.019	0.006	0	0.786	0.792	4.38	—	—	28.5
Long Eaton supply: well in New Red Sandstone, Sept., 1911	48.32	0.038	0.008	0.002	0.295	0.305	2.50	22.3	13.4	35.7
Eastbourne supply: well in chalk, August, 1911	28.56	0.028	0.004	0	0.378	0.382	3.03	15.1	3.8	18.9
Leicester: well 200 ft. deep in Grey Sandstone, Sept., 1901	22.00	0.016	0.004	Trace	Trace	0.004	2.20	9.8	5.9	15.7
Manchester: well in New Red Sandstone, May, 1907	14.92	0.034	0.006	Trace	0.373	0.379	1.30	0.6	8.0	8.6
E. Worcestershire Waterworks; Burcot well in New Red Sandstone, Oct., 1908	17.72	0.028	0.006	Trace	0.314	0.320	1.20	2.1	7.0	9.1
Shanklin: springs in Upper Greensand, June, 1908	34.88	0.036	0.009	0	0.276	0.285	3.40	18.6	5.3	23.9
Exmouth: borehole 338 ft. deep in New Red Sandstone, June, 1909	23.60	0.025	0.006	0	0.386	0.392	2.60	9.1	4.6	13.7
Great Grimsby: well in chalk at Healing, April, 1911	30.00	0.010	0.005	0	0.386	0.391	1.80	18.6	3.6	22.2
" " at Cleethorpes, April, 1911	31.00	0.011	0.004	0	0.149	0.153	2.88	19.4	3.5	22.9

shallow wells. There are, however, many potent influences tending to remove bacteria from water which, on a *priori* reasoning, would have been regarded as almost, if not wholly, inoperative. These causes are mainly the process of devitalisation which pathogenic bacteria undergo in natural, and more especially in surface waters, and the resistance offered by even a comparatively small thickness of soil or other porous material to the passage of micro-organisms. But although these causes are to be looked upon as tending to keep the evils which can result from contaminated drinking water within narrower limits than might have been anticipated, still the possibility of their failure must be constantly kept in view, and they must not be allowed to check the endeavour to substitute unimpeachable for suspicious sources of supply.

Every effort should be made to exclude avoidable sources of contamination, to select the best water which the source affords, and to submit it to the most effective purification available. The improvements which can thus be brought about in water supplies obtained from suspicious sources is conspicuously exemplified in the case of the London supply derived from the rivers Thames and Lea. Here, on the one hand, increasing vigilance has been exercised by the Thames and Lea Conservancy Boards in the exclusion of dangerous matters from the rivers and their tributaries, whilst on the other hand the authorities supplying water have removed their intakes to points on these streams above the most serious pollutions; by increasing their storage capacity they are enabled not only to

avoid drawing from the rivers in times of flood, but also to bring about a great amelioration in the quality of the water during its sojourn in the reservoirs, whilst by improving their filtering appliances they secure a more perfect purification of the water which they have abstracted. Thus the water supplied to London to-day is both chemically and hygienically very different from what it was 60 years ago, although still derived from the same streams, which in the ordinary course of events would be more polluted now than they were then.

Importance to be attributed to various ingredients of drinking water.—It is only possible here to give a brief account of the importance which is usually attributed to the several ingredients which are commonly determined in the analysis of drinking waters.

Dissolved gases.—The gases present in ordinary drinking waters are those of the atmosphere—oxygen, nitrogen, and carbon dioxide. Their quantitative determination is of little or no significance in connection with the quality of the water for drinking, excepting that through the absence of dissolved gases a water has the flat taste of that which has been recently boiled. It is sometimes supposed that the absence of a due proportion of dissolved oxygen in water is an indication of the presence of decomposing organic substances, but this can only be the case with surface waters, as the very purest subterranean waters are almost entirely destitute of it. In the following table the proportion of the several dissolved gases in different kinds of water is recorded:—

Gases dissolved in 100 cub. ins. of water	Rain-water	Cumberland mountain water	Loch Katrine water	Thames water	Deep chalk well water
	cub. ins.	cub. ins.	cub. ins.	cub. ins.	cub. ins.
Nitrogen	1.308	1.424	1.731	1.325	1.944
Oxygen	0.637	0.726	0.704	0.588	0.028
Carbon dioxide	0.128	0.281	0.113	4.021	5.520
	2.073	2.431	2.548	5.934	7.492

The large proportion of dissolved carbon dioxide in the Thames and deep chalk well water is mainly combined with calcium carbonate as bicarbonate.

Total solid residue.—It is only rarely that the amount of the residue left by a water on evaporation affords any evidence of its fitness for drinking. As a general rule, it may be stated that waters which contain very small residues are probably pure and unpolluted, but on the other hand many waters of organic purity contain large proportions of mineral matter in solution. It is impossible to assign limits to the proportion of mineral matter which may be present in water without interfering with its fitness for drinking, more especially as opinion is divided as to the influence of the several constituents on health (*v. also Hardness of water*). Nearly all the best drinking waters in the United Kingdom yield less than 50 parts of solid residue per 100,000, and most of them very considerably less. The use of waters yielding much larger residues is generally attended by the inconvenience which attends

their employment for general domestic purposes, in consequence of their unfitness for boilers and washing.

Organic matter.—As will be pointed out (under *Water analysis*), the accurate determination of the organic matter in water is attended with great difficulties, and none of the methods of analysis in use claims to effect more than a partial determination. Thus in the 'combustion process' the organic carbon and nitrogen are determined with more or less accuracy; in the alkaline permanganate process that portion of the organic nitrogen is discovered which is readily convertible into ammonia; whilst in the 'permanganate' or 'oxygen' process the proportion of permanganate destroyed by the organic matter is taken into account. Although it may be stated generally that the smaller the proportion of organic matter the more desirable is the water for drinking, of still greater importance is the determination of the origin of the organic matter present, whether animal or vegetable. The presence of vegetable matter is of comparatively little consequence

more especially as even small amounts interfere with the palatability of the water, what is known as a 'peaty taste' being imparted by any amount yielding much in excess of 0.2 part per 100,000 of organic carbon. Sometimes much light may be thrown on the origin of the organic matter in water by the proportion which the carbon and nitrogen exhibit towards each other, especially when this is considered in connection with the proportions of ammonia, nitrates, nitrites, and chlorine. Inasmuch as animal matter in general contains a much higher proportion of nitrogen to carbon than does vegetable matter, it follows that the higher the ratio of nitrogen to carbon in the organic matter present in a sample of water, the more probability is there, *ceteris paribus*, of its being derived from animal sources and *vice versa*. The possibility of such diagnosis, however, is considerably limited by the fact that in the oxidation of peaty matter the organic carbon disappears much more rapidly than the nitrogen; whilst, on the other hand, in the oxidation of animal matter there is conversely a tendency for the organic carbon to become concentrated, thus leading to a simulation of animal matter in the case of vegetable, and a simulation of vegetable matter in the case of animal substances after oxidation.

It is thus essential that the evidence afforded by the proportion of organic carbon to nitrogen should be supplemented by an inspection of the source, and by a consideration of the mineral nitrogenous ingredients—ammonia, nitrates, and nitrites—all of which are principally derived from the decomposition of animal matters.

Albuminoid ammonia.—The ammonia yielded on distillation with alkaline permanganate is so frequently made the only measure of the organic matter present in water that a few words are necessary to indicate what is the importance to be attached to the results obtained in this simple process. According to its author, the late Mr. Wanklyn, 'deep spring water is often so pure as not to yield 0.01 part of albuminoid ammonia per million; and unless mixed

with surface water does not yield so much as 0.05 part.' 'The filtered water supplied by water companies—no matter whether derived from a lake, from clean mountain streams, or from defiled rivers—yields from 0.05 to 0.10 part of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to 0.05.' 'When the filters are over-taxed, as happens in the rainy season and in the winter, water companies supply imperfectly-filtered water, in which as much as from 0.10 to 0.20 part of albuminoid ammonia is found.' This statement must be accepted with great reserve, for in the winter months such surface waters almost invariably contain a much larger proportion of organic matter than during the dry season, thus accounting for the increase in albuminoid ammonia quite irrespective of any over-taxing of the filters. On the other hand, the albuminoid ammonia is the chemical ingredient in water which is most affected by filtration. It would appear, therefore, that suspended particles of vegetable and animal matter, which are removed by sand filtration, are particularly productive of ammonia on distillation with alkaline permanganate. In fact, the chemical difference between a water before and after sand filtration is often only attested by the diminished proportion of albuminoid ammonia yielded by the filtered water.

Oxygen or permanganate process.—The analytical value of measuring the proportion of organic matter in water by the amount of permanganate it is capable of decolorising is discussed in the section of this article on *Water analysis*, and it will be sufficient here to give some idea of how the results are to be interpreted. As in the case of the organic elements determined by combustion, it has here again been attempted to establish a scale of classification, which, however, must also be used with the greatest caution and in conjunction with the other analytical data, as well as with regard to the water's source and history. Thus the following artificial standards have been suggested:—

	Oxygen absorbed in three hours at room temperature from potassium permanganate by 100,000 parts of water	
	For Upland Surface Water	For other Water
Class I. Water of great organic purity . . .	0-0.1 part	0-0.05 part
" II. " medium " . . .	0.1-0.3 "	0.05-0.15 "
" III. " doubtful " . . .	0.3-0.4 "	0.15-0.3 "
" IV. Impure water . . .	above 0.4 "	above 0.2 "

It will be readily understood that a great drawback to this permanganate process consists in its not distinguishing between nitrogenous and non-nitrogenous organic matter. Hence it is very desirable that, if the combustion process cannot be resorted to, it should be supplemented by a determination of the 'albuminoid ammonia,' or of the Kjeldahl nitrogen (see p. 403).

Mineral nitrogen (ammonia, nitrates, and nitrites).—The importance of these ingredients is an indirect one. In themselves they in no way influence the wholesomeness of drinking

water; but, on the other hand, they are of consequence as indicating what the previous history of the water has been. Thus, in the ordinary process of decomposition to which organic matters are subjected in nature, the nitrogen is principally liberated in the form of ammonia, and this, by subsequent fermentative oxidation, may become converted into nitrites and nitrates. Moreover, owing to the far greater average richness in nitrogen of animal over vegetable matters, it is evident that these primary and secondary products of decomposition

furnish valuable evidence as to the previous contact of water with nitrogenous, and more especially animal, substances. As a general rule, the presence of ammonia indicates a more recent contact with such matters than does that of nitrates or nitrites, although in the case of some deep subterranean waters it appears that the nitrates originally present in the water have undergone reduction to ammonia, and hence the latter in such cases must be regarded as evidence of a more remote character even than the nitrates themselves. Again, in the ordinary course of nitrification in nature the ammonia is wholly converted into nitrate, the preliminary oxidation to nitrite being rapidly passed over; but if water containing nitrates is brought in contact with organic matter, these nitrates become more or less reduced to nitrites through the agency of certain micro-organisms (P. F. Frankland, Chem. Soc. Trans. 1888, 373; Warington, *ibid.* 742), and hence the presence of nitrites generally constitutes evidence of contamination with organic matter subsequent to the original nitrification, rather than to the latter having been imperfect. The fact must also not be lost sight of that nitrates can be reduced by certain microbes in the presence of organic matter with elimination of the nitric nitrogen in the free state, or as oxides of nitrogen, and that a contamination of the nitrified water may thus lead to the more or less complete removal of the mineral nitrogen. The absence of nitrates may thus, under some circumstances, actually indicate contact with animal matter instead of freedom from it (Munro, Chem. Soc. Trans. 1886, 632).

It must also be remembered that, in the case of surface waters, the mineral nitrogen may undergo removal through being taken up as food by plant-life, and thus the evidence of previous contact with animal matters be destroyed.

As the hygienic significance of contact with animal matters consists in the possibility of the ingress of pathogenic microbes (which may at any time be present in sewage and similar animal refuse), it is obvious that the evidence of such previous contact afforded by the presence of mineral nitrogen in any excessive proportion must be viewed as serious, if the history of the water furnishes no guarantee that any such organised poisons which may have gained access would have been subsequently removed, whilst the evidence is of far less consequence, or may indeed become entirely negligible, if in the subsequent history of the water it has undergone processes of purification which practically preclude the possibility of such poisons being still present. Until the application of bacteriology to questions of water supply, it was not possible to ascertain the efficiency of processes of water purification in this respect. But we now know that the exhaustive filtration through porous strata which spring and deep well water has undergone practically guarantees the removal of any micro-organisms which may have been originally present; in the case of river and shallow well waters, on the other hand, the chance of such removal is much less, and hence in such waters the evidence afforded by mineral nitrogen of previous contact with animal matters must be viewed with suspicion, whilst

in the spring and deep well waters it may often be disregarded altogether.

Chlorine.—This element is invariably in a state of combination—generally as sodium chloride, and hence quite innocuous. Its determination in potable water, however, is of importance as often affording information as to whether the water has been in contact with refuse animal matters or not. In this respect it is often more useful than the mineral nitrogen, as, once present in water, it cannot by any natural processes be removed. Its diagnostic value is due to the fact that human urine contains 500 parts of chlorine, or 824 parts of common salt in 100,000 parts. It is, of course, inapplicable in the vicinity of the sea and of natural salt deposits. In British waters free from animal pollution the average proportion of chlorine may be taken as 1 part per 100,000; but it is subject to very great variations.

There are, however, many other refuse liquids besides sewage which contain large quantities of chlorides, such as the effluents from dye and bleach-works, tanneries, paper-mills, alkali-works, and especially tin-plate and galvanising works, the proportion being often far in excess of anything ever found in sewage.

In America much attention has been bestowed on the proportion of chlorine present in unpolluted water at different distances from the sea-board. The points at which such waters exhibit the same amount of chlorine are joined by lines termed 'isochlors,' and these isochlors are found to be roughly parallel to the coastline. Any water submitted for examination is then remanded for further inquiries if it exhibits more chlorine than is normal for the isochlor upon which the source of the particular water is situated. This is an attempt to make the chlorine a measure of the sewage contamination past and present, in much the same way as the proportion of total combined nitrogen has been employed by others. It has the advantage over the latter, inasmuch as the chlorine is practically permanent whilst the nitrogen is removable in various ways; but, on the other hand, the chlorine is subject to great variations within a small area, according to local circumstances, more especially geological. The chlorine, moreover, only testifies to contamination by liquid, and not by solid, excrements, and in this respect also is of less general applicability than the total combined nitrogen.

Hardness.—This term is applied to those ingredients in water which react with soap and produce an insoluble 'curd,' the principal substances in question being the various salts of calcium and magnesium, which, entering into double decomposition with sodium stearate (hard soap) or potassium stearate (soft soap), give rise to calcium and magnesium stearates, both of which are insoluble bodies, and soluble salts of sodium or potassium. On this account the salts of calcium and magnesium are manifestly detrimental to the fitness of the water for washing. As regards the influence of these salts upon the quality of drinking water, opinion is divided. Some consider the presence of a certain proportion of these salts desirable as furnishing the materials necessary for bone-formation; others contend that if present in more than a moderate proportion, they tend to

these calcareous concretions in the system, whilst, lastly, others regard their presence or absence as immaterial from a hygienic point of view. Further, by some authorities the sulphates and chlorides of calcium and magnesium (the so-called 'permanent hardness') are regarded as more objectionable than the bicarbonates or 'temporary hardness.' Again, there are many who view the presence of the salts of magnesium with more suspicion than those of calcium, and, indeed, magnesian waters are very generally credited with the power of causing phosphatic calculi, goitre, and cretinism. On this account it has sometimes happened that waters which were otherwise of most unimpeachable quality have been discarded in consequence of their containing a few parts per 100,000 of magnesia. All these views concerning the influence of calcium and magnesium salts are, however, based upon very unsatisfactory evidence. The Rivers Pollution Commissioners, in prosecuting their inquiry into this subject, found that 'where the chief sanitary conditions prevail with tolerable uniformity, the rate of mortality is practically uninfluenced by the softness or hardness of the water supplied to the different towns, and the average rate of mortality in the different water divisions varies far less than the actual mortality in the different towns of the same division. They were of opinion that, whilst waters of excessive hardness may be productive of calculus and perhaps other diseases, soft and hard water, if equally free from deleterious organic substances, are equally wholesome.' The question of magnesia in drinking water has been discussed by the writer ('What is the Importance of Magnesia in Drinking Water,' P. F. Frankland, Transactions of the Internat. Congress of Hygiene and Demogr. London, 1891), from whose inquiry it appears that whilst the amount of magnesia in the water supplied to most large towns is very small—generally not more than 1-2 parts of MgO per 100,000—it is much larger than is generally supposed in the well-water consumed by such a large portion of the population. Thus in the case of fifty brewery waters from all parts of the kingdom, the average amount of magnesia (MgO) was 3.41 parts per 100,000. It must also be remembered that the geological formation richest in magnesia (the magnesian limestone) is only very slightly represented in this country, so that the proportions of magnesia met with in the dolomitic districts of the Continent must be much larger.

Until, therefore, a far more searching inquiry than hitherto has been made into the alleged effect of such waters upon health, it would appear undesirable that any importance should be attributed to such proportions of magnesia as the above in drinking waters which are otherwise of unimpeachable purity.

The effect of Clark's process on magnesian waters is noteworthy. As a general rule, the proportion of magnesia removed by the treatment with lime is small—much smaller than that of the lime removed; but it is particularly worthy of notice that in cases where caustic soda was used in conjunction with lime, as in the softening done in the softening of water for industrial purposes, the magnesia may be removed in greater proportion than the lime,

and as a matter of fact magnesium hydroxide is less soluble even than calcium carbonate.

The hardness of water not infrequently throws light upon its previous history, for the food of both man and animals is of necessity rich in lime, and nearly the whole of this is in adult life again found in the liquid and solid excreta; hence water obtained from soil which has been much polluted with animal matters always exhibits a large amount of permanent hardness.

PURIFICATION OF DRINKING WATER.

Inasmuch as the impurities are either suspended or dissolved, mineral or organic, and the organic either animate or inanimate, it follows that the subject of purification may be considered from different points of view, according to the particular class of impurities the removal of which is under discussion. Until recently all the more important processes of drinking water purification were filtration processes, those depending upon precipitation being more especially of importance in connection with water for industrial purposes (see p. 391). Now, however, methods of more or less sterilising water by means of hypochlorites, ozone, or ultra-violet light are sometimes being resorted to (see p. 417).

Purification of drinking water on large scale.—All surface water is liable to turbidity, and in times of rain and flood the amount of suspended matter may become excessive. It is, therefore, desirable that all surface water, even that from upland sources, should be submitted to purification before distribution for domestic purposes. The purification of surface water is best initiated by permitting the water to remain at rest in storage reservoirs for some days or even weeks, the greater part of the suspended matter thus becoming precipitated, and some destruction even of the dissolved organic matter also taking place. During storage most important biological changes also take place (see later). The process of filtration resorted to on the large scale is almost invariably that through sand of different degrees of coarseness. This method was inaugurated by Simpson, the engineer to the Chelsea Company in 1829, and has since been adopted in an ever-increasing number of places all over the world. The filter beds, as usually constructed, are 10-16 ft. in depth, often upwards of an acre in area, made water-tight with masonry, concrete, or puddled-clay walls. On the bottom are collecting drains, upon which is placed a layer of broken stone about 6 ins. in thickness, following upon which are layers of coarse gravel, fine gravel, and uppermost a stratum of fine sand, 1-4 ft. in thickness. The water is kept at a depth of 1-4 ft. above the surface of the fine sand, the rate of filtration varying in different works. For construction and cost of filtration plant, see Donald Chisholm, *Modern Methods of Water Purification*, London, 1911, 125. The greater part of the suspended impurities is retained in the downward passage of the water by the first few inches of fine sand, and sooner or later, sometimes in the course of a few weeks, causes the clogging of the filter. When the rate of filtration is too much retarded for practical purposes, the water

surface of the sand is removed, after which the filtration can be continued until the filter is again choked, when the surface is again scraped off, the process being repeated until the stratum of sand becomes too thin to be efficient, after which the original thickness of the sand-layer is restored by means of washed sand. The sand scraped off is generally thoroughly washed, allowed to dry, and then used again. The particulars for the several sections of the Metropolitan supply, shown below, will serve to illustrate the method of working.

Besides the filter beds just described, some of the works drawing from the Thames are now using an auxiliary process of filtration through the natural gravel beds which form the banks of the Thames at Hampton. These gravel beds are at all times full of water, which forms, as it were, an underground river, and underground pipes are laid in this gravel and connected with a pumping well in order to utilise this water, which is always clear and bright in consequence of the natural filtration which it has undergone. In order to increase the supply of this underground water the gravel bed is flooded with water directly from the Thames, for which purpose a second series of perforated pipes are laid parallel to the first and placed at a distance of about 30 yards from them. This second series of pipes is placed in direct communication with the Thames, but at the point of ingress is

placed a small vertical sand filter to arrest the coarser impurities.

Such sand filters, although very efficient in removing the suspended matter, have comparatively little action upon that which is dissolved. Thus the following figures exhibit the composition of the York water supply, before and after filtration through sand:—

(Results of Analysis expressed in parts per 100,000.)

	Before filtration	After filtration
Total solid matters	28.40	26.20
Organic carbon	0.123	0.119
Organic nitrogen	0.023	0.022
Ammonia	0	0
Nitrogen as nitrates and nitrites	0.077	0.089
Chlorine	1.6	1.6
Temporary hardness	11.5	10.9
Permanent hardness	7.1	7.1
Total hardness	18.6	18.0
Micro-organisms (colonies yielded by 1 c.c. of water on cultivation with gela- tin-peptone)	31,200	122

It was formerly supposed that such sand filtration could have little or no effect in removing the micro-organisms present in water, as the interstitial spaces between the grains of sand are so large in comparison with the minute dimensions of the microbes. It was first shown

METROPOLITAN WATER SUPPLY, JANUARY, 1911.

District works	Number of days' storage	Filtering area per million gallons of the average daily supply of 1910	Thickness of sand on filters		Average rate of filtration per square foot per hour
			Maximum	Minimum	
		acres	ft. ins.	ft. ins.	gallons
Eastern	52.5	0.676	2 6	1 6	1.37
New River	10.7	0.590	2 3	1 7	1.84
Southern, Lambeth Works	35.7	0.986	3 0	2 6	2.13 Kempton Park
Southwark "			3 0	2 3	1.05
Western, Chelsea Works			4 3	3 3	1.17
" Grand Junction Works	11.5	1.007	3 0	2 3	1.43
" West Middlesex Works			2 9	2 6	0.82 Hampton 0.70 Kew Bridge 1.17

Monthly Reports by Metropolitan Water Examiner to Local Government Board.

by Koch in Germany, and by the writer in this country, that nearly all the microbes in water may be removed by the sand-filters (Koch, Bericht der Deputat. f. die Verwaltung der Canalisationwerke, Berlin, 1883; P. F. Frankland, Proc. Roy. Soc. 1885; Proc. Inst. Civ. Engineers, 1885-6; J. Soc. Chem. Ind. 1885, 1887), and this result has been since confirmed by many other investigators.

It was, in fact, supposed by Koch and his pupils that the sand filtration really removed all the microbes originally present in the water, and that those always found in the filtered water had gained access subsequent to filtration. The writer had, however, from the first shown that in the case of the monthly examinations of the

London water supply there was an obvious relationship between the numbers of microbes in the unfiltered and filtered waters respectively, necessitating the conclusion, therefore, that the sand filters can only be credited with removing a portion and not the whole of the micro-organisms present. This is sufficiently conspicuous from the tables on next page, which record some of the writer's results obtained with the London water supply during the year 1886, and reported to the Local Government Board (P. F. Frankland, J. Soc. Chem. Ind. 1886). The unfiltered Thames water was in every case collected near the intakes of the several water companies at Hampton, and the filtered water from the mains of the Chelsea, West Middlesex, Southwark,

TABLE I. 1886.

Total number of Colonies obtained by cultivation of one cubic centimetre of water.

— *	Description of water					
	Thames unfiltered	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	45,400	159	180	2270	4894	2587
February	15,800	305	80	284	208	265
March	11,415	299	175	1562	379	287
April	12,250	94	47	77	115	209
May	4,800	59	19	29	51	136
June	8,300	60	145	94	17	129
July	3,000	59	45	380	14	155
August	6,100	303	25	60	12	1415
September	8,400	87	27	49	17	59
October	8,600	34	22	61	77	45
November	56,000	65	47	321	80	108
December	63,000	222	2000	1100	1700	305
Average	20,255	146	234	524	630	475

TABLE II. 1886.

Percentage reduction in the number of developable micro-organisms present in the river waters before delivery by the companies.

—	Description of water				
	Chelsea	West Middlesex	Southwark	Grand Junction	Lambeth
January	99.7	99.6	95.0	80.2	94.3
February	98.1	99.5	98.2	98.7	98.3
March	97.4	98.5	86.3	96.7	97.5
April	99.2	99.6	99.4	99.1	98.3
May	98.8	99.0	99.4	98.9	97.2
June	99.3	98.3	98.9	99.8	98.5
July	98.0	98.5	87.3	99.5	94.8
August	95.0	99.6	99.0	99.8	76.8
September	99.0	99.7	99.4	99.8	99.3
October	99.6	99.7	99.3	99.1	99.5
November	99.9	99.9	99.4	99.9	99.8
December	99.7	96.8	98.3	97.3	99.5
Average percentage reduction	98.6	99.1	96.7	98.2	96.2

Grand Junction, and Lambeth Companies respectively.

C. Fraenkel and Piefke (Zeitsch. Hygiene, 8, 1890, 1-40) subsequently demonstrated by direct experiment that particular species of bacteria purposely introduced into the unfiltered, were still present, although in greatly diminished numbers, in the filtered water.

The wonderful efficiency of these sand filters in removing microbes was at first very difficult to account for, but it is now recognised to depend upon the impervious nature of the slimy deposit which forms upon the surface of the sand, and until such a coating has been established the filter has but little effect in removing micro-organisms (Piefke, Aphorismen über Wasser-versorgung, Zeitsch. Hygiene, 7, 1889, 115-179). This slimy deposit consists not only of silt, mud, and colloidal matter, but also of a multitude of living forms—diatoms, green and blue algae, innumerable bacteria, fungi, and protozoa. Many of these forms actually feed on

bacteria. The rate at which filtration is carried on is also a most important factor, the more rapid the rate the less efficient being the purification (P. F. Frankland, Proc. Inst. Civ. Engineers, 1885-6). Although the removal of bacteria is not attributable to the sand particles as such, there is abundant evidence that the finer the sand and the greater its depth the more efficient is the filtration. This is doubtless due to a better support being given to the filtering skin, and to the finer and thicker layer of sand regulating the passage of water through the medium, whilst the water is also brought into more intimate and prolonged contact with the colloidal matter with which the sand of a matured filter is clothed. The statistics of the London water-works show that the cost of filtration as carried out by them averages about 0.1d. per 1000 gallons.

In countries liable to extreme cold—indeed, even in cold winters in this country—the process of sand filtration offers great difficulties, in consequence of the freezing of the filters; and this

has, in Berlin, been guarded against by the construction of a number of covered filter-beds. In the United States, where the same difficulty exists, the Hyatt system of filtration has been employed on a considerable scale. In this the water is first treated with a minute quantity of alum (about $\frac{1}{2}$ grain per gallon), after which it passes through a steel filtering chamber, consisting of a vertical cylinder the diameter of which is nearly twice its height. This cylinder is divided by a horizontal diaphragm, capable of withstanding the hydrostatic pressure necessary for rapid filtration. The lower half contains the filtering material, composed of 2 parts coke and 3 parts sand. The upper part of the cylinder is used for washing the filtering material, which at regular intervals is transferred into it in a state of violent agitation by hydraulic currents, the impurities flowing away through pipes situated near the top of the cylinder. In the process of filtration the water is admitted through pipes to the upper part of the lower section of the cylinder, and it is drawn off through perforated cups, which permit the water, but not the sand, to pass. It is claimed that the efficiency of the system depends more upon the successful precipitation and entanglement of germ life by the coagulant alumina than upon any special merits of the filter (Potable Water, Floyd Davis, Iowa, U.S. 1891). The cost of maintenance is said to be only one-fifth of that entailed by filter beds.

In recent years the use of mechanical filters has been gaining ground in Great Britain also, the Jewell, Bell, and Candy filters being those most commonly employed (see Modern Methods of Water Purification, Don and Chisholm, London, 1911; see also *Bacteriology of water*, below). The Pusch-Chabal system consists in submitting the water to successive processes of filtration, sometimes as many as six stages, beginning with coarser grades of gravel and ending with fine sand, being employed. It is specially suitable for very turbid waters, as the life of the fine sand filter is greatly prolonged. It has been used at Magdeburg and other places (see Don and Chisholm, l.c.).

Of other methods of drinking-water purification on the large scale the only one that need be mentioned is Anderson's. The method consists in passing the water slowly through revolving iron cylinders about two-thirds filled with iron borings. A small quantity of the iron continuously passes into solution, so that the water becomes impregnated with ferrous iron, which subsequently, when the water flows into a settling tank, is converted into the ferric state with precipitation, a large proportion of the organic matter in solution being removed in the process, whilst a very considerable diminution in the number of vital germs is also effected. After undergoing oxidation in the settling tank, the water is finally filtered through sand before distribution. It takes $\frac{3}{4}$ mins. for the water to pass through the rotating cylinder, the entire process occupying about 6 hours (Anderson, Proc. Inst. Civ. Engineers; Engineering, 39, 525). This process has been used on a large scale at Antwerp and Paris.

Purification of drinking water on the small scale.—The filtration of water on the small scale was already known to the ancients. Thus Pliny mentions a process in which water was clarified by

passage through wool. An immense number of different materials have been employed during recent years, but space will only permit of the brief consideration of a few of the more important ones.

Animal charcoal is employed in a number of common household filters, and from the invaluable services which it yields in sugar-refining it was anticipated that it would be highly efficient as a water filter. Unlike sand, it not only acts upon the suspended matters, but also removes a considerable proportion of the dissolved organic matter, and even some of the temporary hardness. Unfortunately, however, its action is very transient, and it generally soon becomes the seat of numerous organic growths, which are favoured by the calcium phosphate it contains, and the filtered water is then often rendered more impure than the unfiltered.

Vegetable charcoal has but little effect on the dissolved organic matters, although if in a sufficiently fine state of division it is an excellent strainer for suspended impurities (see table below).

Bischof's spongy iron, obtained either by reduction of hematite or of roasted pyrites, has a remarkable power of removing dissolved organic matters, as well as temporary hardness and nitrates, and this power is far more permanent than that of animal charcoal. It was for some time also employed on the large scale, in conjunction with sand, at the Antwerp Waterworks. The effect of filtration through animal charcoal and spongy iron respectively is exhibited in the table below.

Since the recent great advances in bacteriological science, it has become evident that the removal of micro-organisms from drinking water is a matter of much greater importance than the removal of organic matter, and hence it is in respect of this property that the value of filters is now generally estimated. The writer has shown (The Removal of Micro-Organisms from Water, P. F. Frankland, Proc. Roy. Soc. 1885) that several substances—such as coke, wood-charcoal, spongy iron, &c.—in a sufficiently fine state of division are capable of entirely removing all microbes in water passed through a stratum of a few inches of these materials. This power, which is quite independent of any chemical action (thus in the case of coke and wood-charcoal there is little or no removal of dissolved organic matter), is, however, not maintained unless the materials are frequently renewed; and in the case of animal charcoal which has been in use for a short time (one month) the number of microbes was found to be far greater in the filtered than in the unfiltered water. The most conspicuous instance of biological, as opposed to chemical, filtration is furnished by Chamberland's unglazed porcelain filter, which entirely removes microbes, but has no chemical action whatever (see table on next page).

A number of household filters in actual use have been examined with regard to their power of removing microbes by Plagge (Public Health Section of Germ. Assoc. of Naturalists and Physicians, 1886), who divides them into six classes, according to the materials used: (1) carbon filters, (2) stone and sand filters, (3) spongy-iron filters, (4) paper filters, of various kinds, (5) porous earthenware filters (Chamberland), (6) asbestos filters (Brewer, Hays, &c.).

and Schirmer). The carbon filters were found not only to admit of the free transmission of microbes, but in some cases the numbers in the filtrate greatly exceeded those in the unfiltered water. Thus in one case 68 colonies were obtained from 1 c.c. of the unfiltered, and 12,000 from 1 c.c. of the filtered water. The stone and sand filters were all found to be worthless. The spongy-iron filter yielded the following results: unfiltered water, 38,000 colonies from 1 c.c.; filtered, 18,000-24,000 colonies from 1 c.c. The paper filters all yielded very unsatisfactory results; the earthenware and asbestos filters, on the other hand, gave in nearly every instance a filtrate practically free from microbes. (For par-

ticulars concerning the sterilising power of the Chamberland filter, see also Miquel, *Analyse Bactériologique des Eaux*, Paris, 1891.) The principal drawback to these porous earthenware filters is the rapid diminution in the rate of filtration which they exhibit. More satisfactory in this respect are the Berkefeld filters, similarly constructed of burnt infusorial earth (Nardt-meyer, *Zeitsch. Hygiene*, 1891, 10, 145; Bitter, *ibid.* 155). Neither the Chamberland nor Berkefeld filters permanently yield sterile water, some of the bacteria in the unfiltered water sooner or later growing through the pores. It is, however, doubtful whether any of the ordinary pathogenic bacteria would do this, as none of them are

(Results of Analysis expressed in parts per 100,000.)

Description	Total solid matters	Organic carbon	Organic nitrogen	Ammonia	Nitrogen as nitrates and nitrites	Total combined nitrogen	Chlorine	Hardness			No. of developable micro-organisms in 1 c.c. of water
								Temporary	Permanent	Total	
London water, unfiltered ¹	24.60	0.129	0.023	0	0.188	0.211	1.6	—	—	19.4	—
Ditto, after filtration through fresh animal charcoal ¹	19.40	0.029	0.007	0.013	0.194	0.212	1.6	—	—	15.2	—
London water, unfiltered ¹	25.94	0.164	0.030	0.002	0.062	0.094	1.9	—	—	19.7	—
Ditto, after filtration through animal charcoal in use 11 months ¹	25.10	0.010	0.002	0.002	0.125	0.129	1.9	—	—	19.1	—
London water, unfiltered ¹	25.28	0.120	0.013	0	0.166	0.179	1.7	14.5	0.7	21.2	—
Ditto, after filtration through fresh spongy iron ¹	13.70	0.025	0.004	0.002	0.031	0.037	1.7	7.4	4.6	12.0	—
London water, unfiltered ¹	24.10	0.188	0.034	0.001	0.120	0.155	1.95	11.8	7.3	19.1	—
Ditto, after filtration through spongy iron in use 8 months ¹	14.84	0.089	0.020	0.001	0	0.021	1.95	5.3	4.3	9.6	—
Water, before filtration ²	24.80	0.144	0.050	0	0.190	0.240	1.9	11.3	5.6	16.9	24,000
Ditto, after filtration through fine coke ²	25.00	0.107	0.038	0	0.202	0.240	1.9	11.3	5.6	16.9	0
Ditto, after filtration through fine wood charcoal ²	24.68	0.090	0.024	0	0.221	0.245	1.9	12.5	4.6	17.1	0
London water, before filtration ²	33.70	0.282	0.028	0	0.288	0.316	1.9	15.7	4.9	20.6	54
Ditto, after filtration through Chamberland filter ²	30.04	0.284	0.027	0	0.289	0.316	1.9	14.4	5.3	19.7	0

¹ Riv. Commis. 6th Rep.

² P. F. Frankland, *J. Soc. Chem. Ind.* 1885.

³ P. F. Frankland, *Proc. Roy. Soc.*, 1885, 300.

known actually to multiply extensively in ordinary drinking water (Kühler, *Zeitsch. Hygiene*, 1890, 10, 48).

W. E. Hall has described a simple apparatus for the extraction of micro-organisms from samples of water. The sample is collected in a small straining jar through which any quantity of water can be passed, and the organisms retained in a quantity of water convenient for carriage.

From this concentrated sample the organisms can be extracted by passing it through a filter paper about 1½ in. diameter placed over a small funnel attached to a vessel from which the air is extracted by means of an exhaustor consisting of a modified form of filter pump.

The organisms are finally washed off the filter paper by means of a wash bottle with about 2 c.c. of water in which the organisms can readily be examined in a stage trough or placed in small quantities on a compressor slide (*J. Soc. Chem. Ind.* 1924, 43, 290).

Purification of drinking water by distillation.—This is, of course, the most effectual mode of freeing water from all its impurities. It is

resorted to, on a considerable scale, at sea, both for steam and sailing vessels. (For description of forms of apparatus in actual use v. Fischer, *Technologie d. Wassers*, Brunswick, 1880, 201-208.) The insipid taste of the distilled water can be removed either by aëration, or by filtration through animal charcoal or other porous substances. Distilled water is also employed to some extent for the manufacture of aerated waters and for artificial ice.

Purification of drinking water by boiling.—The purification consists, of course, only in the destruction of living organisms present in the water, but this is from an hygienic point of view of the greatest importance. In its action it is far more reliable than any process of filtration, and should be invariably resorted to in the case of waters which bear any suspicion of sewage contamination. The rapid taste of the boiled water may be removed by passage through a filter, which, however, should be exclusively employed for this purpose and not for filtering unboiled water. A convenient form of apparatus for sterilising large quantities of water—e.g. for hospitals, barracks, &c.—is described by

Miquel (*Manuel d'Analyse bactériologique des Eaux*, Paris, 1891, 198). The more extensive use of boiled instead of filtered water is one of the chief sanitary desiderata of the day. Although absolute sterility cannot be guaranteed by a few minutes' ebullition, yet the reduction in the number of microbes by this simple process is so great that it may be safely regarded as ample for practical purposes. Thus Miquel and Wada (*ibid.* 185) found in the case of the Ourcq-canal water of Paris:—

Temperature.	Bacteria in 1 c.c.
14°C.	460,800
50° for 10 minutes	600
60° "	(60)
70° "	88.8
80° "	62.4
90° "	26.4
100° "	0.5
100° for 20 minutes	0.0

WATER FOR INDUSTRIAL PURPOSES.

Of the numerous industrial uses to which water is put, the most general and important is the raising of steam. The composition of the water supplied to steam-boilers is a matter of great consequence, as the use of unsuitable water may cause the corrosion of boiler-plates and the formation of deposits, which not only occasion a serious loss of heat but may also lead to most disastrous explosions (*v.* **BOILER INCURSTATIONS AND DEPOSITS**).

Water for other industrial purposes.—(1) For *brewing*, see art. **BREWING**. For use in bakeries, the water should be in all respects of the same degree of purity as is demanded for drinking purposes.

(2) For the *textile industries* the character of the water employed is often of great consequence. Thus in bleaching and dyeing the presence of iron and manganese, even in very small quantities, is highly deleterious, giving rise to iron and manganese stains on the bleached goods, and causing spots and modifications in the shades of dyed materials. Hard water, again, involves the use of larger quantities of alkali and soap in the several operations of boiling, scouring, and milling, and the insoluble lime-soap is left adhering to the fibre, often preventing the subsequent application of mordant or dye. In those operations, again, in which dyed fabrics are soaped, the lime-soap often injures the brilliancy of the colour, whilst in other cases the earthy soaps precipitated on the fibre act as mordants, and attract the colouring matters on those parts of the goods where it is not wished to fix them. In general, hard water has the effect of dulling many colours, and if due to bicarbonates retards, or even prevents, the dyeing of such colours as require an acid bath (*e.g.* cochineal scarlet). In some cases hard water containing bicarbonates wastes the mordants by precipitation in the bath instead of on the fibre, whilst it is sometimes actually beneficial for the washing of goods which have been mordanted with basic mordants. Such water is unsuitable for the solution of many coal-tar colours—*e.g.* methyl violet—a portion of the latter being lost as a tarry precipitate, whilst the goods are often spotted. For dyeing with some colours—*e.g.* alizarin and logwood—the

presence of a certain amount of lime is almost indispensable; a pure water to which a known quantity of lime-salt has been added is, however, preferable to a naturally hard water, especially if the latter is of variable composition. Water containing alkaline carbonates is sometimes advantageous, *e.g.* in wool-scouring, and in those dyeing operations in which the addition of sodium carbonate is prescribed; but in mordanting, in the dyeing with many colours, and in the washing of dyed goods, it is often very prejudicial; in these cases it should be neutralised with sulphuric or acetic acid. Acid waters are generally highly injurious, and should be neutralised with sodium carbonate. Sulphuretted hydrogen in water is also very objectionable in many operations of dyeing, more especially in mordanting with metallic salts (*Hummel, Dyeing of Textile Fabrics*). For the manufacture of paper, water containing iron is highly objectionable, giving rise to stains, whilst the presence of hardness is objectionable in causing the decomposition of the rosin-soap.

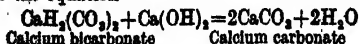
(3) For *tanning*, pure water is also a desideratum. Water much contaminated with organic matter causes injury to the surface of the leather, and sometimes a corrosion from the flesh-side of the skin. Water containing carbonic acid, or the bicarbonates, or calcium and magnesium sulphates, causes the hides to swell, whilst the chlorides prevent the swelling, and hence sea-water cannot be employed for the purpose. Hard water occasions a less perfect utilisation of the tanning materials, and an excess of chlorides retards the tanning process and causes the leather to attract moisture; the presence of iron is not so objectionable as is commonly supposed (*Fischer, Das Wasser*, 49–51).

(4) In *sugar-refining* the sulphates and alkaline carbonates are more productive of molasses than the chlorides, whilst nitrates are specially objectionable, as they prevent the crystallisation of six times their weight of sugar (*Fischer, Technologie d. Wassers*, p. 286).

Purification of water for industrial purposes.

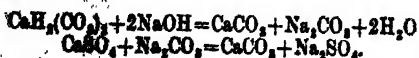
As already pointed out, some substances, although unobjectionable in drinking water, operate prejudicially when the water is employed for many industrial purposes, and numerous methods have been devised for removing these impurities or for counteracting their effects. But few methods of purification have found favour in actual practice, and to these alone will any attention be given here. The processes which have for their object the removal of matters in suspension and organic substances have been already described under *Purification of drinking water* (*v.* p. 396), whilst the processes intended for the improvement of industrial water supplies are chiefly directed to the removal of lime and magnesia salts in solution, which, as has been shown above, interfere with the success of so many industrial operations. This removal of lime and magnesia salts is frequently spoken of as 'water-softening,' in consequence of the water after such treatment requiring less soap when used for washing purposes.

Purification with lime (Clark's process).—This method of purification was first proposed by Clark, of Aberdeen, in 1841, and consists in the decomposition of calcium bicarbonate or 'temporary hardness' of water by the addition of a suitable quantity of slaked lime, according to the equation



Thus both the lime in solution as bicarbonate as well as that added in the form of hydroxide are precipitated as normal carbonate, which is almost insoluble in water. The calcium hydroxide is sometimes added in the form of milk of lime, sometimes in that of clear lime-water, but the latter is far preferable, as the quantity added can be more easily controlled and an excess avoided. The necessary quantity of calcium hydroxide is most easily ascertained by adding such an amount that, after thorough mixing, a small quantity of the water taken out yields a yellow or brown colour with a solution of silver nitrate, more water is then added, until, on similarly testing, no coloration with the silver nitrate is obtained. This test should invariably be resorted to even in the case of such waters as are of very constant composition, and which, therefore, admit of the lime being proportioned by experience, as otherwise an excess or deficiency of lime is nearly sure to result. In its original form the Clark process is carried out in large tanks in which the water can remain at perfect rest for about 16 hours, although by the use of a floating exit-pipe the clear surface water can often be drawn off after 2 or 3 hours, and before the whole of the precipitate has reached the bottom. This method has been most successfully employed on a large scale at the Colne Valley Waterworks, near Bushey, at Canterbury, Caterham, and many other places on a small scale. The 'temporary hardness' only is, of course, removed, and even this not completely, as under the most favourable circumstances a small proportion of calcium carbonate remains in solution, whilst in the case of waters containing magnesium bicarbonate the removal of the latter is generally far less complete. In addition to these bicarbonates, the salts of iron and much organic matter are also removed.

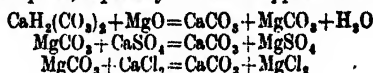
In order to obviate the large amount of storage capacity required for Clark's process, several modifications have been introduced, in which the precipitate formed by the treatment with lime is either removed by filtration or made to subside rapidly by artificial means. The most notable of these improved processes are the so-called 'Porter-Clark,' in which the precipitate is removed with a filter-press, and Gaillet and Huet's process, in which subsidence is promoted by causing the water to take a circuitous zig-zag and upward path after the addition of the lime. In this latter process both lime and caustic soda are frequently employed in conjunction as the softening agents; in this manner both 'temporary' and 'permanent' hardness can be, to a great extent, removed, thus:—



Space does not permit the description of a number of other water-softening apparatuses

which are now on the market, and which only differ from each other in the special mechanical devices for supplying the chemicals (milk of lime, lime water, sodium carbonate, or caustic soda, as the case may be) and for removing the deposit. The Archbutt-Deeley process, however, possesses certain features of interest. In this the clarification of the treated water is accelerated by stirring it up with the sludge of calcium carbonate obtained in previous precipitations, this being effected by blowing in compressed air through perforated pipes. The subsequent sedimentation takes place very rapidly, and the clear water is drawn off from the surface by means of a floating arm. Further, the danger of subsequent deposition of calcium carbonate in the service pipes, which often occurs when an insufficient time is allowed for sedimentation, is avoided by injecting carbon dioxide (obtained from a coke-stove, the gas being scrubbed with limestone to remove sulphur compounds) into the clarified water as it is drawn from the settling tank.

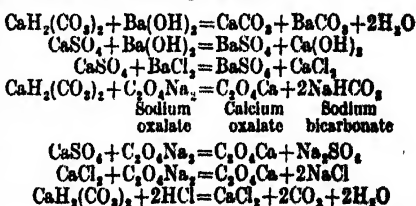
Magnesia has also been employed to a limited extent for softening instead of lime. Under these circumstances the following reactions may take place, especially if heat is applied:—



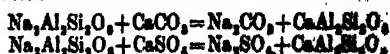
(Fischer, Chem. Technol. d. Wassers, Brunswick, 1880, 264).

The formation of magnesium chloride is obviously disadvantageous for boiler purposes.

A number of other processes of chemical purification have from time to time been suggested, but none of them have met with any great success. Thus attempts have been made to utilise the following reactions:



In the *Permutite* process, devised by Dr. Gans of Berlin, the water is softened by filtration through artificial zeolite (a hydrated silicate of alumina and soda) to which the name of *Permutite* has been given. The latter is made by fusing together silica or quartz, alumina or china-clay, and sodium carbonate. The fused mass is extracted with water, a crystalline body ($\text{SiO}_2=46$, $\text{Al}_2\text{O}_3=22$, $\text{Na}_2\text{O}=13.6$, $\text{H}_2\text{O}=18.4$ p.c.) being obtained. When waters containing calcium or magnesium salts are filtered through this material, the following reactions take place:—



It is claimed for this process that the whole of the hardness is removed and that the calcium or magnesium zeolite formed can be reconverted into the original permutite or sodium zeolite by treatment with a strong solution of common salt. Gans uses a manganese-permutite (zeolite,

alkalis, and a higher oxide of manganese) for the removal of iron and manganese in water. This material can be regenerated by treatment with a solution of potassium or calcium permanganate. The manganese-permutite can also be employed for the sterilisation of water; the water is treated with permanganate in sufficient concentration to destroy bacteria, and, on subsequent filtration through manganese-permutite, the whole of the manganese is said to be retained by the filter. Calcium-permutite has been used for removing potash from molasses, lime passing into solution; the lime may be replaced by soda by passing through sodium-permutite. The plant and materials for the Permutite process can be obtained from 'Water Softeners, Ltd.,' Kingsway, London, W.C.

For the effect of softening processes on the bacteria in water, v. p. 417.

The action of water on lead, zinc, copper, and aluminium.—The action of water on these metals, and especially on lead, is of great importance in connection with the distribution and storage of water. The Romans employed leaden pipes, and Vitruvius and Galen were aware that some waters were thereby rendered deleterious. On the other hand, certain waters have so little action on lead that pipes of this material have been in use for upwards of 200 years without showing any trace of corrosion (Fischer, *Technologie d. Wassers*, 317). As a general rule, hard waters, and more especially those containing bicarbonates, do not act on lead; the greater number of active waters are soft, and generally entirely destitute of bicarbonates. The activity has been ascribed by different authorities to the presence or absence of a great variety of ingredients in the water—e.g. the presence of dissolved air (Yorke), ammonium nitrite (Medlock), ammonium carbonate (Böttcher). Some have contended that organic matters diminish the activity (Horsford), others that they increase it (Hofmann, Graham, Miller, and Noad). The latter authorities were of opinion also that the presence of dissolved oxygen and the absence of more than 3 vols. of carbon dioxide in 100 vols. of water are amongst the conditions necessary for the attack upon lead. It has also been contended that a minute proportion of calcium phosphate prevents a soft water from attacking lead (Riv. Pollut. Commis. 6th Rep. 224), whilst according to others, again, the protecting ingredient is silica (Crookes, Odling, and Tidy, Report on the Action of Water on Lead, London, 1886). In many cases the activity of the water is due to the presence of organic acids (Allen), this being doubtless a fruitful cause of moorland waters acting on lead. The activity of many waters is confined to new untarnished lead, whilst others continue to act, sometimes with increased vigour, on the old and tarnished metal (P. F. Frankland, *The Action of Water on Lead*, J. Soc. Chem. Ind. 1889, 241).

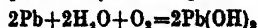
Numerous expedients have been resorted to in order to destroy this activity of some soft waters. When acidity is the presumable cause the most obvious remedy is the filtration of the water through finely-divided limestone; in practice, however, this is found to be only of temporary service, as the surfaces of the limestone become coated with a film which prevents their

being further acted on by the water. It has been found more effective to mix the water continuously with a milk of finely-divided calcium carbonate, and allowing this to subside before the water is distributed.

It is now generally admitted that the action of water on lead is of two different kinds. Of these the most obvious is that due to the acidity¹ of some waters; such acidity may be due to organic or even mineral acids, and can be determined by titration with appropriate indicators. Such acid waters have, in general, a continuous action on lead. The acidity can, of course, be neutralised by the addition of lime, finely-divided calcium carbonate, or most effectively by sodium carbonate. It was, however, shown many years ago by the writer that such neutralisation does not necessarily entirely stop the action of the water on lead, and that this is often only secured by adding a considerable excess of sodium carbonate. Similarly there are many natural waters, which, although slightly alkaline with small proportions of calcium bicarbonate, nevertheless act on lead. Such action of neutral or even slightly alkaline waters is now usually termed '*erosive*' as distinguished from the '*plumbosolvent*' action of acid waters. These remarkable phenomena have only received a satisfactory explanation since the recent advances in physical chemistry have illuminated the subject of chemical equilibrium.

This matter is very ably dealt with in an important paper by Paul, Ohlmüller, Heise, and Auerbach (*Arbeiten a. d. kais. Gesundheitsamte*, 1906, 23; *Untersuchung über die Beschaffenheit des zur Versorgung der Haupt- und Residenzstadt Dessau benutzten Wassers, insbesondere über dessen Bleilösungsfähigkeit*). The conclusions arrived at by these authors are:—

1. *Dissolved oxygen* is necessary for the solution of metallic lead in pure water. Experiments made with distilled water, which had been saturated with air freed from carbon dioxide, showed that nearly the whole of the oxygen (amounting to about 9 mgms. per 1 litre) was taken up presumably according to the equation:



The water, which was at 18°, took up about 115 mgms. of lead per 1 litre. By increasing the proportion of oxygen in the air used for saturating the water the amount of lead taken up was at first also increased (up to about 140 mgms. Pb per 1 litre), but this was followed by a sudden drop to an amount which remained practically constant (about 108 mgms. per 1 litre for about 14.5 mgms. O₂ dissolved in 1 litre water). This sudden drop is referred to the appearance of a precipitate (*solid phase*) preventing further supersaturation of the water with lead hydroxide. (The authors did not determine the exact composition of the solid phase, which may have been Pb(OH)₂, or more probably one of its anhydrides.)

2. *Free carbonic acid* diminishes the plumbosolvent effect of the simultaneously present dissolved oxygen. Thus, in an experiment with distilled water made to contain about 8 mgms. O₂ and 40 mgms. CO₂ in 1 litre, the amount of lead

¹ See a very important paper on 'The Acidity and Alkalinity of Natural Waters,' by James Walker and S. A. Kay (*J. Soc. Chem. Ind.*, 1912, 31, 1979).

taken up was about 11 mgms. per 1 litre, or about $\frac{1}{2}$ of that dissolved when the same proportion of dissolved oxygen was present in the absence of carbonic acid. This diminished plumbosolvency is, of course, attributable to the formation of a more insoluble solid phase, viz. either PbCO_3 , or more probably some basic carbonate such as $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$.

3. Sodium bicarbonate in the absence of any appreciable quantity of free carbonic acid greatly reduces the plumbosolvency of water; thus in similar experiments, in which the same proportion (about 9 mgms. O_2 per 1 litre) of dissolved oxygen was retained, but along with 35 mgms. of NaHCO_3 per litre, the amount of lead taken up was only 0.6 mgm. per litre of water. This, again, is attributable to the diminished solubility of the solid phase in the solution of the sodium bicarbonate. The amount of lead taken up by the water is limited by the *solubility product*; thus a saturated solution of lead carbonate will contain a small concentration of PbCO_3 molecules, together with $\text{Pb}^{++}\text{CO}_3^{--}$ ions, of which only the PbCO_3 molecules are in direct equilibrium with the solid phase (precipitated lead carbonate). The concentration of the PbCO_3 molecules will always remain constant as long as there is any of the solid phase present, but this concentration is very small. The concentration of the ions, on the other hand, is determined by the dissociation equilibrium. Thus, representing the molecular concentrations of the respective bodies by the formulæ enclosed in brackets, we have—

$$[\text{Pb}^{++}] \times [\text{CO}_3^{--}] = k \times [\text{PbCO}_3]$$

in which k is a constant. But in saturated solutions, as already seen above, $[\text{PbCO}_3]$ is constant, therefore $k \times [\text{PbCO}_3]$ is also constant, and can be represented by S , which is termed the *solubility product*, thus—

$$[\text{Pb}^{++}] \times [\text{CO}_3^{--}] = S$$

$$\therefore [\text{Pb}^{++}] = \frac{S}{[\text{CO}_3^{--}]}$$

which obviously signifies that the concentration of the Pb^{++} ions will be the smaller the greater the concentration of the CO_3^{--} ions. (If the solid phase is a basic carbonate, then it can be shown that the concentration of the Pb^{++} ions must be inversely proportional to the concentrations of the CO_3^{--} and the OH^- ions.)

In solutions of free carbonic acid the concentration of CO_3^{--} ions is very small (because carbonic acid being a very weak acid is only very slightly dissociated into ions), whilst in solutions of NaHCO_3 the concentration of CO_3^{--} ions is much greater, and, therefore, the concentration of the Pb^{++} ions will be correspondingly diminished, or, in other words, a much smaller proportion of lead will pass into solution. (It should be mentioned that the phenomena may be complicated by the circumstances that the nature of the solid phase may be different according as the metallic lead is placed in contact with a solution of free carbonic acid or bicarbonate respectively.)

4. The simultaneous presence of free carbonic acid and sodium bicarbonate leads to the following considerations:—



further $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, whilst to a much less degree $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$. These dissociations are expressed by the equations

$$(1) [\text{H}^+] \times [\text{HCO}_3^-] = k_1 \times [\text{H}_2\text{CO}_3]$$

$$(2) [\text{H}^+] \times [\text{CO}_3^{--}] = k_2 \times [\text{HCO}_3^-]$$

in which the values

$$k_1 = 3.04 \times 10^{-7}$$

$$k_2 = 1.3 \times 10^{-11}$$

are known (J. Walker and W. Cormack, Chem. Soc. Trans. 1900, 77, 5; Bodländer, Zeitsch. physikal. Chem. 1900, 35, 23).

From equation (2)

$$[\text{CO}_3^{--}] = k_2 \times \frac{[\text{HCO}_3^-]}{[\text{H}^+]}$$

and combining this with equation (1) we have

$$[\text{CO}_3^{--}] = \frac{k_2}{k_1} \times \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3]}$$

but with PbCO_3 as solid phase we had

$$[\text{Pb}^{++}] = \frac{S}{[\text{CO}_3^{--}]}$$

which can, therefore, be written

$$\text{Pb}^{++} = \frac{S \times k_1}{k_2} \times \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]^2}$$

But, inasmuch as free carbonic acid is very little, and sodium bicarbonate very much dissociated, the value of $[\text{H}_2\text{CO}_3]$ may be taken as proportional to the molecular concentration of the free carbonic acid, and $[\text{HCO}_3^-]$ to that of the sodium bicarbonate, and thus the concentration of the Pb^{++} ions will be directly proportional to that of the free carbonic acid, and inversely proportional to the square of that of the sodium bicarbonate.

This important theoretical deduction was experimentally verified by placing lead in contact with water containing 8.3 mgms. O_2 , 35.3 mgms. NaHCO_3 , and about 33 mgms. CO_2 per 1 litre, with the result that the amount of lead in solution was found to be about 1 mgm. per 1 litre, and thus slightly but distinctly greater than in the previous experiment in which there was no free carbonic acid present, and in which 0.6 mgm. Pb per 1 litre was taken up by the water.

In ordinary natural waters the phenomena are complicated by the simultaneous presence of other salts, especially chlorides and sulphates. Both PbCl_2 and PbSO_4 are considerably more soluble than the carbonate. On adding 71 mgms. Na_2SO_4 per 1 litre to the last artificial water mentioned above, it was found that the proportion of lead taken up was about tripled, being about 3 mgms. per litre. This increase must, of course, depend on the presence of PbSO_4 molecules in solution, and not on an increase in the concentration of the Pb^{++} ions, which it was shown was already fixed by the concentrations of the carbonic acid and bicarbonate. Now by removing some of the free carbonic acid (e.g. by adding Na_2CO_3) the concentration of the Pb^{++} ions will be diminished, and this will have the effect of also diminishing the amount of lead in solution due to the solubility of the PbSO_4 , for the amount of undissociated PbSO_4 is dependent on the concentration of the Pb^{++} ions, and if the latter be, through any cause,

diminished, the amount of undissociated $PbSO_4$ must be diminished also, with the result that the total amount of lead passing into solution will be less. This was experimentally verified by using the same artificial water as in the last-mentioned experiment, excepting that by the addition of Na_2CO_3 the free carbonic acid was reduced to about 9.5 mgms. CO_2 per litre, and the $NaHCO_3$ consequently raised to about 128 mgms. per litre, with the result that the lead taken up amounted to only 1.3 mgm. per litre of water.

Experience has also shown that some waters act powerfully on lead when the pipes are charged intermittently, whilst the action becomes very much diminished if they are kept under constant pressure. The effect of pressure on the activity ought, therefore, always to be specially determined (P. F. Frankland, *J. Soc. Chem. Ind.* 1889).

In investigating the action of water on lead, the water should either be put in contact with strips of the metal or placed in leaden pipes for a definite period of time, after which it should be removed and tested for lead both in solution and suspension, fresh portions of the water under examination are then placed in contact with the metal and again tested after a definite interval of time, this procedure being repeated a number of times. Thus it is often found that a water has a considerable initial action on the metal, but as the latter becomes coated with deposit, the action moderates and may practically cease altogether. Some waters, on the other hand, act continuously on the metal.

Some polluted waters have a very strong and continuous action on lead (*Riv. Pollut. Commiss.* 6th Rep. 226), and in such cases the obvious remedy is the abandonment of the source.

It is worthy of note that hot water generally acts much more violently on lead than cold, and further that the lead dissolved in water is entirely removed by passage through any of the numerous forms of animal charcoal filters.

As regards the quantity of lead in water from which danger to health is to be apprehended, it is now generally admitted that water containing anything above one-twentieth grain of lead per gallon, or 0.07 part per 100,000, may, by continued use, produce mischief.

Of the action of water on zinc but little is known beyond the fact that many waters do act on it, and that it is therefore not to be recommended for the construction of cisterns, &c., in which drinking water is to be stored. The solution of the zinc takes place with special facility if metallic iron is also in contact with it (*Heaton, Chem. News*, 49, 85; P. F. Frankland, *ibid.* 115; Stevenson, *ibid.* 107).

Copper appears to be continuously acted on by water, especially if simultaneously in contact with air, and hence should not be used in connection with drinking water.

The action of water and other liquids on aluminium is now a matter of some importance owing to its use for domestic and industrial purposes (see *An Investigation of Aluminium, with Special Reference to its Suitability for the Construction of Brewery Plant*, A. C. Chapman, *J. Inst. Brewing*, 1911). Although acted on by moist air the layer of oxide exerts a marked protection to further attack; alkalis and alkali

chlorides increase the tendency to corrosion. Chapman considers that it may be safely used for the construction of brewing plant, especially fermenting tuns and vessels intended for the treatment of chilled and filtered beers.

THE CHEMICAL ANALYSIS OF WATER.

As the qualitative analysis of the ingredients of water is of no practical importance, and involves no special methods, the quantitative examination will alone be considered here. In order that the analysis may be of any value, especially for sanitary purposes, it is of the greatest importance that the samples should have been collected with care.

Suspended matter.—The suspended matter, if considerable in amount, should be separately determined, but if only present in minute quantity it is advisable to regard it as part of the dissolved matter, in which case it is necessary that the sample should be well shaken before taking out each portion for analysis, so that the suspended particles may be uniformly distributed. If it is decided to determine the suspended matter separately, the sample should be well shaken, and 250 or 500 c.c. measured out and passed through a filter previously dried at 100° and weighed. The matter on the filter is washed with distilled water, and dried at 100° until of constant weight. Some analysts prefer to dry at 105° , 110° , or even 120° , but in all cases the temperature should be specified. The filter and its contents are then incinerated in a coil of platinum wire and dropped into a weighed platinum crucible, gently ignited until free from organic matter, and then treated with a few drops of a solution of ammonium carbonate, and dried at 150° . The loss in weight represents organic matter and water of hydration. It is sometimes of importance to determine the proportion of carbon to nitrogen in the organic part of the suspended matter. For this purpose some of the suspended matter is collected on an ignited plug of asbestos or glass wool, transferred to a small flask, and boiled with 20 c.c. of sulphurous acid and some distilled water free from ammonia and organic matter, and then further treated, as in the determination of organic carbon and nitrogen, by the combustion process (p. 402). If the suspended matter has been thus separately determined, the remainder of the analysis should be performed on the water, after filtration through Swedish paper, rejecting the first 250 c.c. which pass through; or if the suspended matter completely settles on standing the clear water may be siphoned off. The suspended matter may, of course, in exceptional cases also have to be submitted to a complete mineral analysis, or examined for some special ingredient.

An ingenious method of determining minute traces of suspended matter has been devised by Dibdin (*Analyst*, 1896, 21, 2). In this method the volume of the moist suspended matter is measured in a capillary tube.

MATTERS IN SOLUTION.

Total solids.—250 or 500 c.c. of the water are evaporated to dryness in a weighed platinum dish on a water- or steam-bath, the dish being

supported on a glass or porcelain, but not on a metallic, ring. The dish and residue are then dried until constant at 100°, 105°, 110°, 120°, or even at 180°. The residue may be further utilised for the determination of nitrates and nitrites by the mercury method (*v. infra*).

Ammonia.—A measured volume of the water (varying from 100–1000 c.c., according to the proportion of ammonia present) is distilled in a capacious flask or retort connected with a Liebig's condenser, about 1 gm. of recently ignited sodium carbonate having been previously added. It is essential that the whole apparatus should have been carefully freed from ammonia immediately before use, which can be done by distilling some water in the apparatus until the distillate gives no reaction with Nessler solution. The remainder of the water in the flask or retort is then thrown away, and the measured quantity of the sample under examination introduced along with the sodium carbonate. The distillation should be carried on briskly, and the distillate collected in colourless glass cylinders of 50 c.c. capacity. If less than 500 c.c. has been used, this volume should be made up with distilled water free from ammonia before distillation. If the quantity of water has been well chosen, the whole of the ammonia will be found in the first three cylinders of the distillate, and in most cases it will all be contained in the first. The quantity of ammonia in each cylinder is estimated by adding 1 c.c. of Nessler solution, and comparing the coloration obtained with that similarly produced by known quantities of a standard solution of ammonium chloride, added to 50 c.c. of distilled water free from ammonia. The Nessler reaction is so delicate that by its means 1 part of NH_3 in 100,000,000 parts of water can be easily detected. The colour produced by more than 10–15 c.c. of a solution of NH_4Cl (containing 0.00001 gm. NH_3 per litre) is too deep for accurate comparison, and should one of the cylinders require more than this the determination must be repeated on a smaller volume of water. This may be generally avoided, however, by adding the Nessler solution to the second and third cylinders of distillate before the first, and if it is found that the second cylinder gives a colour requiring more than 5 c.c. of the above solution of ammonium chloride for its imitation the first cylinder should be diluted, and an aliquot part taken for testing with the Nessler reagent.

The Nessler solution is prepared by dissolving 62.5 grms. of potassium iodide in 250 c.c. of distilled water; set aside 10 c.c. of this, and run into the remainder a cold saturated solution of mercuric chloride until a permanent precipitate is formed, then add the above 10 c.c. of potassium iodide, which will cause its solution, after which very carefully add more of the mercuric chloride until a slight precipitate remains on stirring. Now add 150 grms. of potassium hydroxide dissolved in distilled water, and dilute the whole to 1000 c.c. After settling, decant the clear liquid into a bottle for use.

As the 'albuminoid ammonia' is commonly determined in one operation with the 'free' ammonia, the method of estimating the former will now be described, instead of considering it under the methods for determining organic matter, where it more properly belongs.

'Albuminoid ammonia' process.—Whilst the determination of the free ammonia is being proceeded with as above, the solution of alkaline permanganate must be prepared for this process, as it is required immediately the free ammonia has passed over. The volume of the alkaline permanganate (for preparation *v. below*) taken must be at least one-tenth of the volume of the sample being distilled for ammonia, and it should not exceed that volume unless the water contains a very large amount of organic matter. The alkaline permanganate taken is then diluted with four times its volume of distilled water, and boiled in a flask during the whole of the time that the distillation for free ammonia is going on as above, and when the latter is finished it is added to the water remaining in the distilling flask or retort (the whole volume in this must now be not less than 500 c.c.), and distillation is then continued until the distillate is free from ammonia. The distillate is collected and Nesslerised, as in the determination of free ammonia above. The ammonia thus evolved by distillation with alkaline permanganate is generally recorded as 'albuminoid ammonia' (*v. 403*). The alkaline permanganate solution is prepared by dissolving 200 grms. of potassium hydroxide and 8 grms. of pure potassium permanganate in 1100 c.c. of distilled water, then boiling the solution rapidly until concentrated to about 1000 c.c.

Chlorine.—(a) *Mohr's method.* 50 or 100 c.c. of water are treated with a few drops of a solution of potassium chromate, and a standard solution of silver nitrate is then run in from a burette until the precipitate becomes of a faint but distinctly red colour. The water must be well agitated after each addition of the nitrate, the reaction depending upon the decomposition of the red silver chromate by dissolved chlorides with formation of silver chloride and soluble chromate. As soon as the last trace of chloride is precipitated as silver chloride, the red colour of the silver chromate makes its appearance. By using a solution of silver nitrate containing 2.3944 grms. per litre, the number of c.c. employed gives at once (if 50 c.c. of water have been taken) the parts of Cl per 100,000, whilst if 100 c.c. of water are taken the silver nitrate solution should be of double this strength.

Mohr's method cannot be employed if the water is acid, and if this is the case a given volume of the water should be boiled with an excess of pure calcium carbonate (free from chlorides), filtered, the filtrate made up to known volume, and the chlorine determined in a part of this. In the presence of reducing substances, much organic matter, sulphuretted hydrogen, and sulphites, the method is also inapplicable, and in such cases it is desirable to determine the chlorine gravimetrically, which should also be done if the proportion of chlorine is large.

(b) *Folhard's method.* 50 or 100 c.c. of the water are treated with an excess of decinormal silver nitrate, the mixture being well agitated so as to cause the silver chloride to settle in flakes; the latter is filtered off and washed, and then to the filtrate about ten drops of a cold saturated solution of iron-alum are added, and subsequently enough strong nitric acid (free from nitrous acid) to remove the colour of the ferric

salt. Decinormal ammonium thiocyanate is then added from a burette, stirring well all the time, until the liquid acquires a light yellow-brown colour, which remains permanent on leaving the liquid at rest for about 10 mins. By deducting the number of c.c.'s of thiocyanate from that of the silver nitrate added, the remaining silver nitrate indicates the proportion of chlorine present in the water. The advantage of this method consists in its being applicable to acid liquids. The method depends upon there being no formation of red ferric thiocyanate until the whole of the silver in solution has been precipitated as thiocyanate (*Annalen*, 190, 24).

Nitrogen as nitrates and nitrites.—A number of different methods have been devised for the determination of oxidised nitrogen; there are, however, only a few which have been largely adopted in practice, and such alone will be described here.

(a) *Crum's method.* This depends on the decomposition which nitrates and nitrites undergo when dissolved in strong sulphuric acid on being shaken up with mercury, and which leads to the evolution of the whole of the nitrogen as nitric oxide, the volume of which is then determined. The residue obtained in the estimation of the total solids (*see* p. 395) may be conveniently used for this determination also. This residue in the platinum or glass dish is repeatedly treated with a very small quantity of hot distilled water, which is brought into thorough contact with the residue by detaching the latter with a small glass rod covered with a piece of india-rubber. The aqueous extracts, which should in all not exceed about 10 c.c., are passed through a small filter and collected in a little beaker. This aqueous extract, containing all the soluble salts in the water residue, is evaporated nearly to dryness on a water-bath, after which it is dissolved again in a minimum quantity (1 or 2 c.c.) of water, and introduced into a Lange nitrometer (*Ber.* 11, 434); the beaker is repeatedly rinsed with a few drops of hot water, and these rinsings added to the nitrometer. The beaker is then further rinsed with pure strong sulphuric acid (free from oxides of nitrogen), and this also is transferred to the nitrometer. About $1\frac{1}{2}$ volumes of sulphuric acid must in all be used to 1 volume of aqueous extract. If the water contains soluble carbonates there will be an evolution of carbon dioxide when the sulphuric acid mixes with the aqueous extract; the gas should be allowed to collect without shaking the tube, and should then be expelled. The contents of the nitrometer tube are now violently agitated with the mercury, and then in the course of a minute or so the evolution of nitric oxide will commence, and the agitation should be continued as long as any gas continues to come off. If the water contains a considerable quantity of chlorides some hydrogen chloride may have been given off with the nitric oxide, but this may be removed by admitting a little water into the nitrometer. When the gas has cooled to the temperature of the air, its volume is measured at atmospheric pressure. The determination is rendered more accurate, especially if the quantity of nitrates and nitrites is only small, by measuring the nitric oxide in Frankland's gas apparatus, in

which case the decomposition with mercury and sulphuric acid is effected in a small tube standing in a mercury trough, the evolved nitric oxide being then transferred to the gas apparatus (*see* Sutton's Volumetric Analysis). This method, which is by far the most convenient for ordinary water analysis, becomes inapplicable in the presence of very large quantities either of organic matter or of chlorides.

(b) *Methods of Schloësing-Tiemann, and of Schloësing-Reichardt,* depend upon the decomposition of nitrates and nitrites by ferrous chloride and hydrochloric acid, and the measurement of the evolved nitric oxide. Of these methods, which closely resemble each other, the former, as the more convenient, need alone be considered here.

100–500 c.c. of the water are concentrated by evaporation to about 50 c.c., which are then introduced into a flask of about 150 c.c. capacity, provided with an india-rubber stopper, perforated by two narrow pieces of glass tubing, of which one (A) extends about an inch into the flask, and is constricted below, whilst the other (B) only just penetrates the stopper; the tube (B) is externally connected by means of a short piece of india-rubber tubing provided with a pinch-cock, with a delivery tube dipping into a trough containing 10 p.c. caustic soda solution previously boiled to expel air. The tube (A) is also connected with india-rubber and pinch-cock to another piece of glass tubing, which is allowed to hang vertically downwards. The water in the flask is vigorously boiled with the pinch-cocks open until the air is completely expelled by the steam, then the pinch-cock on (B) is closed whilst that on (A) is left open until the volume of water in the flask is reduced to about 10 c.c.; this pinch-cock is then also closed, and the flame removed from beneath the flask. The glass tube attached to (A) is carefully filled with water up to the pinch-cock; 15–20 c.c. of a saturated solution of ferrous chloride are introduced into the flask, in which there is now a partial vacuum, by siphoning from a small beaker through (A), the pinch-cock being temporarily opened, and about an equal quantity of strong hydrochloric acid is made to follow in the same manner into the flask. The flask is now carefully heated, and when the internal pressure rises the pinch-cock on (B) is opened, and the evolved gas allowed to pass through the delivery tube into a measuring tube filled with the 10 p.c. caustic soda solution standing in the trough. The heating of the flask is continued until the volume of gas in the measuring tube ceases to increase. The measuring tube is transferred to a tall glass cylinder full of water, and after the gas has acquired the temperature of the room the volume is measured at the atmospheric pressure, a correction being of course made for the tension of aqueous vapour.

This method is specially applicable to the case of water containing excessive quantities of organic matter and chlorides (*Ber.* 1873, 1041; Tiemann and Gärtner's *Untersuchung d. Wässern*, 170).

For Schloësing-Reichardt's method, *v. Zeitsch. anal. Chem.* 1870, 24, or Tiemann and Gärtner's *Untersuch. d. Wässern*, 175.

(c) *The aluminium and zinc copper couple methods* depend upon the conversion by means of

hydrogen of the oxidised nitrogen in the water into ammonia, and estimation of the latter by Nessler solution.

Aluminium method.—100 c.c. of the water are introduced into a flask together with 10 c.c. of caustic soda solution free from nitrates and nitrites, the mixture being boiled until it is reduced to about one-fourth of its volume. It is then diluted to about its original bulk with distilled water free from ammonia, and a piece of aluminium foil, about 2 ins. square and wrapped round a piece of glass rod, is dropped into the flask, which is then fitted with a stopper and small U-tube containing glass beads moistened with hydrochloric acid free from ammonia. After the evolution of hydrogen has continued for about 6 hours, the glass beads and washings of the U-tube are transferred to the liquid in the flask, the latter is then attached to a Liebig's condenser, and the ammonia determined by distillation and Nesslerising in the ordinary way (see p. 396). According to Tiemann and Gartner (*Untersuchung des Wassers*, 208), only the equivalent of 72–90 p.c. of the nitric acid is thus recovered as ammonia.

Zinc-copper couple method.—The residue obtained in the determination of 'total solids' is extracted with about 25 c.c. of hot distilled water, and this is boiled down with a fragment of recently-ignited pure lime about the size of a hemp-seed to one-fourth of its bulk. This liquid, together with the washings of the dish containing the residue, is transferred through a stoppered funnel into an eight-ounce Wurtz flask, attached to a Liebig's condenser, and containing the requisite amount of the zinc-copper couple. The distillation is carried on until the greater part of the water has passed over, after which hot distilled water is repeatedly run into the flask and the distillation continued until about 100 c.c. of distillate have been collected; the latter is then 'Nesslerised' in the ordinary way (Thorpe, *Chem. Soc. Trans.* 1873, 541). According to Tiemann and Gartner, from 88 to 95 p.c. of the nitric acid is thus obtained.

In the writer's laboratory the process is carried out as follows: A stoppered bottle (about 200 c.c. capacity) is loosely filled with strips of zinc, which, after cleaning with dilute sulphuric acid, are covered with copper sulphate solution (1 p.c.). The copper-coated strips are repeatedly washed with distilled water, and finally with the water under examination, care being taken not to detach the copper film. The bottle is then completely filled with the sample of water and a crystal of oxalic acid is added, and the bottle, loosely stoppered, is allowed to stand over night. A definite volume is withdrawn by means of a pipette, and this is distilled with a suitable volume of ammonia-free water in the ammonia apparatus as usual, a small quantity of ignited sodium carbonate being added. Before withdrawing the water from the bottle for distillation, a small quantity should be tested for nitrite to ensure that the reduction to ammonia is complete. Waters containing free or saline ammonia must have this distilled off before being placed in contact with the zinc-copper couple.

A rapid method of estimating nitrates in water is due to Harrow (*Chem. Soc. Trans.* 1891, 397), depending on the reduction to nitrite

by zinc-dust and estimation of the nitrous acid by sulphanilic acid and α -naphthylamine (Griess test). This reagent is prepared by dissolving 1 grm. of α -naphthylamine, 1 grm. sulphanilic acid, and 25 c.c. strong hydrochloric acid in about 200 c.c. distilled water; boiling with a small quantity of animal charcoal, filter, and making up to 500 c.c. The process is conducted thus: 50 c.c. of the water are placed in a beaker of 100 c.c. capacity, and in three similar beakers 50 c.c. of three standard solutions of potassium nitrate, containing (1) 1.0 part N, (2) 0.1 part N, (3) 0.01 part N per 100,000; to each beaker 10 c.c. of the above test-solution are added, and afterwards a very small quantity (7–8 mg.) of zinc-dust. If nitrate is present in the water a pink colour appears, which must be compared with that yielded by the three standard solutions after 15 mins. This gives an approximate idea of the amount of nitrate present, whilst in order to obtain an accurate result the water must be diluted until the colour produced is almost identical with that given by one of the standards. The results appear to be accurate, but it is especially necessary to avoid the addition of large quantities of zinc-dust, which would decolorise the solution.

(d) *The indigo method* differs from those previously described in being a simple volumetric method depending upon the decolorising action of nitric acid on indigo solution. The results are only accurate when the greatest uniformity is preserved in the conditions under which the experiments are made—the process is, in fact, entirely empirical. It may be carried out as follows: 25 c.c. of the water are mixed with 50 c.c. of pure strong sulphuric acid; a dilute solution of indigo is then immediately added from a burette, shaking the whole time, until the solution acquires a bluish-green colour. In a second experiment nearly the whole volume of indigo which was found necessary in the first experiment is added at once, and the blue colour is then obtained by further small additions, and in this manner, by shortening the time taken in the titration, a more accurate result, generally higher than in the preliminary experiment, is obtained. The solution of indigo must be standardised under precisely similar conditions by means of a solution of potassium nitrate of known strength. The indigo solution should be chosen of such strength that 5–8 c.c. correspond to 0.001 grm. N_2O_5 ; and if 25 c.c. of the water contains more than 0.003–0.004 grm. N_2O_5 , it should be diluted before a final titration is made. The method is only suitable for use by an operator in continual practice (Warington, *Chem. Soc. Trans.* 1879, 578; *Water Analysis*, E. Frankland, 31). The results are too low if there is a large amount of organic matter in the water.

The methods described above do not distinguish between nitrous and nitric acids. Indeed, the indigo method is altogether unreliable in the presence of any notable proportion of nitrous acid, as is also Crum's method, should it be necessary to allow any carbon dioxide to escape before shaking with mercury (see p. 397). As nitrous acid is, however, generally only present in natural waters in minute traces, these difficulties do not frequently arise, and the

nitrous acid may be most conveniently estimated by colorimetric methods, of which there are several in vogue. Of these may be mentioned:

(a) *Preuss-Tismann's method*, depending upon the production of Bismarck brown when an acid solution of a nitrite acts upon *m*-phenylenediamine. 100 c.c. of the water are placed in a colourless glass cylinder, 1 c.c. of dilute sulphuric acid (1 : 3) is added, and then 1 c.c. of solution of *m*-phenylenediamine (5 grms in 1000 c.c. distilled water, decolorised if necessary with animal charcoal); if the colour appears in less than 1 or 2 mins. the experiment must be repeated with a smaller quantity of water, in each case diluted, however, to 100 c.c. The coloration is then imitated under precisely similar conditions with a standard solution (the standardisation can be effected either by the potassium permanganate, or, better, by the urea method) of potassium or sodium nitrite. The final tint is not arrived at until the mixture in the glass cylinder has stood for 20-25 mins., which is the great drawback of the process (*see also* Warrington, *The Detection of Nitric and Nitrous Acids*, Chem. News, 1885, 51, 39).

A preferable method (Zambelli, Chem. Soc. Abstr. 1887, 533) consists in adding to the water a few drops of a saturated solution of sulphanilic acid in dilute sulphuric acid, then a few drops of a saturated aqueous solution of phenol, after which the mixture is rendered alkaline with ammonia. The presence of nitrous acid is indicated by the appearance of a coloration, varying from faint yellow to intense reddish yellow, according to the quantity of nitrous acid present. The author claims that this method is capable of revealing the presence of 1 part of nitrous nitrogen in 40,000,000 parts of water. It has the great advantage that the reagents employed are permanent in solution.

For larger quantities of nitrous acid, as also for the standardisation of solutions of sodium and potassium nitrite, the urea method devised by the writer is to be recommended (Chem. Soc. Trans. 1888, 364).

Hardness.—The determination of the hardness of a water consists in empirically ascertaining the amount of soap which has to be destroyed by a given volume of the water before a lather can be obtained, and expressing this in terms of the amount of calcium carbonate which must be dissolved in the same volume of water to destroy the same amount of soap. Accurate results can only be obtained by preserving uniformity in the conditions of experiment.

50 c.c. of the water are measured into an 8-oz. stoppered bottle, which is then violently agitated and the air sucked out by means of a glass tube to remove any carbon dioxide which may be given off by the water. A standard solution of soap (*v. infra*) is then added in diminishing quantities not exceeding 0.5-0.10 c.c. at a time, even at first, violently shaking after each addition, until the froth produced remains unbroken over the surface for a period of 5 mins. when the bottle is placed at rest on its side. The quantity of calcium carbonate corresponding to the volume of soap solution employed can then be ascertained by reference to the empirical table which follows.

Table of hardness in parts per 100,000, 50 c.c. of water being used.

G.c. of soap solution	CaCO ₃ per 100,000	G.c. of soap solution	CaCO ₃ per 100,000	G.c. of soap solution	CaCO ₃ per 100,000
·7	0·00	5·9	7·29	11·0	14·64
·8	·16	6·0	·43	·1	15·00
·9	·32	·1	·57	·2	·16
1·0	·48	·2	·71	·3	·32
·1	·63	·3	·86	·4	·48
·2	·79	·4	8·00	·5	·63
·3	·95	·5	·14	·6	·79
·4	1 11	·6	·29	·7	·95
·5	·27	·7	·43	·8	16·11
·6	·43	·8	·57	·9	·27
·7	·56	·9	·71	12·0	·43
·8	·69	7·0	·86	·1	·59
·9	·82	·1	9·00	·2	·75
2·0	·95	·2	·14	·3	·90
·1	2·08	·3	·29	·4	17·06
·2	·21	·4	·43	·5	·22
·3	·34	·5	·57	·6	·38
·4	·47	·6	·71	·7	·54
·5	·60	·7	·86	·8	·70
·6	·73	·8	10·00	·9	·86
·7	·86	·9	·15	13·0	18·02
·8	·99	8·0	·30	·1	·17
·9	3·12	·1	·45	·2	·33
3·0	·25	·2	·60	·3	·49
·1	·38	·3	·75	·4	·65
·2	·51	·4	·90	·5	·81
·3	·64	·5	11·05	·6	·97
·4	·77	·6	·20	·7	19·13
·5	·90	·7	·35	·8	·29
·6	4·03	·8	·50	·9	·44
·7	·16	·9	·65	14·0	·60
·8	·29	9·0	·80	·1	·76
·9	·43	·1	·95	·2	·92
4·0	·57	·2	12·11	·3	20·08
·1	·71	·3	·26	·4	·24
·2	·86	·4	·41	·5	·40
·3	5·00	·5	·56	·6	·56
·4	·14	·6	·71	·7	·71
·5	·29	·7	·86	·8	·87
·6	·43	·8	13·01	·9	21·03
·7	·57	·9	·16	15·0	·19
·8	·71	10·0	·31	·1	·35
·9	·86	·1	·46	·2	·51
5·0	6·00	·2	·61	·3	·68
·1	·14	·3	·76	·4	·85
·2	·29	·4	·91	·5	22·02
·3	·43	·5	14·06	·6	·18
·4	·57	·6	·21	·7	·35
·5	·71	·7	·37	·8	·52
·6	·86	·8	·52	·9	·69
·7	7·00	·9	·68	16·0	·86
·8	·14				

In performing the titration as above, the experienced operator is guided by the ear as well as by the eye, for the sound produced on shaking serves to indicate how the reaction between the hardening constituents of the water and the soap is progressing, for as this approaches completion the sound becomes softer, and when an excess of soap has been added the agitation is all but noiseless.

In the case of waters requiring more than

16 c.c. of soap solution for the 50 c.c. of water, it is necessary to take a smaller volume of the water and dilute to 50 c.c. with boiled distilled water. The presence of magnesia salts is indicated in the soap test by the formation of a characteristic light curd, and also by the premature formation of a lather, which again disappears on the further addition of soap solution and shaking. If these signs are exhibited, only such a volume of water should be taken as, when diluted to 50 c.c., requires not more than 7 c.c. of the soap solution; indeed, it is a very good practice invariably to dilute waters so that not more than 7 or 8 c.c. of soap solution are required. In the presence of magnesia salts the results are always less accurate, and, unless great care is exercised, may become wide of the truth.

Permanent hardness.—The permanent hardness is most conveniently determined by taking a small flask with a *very short neck* (the Erlenmeyer shape is very suitable), and adding the water to it until a definite weight (e.g. 250 grms.) has been made up. The water is then maintained in gentle ebullition for exactly half-an-hour, and, after cooling, the weight is again made up to the original by the addition of boiled distilled water, the soap titration being then performed on a measured portion of this, as described above.

Some analysts prefer to take a given volume of water and restore the volume after boiling, then removing the precipitated carbonates of lime and magnesia by passing through a dry filter.

The *standard solution of soap* is prepared as follows. A cake of Castile soap is scraped with a knife, and about 7 grms. of the shavings are dissolved in 500 c.c. of a mixture of 2 vols. of methylated spirit with 1 vol. of distilled water. Filter off the insoluble matter, and dilute the soap solution with half its volume of water. A portion of this solution is then further carefully diluted with a mixture of 2 vols. methylated spirit and 1 vol. water until 7·8 c.c. are required to form a permanent lather with a mixture of 25 c.c. of the standard calcium chloride solution (prepared by dissolving 0·2 gm. of Iceland spar in dilute hydrochloric acid, and, after driving off excess of acid on the water-bath, making up to 1000 c.c. with distilled water) and 25 c.c. of distilled water.

Poisonous metals.—Of these the only ones which are of practical importance in water analysis are lead, zinc, copper, arsenic, and barium. As they are generally present in only very minute proportions, it is necessary to evaporate large volumes (5 litres and upwards) of water in order to obtain gravimetric determinations in the ordinary way; but the following *special methods* may be generally employed.

For *lead*, take 100 c.c. of the water, acidify with a few drops of acetic acid, and then add about 5 c.c. of a saturated solution of sulphuretted hydrogen. The colour produced is imitated by adding a known quantity of a standard solution of a lead salt to 100 c.c. of distilled water. Even such small proportions as 0·03 part Pb per 100,000 should invariably be recorded. (For the standard solution of lead, dissolve 0·1831 gm. crystallised normal lead acetate in 1000 c.c. distilled water; 1 c.c. = 0·0001 Pb.)

For *copper*, the same colorimetric method may be employed as for lead, using for comparison a solution of copper sulphate containing 0·0001 gm Cu in 1 c.c. (0·3929 gm. crystallised copper sulphate per litre). In the absence of iron a very delicate colorimetric method may be employed, based upon the reaction between copper salts and potassium ferrocyanide, the water being acidified with hydrochloric acid, whilst in the presence of iron the blue coloration produced by ammonia may be used.

The presence of *zinc* is generally indicated by the gradual formation of a film of carbonate on the surface of the water when the latter is exposed to the air. Some of this film ignited on platinum foil should leave a residue, which is yellow when hot and white on cooling. The quantity of the zinc may be approximately determined, in the absence of other heavy metals, by acidifying 100 c.c. of the water with dilute hydrochloric acid, and then adding a solution of potassium ferrocyanide. The white turbidity produced is then compared with that obtained from a known quantity of a standard solution of a zinc salt (Snijders, Ber. 1878, 939).

Arsenic is best detected and estimated by Marsh's test; 500 c.c. of the water are rendered slightly alkaline with caustic soda or potash free from arsenic, and evaporated to dryness. The residue is extracted with strong hydrochloric acid, and the liquid introduced into a Marsh's apparatus. The gas is passed through a small U-tube containing pumice soaked in solution of lead acetate, and then through a piece of combustion tube constricted in the middle, where it is heated to redness. The passage of gas through the heated tube is continued for an hour, although nearly all the arsenic is liberated in 5 or 10 mins. The metallic ring formed is compared with a number of standard rings similarly obtained with known quantities of arsenic. A blank experiment must invariably be performed previously, to control the purity of the chemicals employed.

Barium may be detected and determined by concentrating a considerable volume of the water, acidifying with hydrochloric acid, and after filtering, if necessary, adding a solution of calcium sulphate. The barium sulphate precipitated is then collected and weighed in the ordinary manner.

Iron can generally be estimated colorimetrically by means of ferrocyanide or thiocyanate. Its determination is frequently of importance in waters used for industrial purposes.

In the ferrocyanide method, the water residue is dissolved in hydrochloric acid and diluted to 100 c.c. Of this 10 c.c. are transferred to a 100 c.c. cylinder; add 1 c.c. of strong nitric acid, dilute to 100 c.c., stir, and then add 1 c.c. of potassium ferrocyanide solution and mix well. The colour produced is compared with that obtained from a standard iron solution, but the same quantity of nitric acid must be present in each case (Sutton, Volum. Anal. 6th ed. 194; v. also Carter Bell, J. Soc. Chem. Ind. 8, 175).

In the thiocyanate method, two 100 c.c. cylinders are taken, and into each 5 c.c. of dilute hydrochloric acid (1 : 5) and 5 c.c. of dilute nitric acid (1 : 5), together with 15 c.c. of thiocyanate solution, are poured; then introduce a

measured volume of the liquid to be tested into the one cylinder, and after filling up both cylinders to the mark with distilled water, imitate the red colour obtained with the liquid under examination by running in a standard solution of iron from a burette into the other cylinder. In this way one part of iron is said to be recognisable in fifty millions of water (Thompson, Chem. Soc. Trans. 1885, 493).

Determination of organic matter.—A number of processes have been devised for the determination either of the whole or part of the organic substances present in water. Of those which lay claim to discovering the whole of these organic materials, none is entitled to any confidence, whilst even those which attempt to determine a part, or to indirectly obtain a comparative measure of the organic matter, are also open to objections on the score of accuracy. Only those methods more commonly in use by water analysts will be described here.

(1) *Methods depending on the reduction of potassium permanganate.*

(a) *Kubel's process.*—In this the reduction is effected in acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity and treated with 5 c.c. dilute sulphuric acid (1 : 3), and then with such a quantity of standard dilute permanganate (equivalent to centinormal oxalic acid) that the liquid is of a strong red colour. The mixture is then boiled for 10 mins., and the excess of permanganate added must be such that the colour is not discharged in the operation. 10 c.c. of centinormal oxalic acid are now added, and into the resulting colourless liquid standard permanganate is then run until a faint red colour is obtained. The amount of oxygen consumed by the organic matter in the water can then be calculated.

(b) *Schulze's process.*—In this the reduction is commenced in an alkaline and completed in an acid solution. 100 c.c. of the water are placed in a flask of about 300 c.c. capacity, 0.5 c.c. caustic soda solution (1 : 2) are added, as well as 10–15 c.c. of standard dilute permanganate (equivalent to centinormal oxalic acid). The liquid is boiled for 10 mins., allowed to cool to 50° or 60°C. and then 5 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of centinormal oxalic acid are added, the liquid being shaken and gently warmed until the colour has quite disappeared. Then the standard dilute permanganate is run in until a faint red colour, remaining permanent for at least 5 mins., is obtained. The oxygen consumed by the organic matter of the water is then calculated.

(c) *Forchhammer process.*—This resembles Kubel's method, inasmuch as the reduction of the permanganate is effected in an acid solution, but the temperature employed, instead of being defined, is that of the air of the laboratory.

Two flasks are carefully cleaned and into one 250 c.c. of the water, into the other 250 c.c. of distilled water, are introduced. To each 10 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of standard permanganate (containing 0.395 gm. per litre or 0.001 gm. available oxygen in 10 c.c.) are added, and the mixture is allowed to stand for three hours. At the end of this time the excess of permanganate remaining is deter-

mined by adding two drops of potassium iodide (1 : 10) to each flask, and then running in a standard solution of sodium thiosulphate (1 gm. per litre) until the whole of the free iodine is removed, a drop of clear starch solution being added at the close of the operation. The amount of permanganate destroyed in the blank experiment must of course be deducted from that destroyed in the case of the water, and from the difference the oxygen consumed by the organic matter of the water can be calculated (Tidy, Chem. Soc. Trans. 1879, 66).

In this country it is now almost the invariable custom of water analysts to allow the acid permanganate to act for 4 hours at 80°F. (26.7°C.); Thorpe (Metropolitan Water Reports, 1904) has also used 1 hour at 122°F. (50°C.), under which conditions a larger amount of oxygen is consumed.

It must be pointed out that in these several methods depending on the reduction of permanganate, the results are only comparative for the same kind of organic matter, a given weight of organic carbon in different kinds of water consuming different quantities of oxygen from permanganate under the same conditions. Thus it has been found that for surface waters, such as those of the rivers Thames and Lea, by multiplying the oxygen consumed in the Forchhammer process by the factor 2.38, the proportion of organic carbon (as determined by combustion) is approximately obtained, whilst in the case of deep well water the factor which must be employed is 5.8 (Woodland Toms).

Again, all these methods are affected by the presence of nitrites, ferrous salts, and larger quantities of ammonia compounds, all of which exercise a reducing action on permanganate. By determining the nitrous acid, a correction can be made for this, whilst the ferrous can generally be converted into ferric iron by shaking up the water several times in a half-filled bottle previously to the oxidation with permanganate; and the error due to ammonium salts is so small that it can generally be neglected (even one part NH₃ per 100,000 has no appreciable reducing effect) (Preusse and Tiemann, Ber. 12, 1906).

(2) *Determination of organic carbon by oxidation of organic matter with potassium dichromate and sulphuric acid* (Wolff, Degener, and Herzfeld).—500–1000 c.c. of the water are introduced into a capacious retort, the neck of which is drawn out and bent downwards and is connected with a Liebig's condenser. This arrangement enables the retort to be turned upwards and the condenser downwards, thus preventing any loss by spurting during distillation, which is carried on until 250–700 c.c. (according to the volume of water employed) have passed over. The distillate is submitted to Kubel's method (*u. supra*) to ascertain whether any volatile organic matters are present. Alkaline waters should be saturated with carbon dioxide, and acid waters carefully neutralised with sodium carbonate before the above distillation. The water remaining in the retort is evaporated down to 15 c.c. in a glass dish on a water-bath, the access of dust being carefully avoided. This concentrated liquid is introduced into a flask of 250–300 c.c. capacity, and the dish and retort are rinsed with 10 c.c. of dilute sulphuric acid (1 : 3),

these rinsings also being added to the water in the flask. The decomposition of carbonates caused by the addition of this acid is completed by heating to 50°C. and shaking, and the evolved carbon dioxide completely displaced by air. After cooling the flask and its contents, 10 grms. of finely-powdered potassium dichromate are added, and the flask is then attached to the remainder of the apparatus. An india-rubber stopper with three holes is placed in the flask; through one hole passes a thermometer dipping into the liquid, through a second passes nearly to the bottom of the flask the tube of a bulb-funnel (A) provided with a stopcock, whilst through the third passes the bent tube of an inverted Liebig's condenser (B). The upper extremity of the condenser (B) is connected with two U-tubes (C and D) filled with fused calcium chloride, whilst between these is a third U-tube (E) containing coarsely-powdered antimony. Of these, C and D are intended to absorb the moisture passing the condenser, and the intermediate one, E, to retain any chlorine. Following on these tubes is a set of weighed potash-bulbs (F) for the absorption of carbon dioxide, and these bulbs are, of course, protected from ingress of moisture on the other side by means of a calcium chloride tube, which can be attached to an aspirator at the close of the experiment. The apparatus having been thus put together, 50-60 c.c. of diluted sulphuric acid (3:2) are gradually added through the stoppered funnel (A). During the first half-hour the temperature is kept at 50-55°C., whilst during the second half-hour it is gradually raised to boiling, which is maintained from 5-10 mins. The aspirator is then attached, the air which enters by the funnel (A) having been previously freed from carbon dioxide by bubbling through caustic potash. The increase in weight of the potash bulbs (F) gives the weight of carbon dioxide evolved, from which the carbon itself can be calculated (Ber. 1886, 2618; Tiemann-Gärtner, *Untersuch. d. Wassers*, 247).

For a somewhat similar method of determining organic carbon in which permanganate is used instead of dichromate, see Blair, *Organic Analysis of potable Waters*, Churchill, 1891, 83. The method appears worthy of more extended trial.

(3) *Determination of organic carbon and nitrogen by combustion.*—(a) *Frankland and Armstrong's process* (Chem. Soc. Trans. 6, 77). This method, which is unquestionably the most rational and exact, has been adopted to a comparatively limited extent by water analysts in consequence of the special apparatus and manipulative skill which it entails. The method will be described only in outline here, and for full particulars the reader is referred to Sutton's *Volumetric Analysis*, whilst for a critical survey of the methods employed in the organic analysis of water he should not fail to consult Mallet, *Report of the United States National Board of Health*, 1882.

The process is divisible into three parts: (1) the evaporation of the water, (2) the preparation and combustion of the residue thus obtained, and (3) the measurement of the gases evolved in the combustion.

For the evaporation, from 100 c.c. (in the case of sewage and highly polluted waters) to

1000 c.c. (in the case of very pure waters) are measured into a clean flask, 20 c.c. of a saturated solution of sulphurous acid being added together with a drop of a solution of ferric chloride; the liquid is then boiled rapidly for a few seconds. This treatment secures the decomposition of carbonates, nitrates, and nitrites, whilst any ammonia is fixed by the sulphurous acid, and this ammoniacal nitrogen, which has previously been determined, must be deducted from the total amount of nitrogen obtained in the combustion. The water is now rapidly cooled, and the evaporation commenced in an apparatus specially designed for the purpose. This consists of a nearly hemispherical glass dish about 4 ins. in diameter and without a lip. It is floated in a shallow copper basin heated below by a water-bath provided with constant feed, and on the flange of this copper basin there rests a truncated conical ring, constructed of lead or copper, and about 3 ins. in height, whilst upon a flange at the top of this again rests a tall glass shade about 12-18 ins. in height. The water for evaporation is placed in a flask which is provided with a delivery tube of special construction ground on to its neck, and which serves, when the flask is turned upside down, to maintain the water at a constant level in the glass dish in which the evaporation is proceeding, for this delivery tube is made to pass through a notch in the truncated conical metal ring, just beneath the glass shade which the latter supports, and delivers into the centre of the glass dish within. In the writer's laboratory, the evaporation of 500 c.c. of water is found to take from 10-12 hours. The evaporation should be continued until the residue is quite dry, and if the water contains only a small amount of total solids it is advisable to add a little ignited calcium phosphate to the dish before commencing the evaporation. In the analysis of sewage, or waters containing much ammonia and no nitrates or nitrites, it is advantageous to use 10 c.c. of a solution of metaphosphoric acid (1:10) instead of the sulphurous acid, as ammonium phosphate loses much less ammonia during evaporation than ammonium sulphite. A little ignited calcium phosphate should also be added to dry the residue in this case. But if there are no nitrates and nitrites and much ammonia, the more satisfactory, although more laborious, plan is to use a little ignited borax instead of the sulphurous or metaphosphoric acid. In this way the ammonia is completely dissipated on evaporation, and as no correction has, therefore, to be applied to the organic nitrogen found, the result is more correct. But as boric acid does not entirely decompose carbonates the accuracy of the organic carbon found by this method may be seriously affected, and it is advisable to make a separate determination of the carbon in a second experiment in which the sulphurous acid method is employed. Unless this method be adopted the results for organic nitrogen in the presence of much ammonia are nearly sure to be highly inaccurate.

If the water contains more than 0.5 part per 100,000 of nitrogen as nitrates and nitrites, the 20 c.c. of sulphurous acid employed above may not improbably prove insufficient for their complete destruction, and in the case of such waters the residue in the dish should be further treated

with 10 c.c. of sulphurous acid, this evaporated off, and if the amount of nitric or nitrous nitrogen exceed 1 part per 100,000 this treatment of the residue with further quantities of sulphurous acid may be repeated twice or three times to secure complete destruction of the nitrates and nitrites.

The preparation and combustion of the residue thus obtained is effected by thoroughly mixing with the latter in the dish a small quantity of finely divided and carefully ignited copper oxide. This is then completely transferred to a narrow piece of combustion tubing about 18 ins. long and sealed at one extremity. The dish is again rinsed with a little fine oxide, and this also transferred to the tube. Coarse and carefully ignited oxide of copper (preferably from wire) is then introduced to a depth of about 10 ins., whilst the fine oxide previously introduced will occupy about 2 ins. Upon the stratum of coarse oxide follows a copper gauze cylinder 3 ins. in length, and then another layer of coarse oxide about 1 in. long. The open extremity of the tube is now drawn out over the blowpipe, so that it can be connected with a Sprengel mercury pump. The tube is completely exhausted, and the combustion performed *in vacuo* in the ordinary way, the evolved gases being then drawn over by the pump and collected in a test tube filled with mercury and placed over the lower open extremity of the fall tube in the trough below.

The volumetric measurement of the gases (consisting of carbon dioxide, nitrogen, and possibly also nitric oxide and sulphur dioxide) collected as above is carried out in the Frankland gas apparatus, which admits of the measurement of very minute quantities of gas. Three measurements are only necessary. In the first place the gas is treated with a few drops of a saturated solution of potassium dichromate to absorb any sulphur dioxide that may be present. The volume of the gas is then accurately measured, after which it is treated with a few drops of strong caustic potash, which rapidly removes the carbon dioxide, after which the volume of the remaining gas is again carefully ascertained. The residual gas now consists of nitrogen, with possibly a little nitric oxide. It is mixed with a bubble of pure oxygen in order to convert any nitric oxide into nitrous and nitric acids, which are immediately absorbed by the caustic potash present, and then, on adding a drop or two of solution of pyrogallous acid, the excess of oxygen is absorbed and the remaining gas, which consists of nitrogen, is carefully measured. The diminution in volume effected by the caustic potash in the first instance obviously represents the carbon dioxide, whilst the final volume of residual gas, together with one-half of the contraction resulting from the addition of oxygen and pyrogallous acid, represent the total volume of nitrogen. From these volumes the weights of carbon and nitrogen respectively can be calculated. As already pointed out, if sulphurous or metaphosphoric acid has been used in the evaporation, and ammonia is present in the water, the ammoniacal nitrogen (subject to an empirical correction for loss of ammonia during evaporation) has to be subtracted from the total nitrogen found by combustion. A small correction (ascor-

tained by blank experiments made from time to time with the reagents employed in the evaporation and combustion) has also to be applied to the carbon and nitrogen thus determined.

For Dupré and Hake's method, see Chem. Soc. Trans. 1879, 159.

In Dittmar and Robinson's method of determining organic carbon, the gases proceeding from the combustion tube are first passed through a U-tube containing a solution of chromic acid in 60 p.c. sulphuric acid to absorb moisture and sulphurous acid (the water is evaporated with sulphurous acid for the preparation of the residue), the carbon dioxide being absorbed in a weighed soda-lime tube (Chem. News, 1877, 36, 26). A method of determining organic nitrogen has also been devised by Dittmar and Robinson, and is described below.

(4) *Methods for determination of organic nitrogen only.*—Of these the most common one in use is the well-known

(a) '*Albuminoid ammonia*' process of Wanklyn, Chapman, and Smith (Chem. Soc. Trans. 1867, 591), which does not yield the whole, but only very variable proportions, of the organic nitrogen in different nitrogenous organic substances, although in the case of some—such as leucine, aspartic acid, tyrosine, &c.—which frequently appear as decomposition products of albuminous matters, nearly the whole of the nitrogen is obtained as ammonia (Preusse and Tiemann, Ber. 12, 1906; Mallet, U.S. National Board of Health Report, 1882).

The method has already been described on p. 396.

(b) *Dittmar and Robinson's process.*—In this process the residue, obtained in the same way as for the combustion process, is heated with fused caustic soda, or soda and baryta, in a copper or silver boat placed in a combustion tube in a current of hydrogen, the evolved ammonia being absorbed by very dilute hydrochloric acid, which is subsequently 'Nesslerised' (Chem. News, 1877, 36, 26). The results are accurate, and coincide with those obtained by the combustion process of Frankland and Armstrong.

(c) *Kjeldahl's process.*—This well-known and now much-employed method for determining organic nitrogen was adapted for use in water analysis by Drown and Martin (Chem. News, 59, 272). It appears to give accurate results uninfluenced by the presence of nitrates and nitrites in such quantities as are found in ordinary waters, 500 c.c. of the water are placed in a round-bottomed flask of about 900 c.c. capacity; the volume is then reduced to about 200 c.c. by boiling, and to this, after cooling, 10 c.c. of pure concentrated sulphuric acid are added. The mixture is then cautiously boiled, with the flask in an inclined position, until all the water has been driven off and the acid remains of a white or very pale-yellow colour. After removing the source of heat, add a little powdered permanganate until, on shaking, the liquid becomes green, showing that excess has been added. If a purple instead of a green colour appears, it shows that the whole of the water has not been driven off. When cool, 200 c.c. of water free from ammonia are added, care being taken to rinse round the neck of the flask, and thus wash in any acid which may be adhering there.

WATER.

150 c.c. of sodium hydroxide solution are then added, and the mixture distilled with a Liebig's condenser. (The sodium hydroxide solution is prepared by dissolving 200 grms. of good caustic soda in 1250 c.c. of distilled water, adding 2 grms. potassium permanganate, and boiling down until the volume is rather less than 1000 c.c. making up to 1000 c.c. when cold.) The distillate is collected in a flask containing 50 c.c. of water free from ammonia, and 1 c.c. of dilute pure hydrochloric acid, and during the distillation of the first 50 c.c. the delivery tube of the condenser is made to dip into this acid liquid, whilst during the remainder of the distillation the flask is lowered so that the delivery tube is just above the liquid. The distillation is carried on until the whole of the ammonia has passed over, and the contents of the receiver are then 'Nesslerised' in the ordinary way. The most scrupulous care must be exercised to prevent access of ammonia from the air and reagents; a blank experiment should also be made for control.

Determination of dissolved oxygen.—Much importance is, with very little reason, attributed by some analysts to this determination; it can, moreover, be rarely applied, as the samples must be collected with special precautions if the results are to have any value at all. The various processes in use have been examined by Kisch (Chem. Soc. Abstr. 1892, 98). *Reichardt's* method (Zeitsch. anal. Chem. 1872, 11, 271), as modified by Preusse and Tiemann (Ber. 1879, 12, 1768; Tiemann-Gärtner's Untersuch. d. Wassers, 278), consists in boiling a measured volume of water, and collecting the gases over a hot solution of caustic potash, the oxygen being then estimated either by explosion with hydrogen, or by absorption with potassium pyrogallate. In *Mohr's* method (*Mohr's* Titrimethoden) the sample is mixed with an acid solution of ferrous sulphate of known strength, then with caustic soda to throw down ferrous hydroxide, and after remaining for a few hours (air, of course, being rigidly excluded), the precipitate is redissolved in sulphuric acid, and the remaining ferrous sulphate titrated with permanganate. In the *Schützenberger-Riesel* process (Bull. Soc. chim. 1873, [ii.] 19, 152; 20, 145; Tiemann-Gärtner's Untersuch. d. Wassers, 277, 288; Catherine Williams and Ramsay, Chem. Soc. Trans. 1886, 760; Bernthsen, Ber. 13, 2277; Roscoe and Lunt, Chem. Soc. Trans. 1889, 552; Dupré, Analyst, 1885, 10, 156) the water is allowed to act on a solution of sodium hydriodide disulphonate, which oxygen converts into the blue compound; a standard solution of sodium hydrosulphite is then run in until the liquid again becomes colourless. In *Winkler's* process (Ber. 21, 2843) the water is mixed with a solution of manganous chloride, and then with potassium iodide and caustic potash; the precipitated manganous hydroxide absorbs the oxygen, passing into a higher state of oxidation. On adding hydrochloric acid the higher oxide of manganese gives rise to the liberation of an equivalent quantity of iodine, the amount of which is determined by titration with sodium thiosulphate. According to Kisch (*loc. cit.*), the results by the Reichardt-Preusse-Tiemann method are decidedly lower than those obtained by the *Winkler* process, which is in harmony

with the experience of the writer. The results by *Mohr's* and *Schützenberger's* methods accord very well with those of *Winkler*; but *Winkler's* appears, on the whole, to be the most trustworthy, and the easiest to carry out. A modification of *Winkler's* method has been made by Rideal and Stewart (Analyst, 1901, 26, 141), and a more recent one reducing it to a colorimetric process by Rideal and Burgess (*ibid.* 1909, 34, 193).

A full description and discussion of the several methods will be found in Sutton's Volumetric Analysis.

The determination of dissolved oxygen has, in recent years, been much practised in connection with the rate at which dissolved oxygen is absorbed by sewage and effluents from sewage works. This matter is of importance as affording a measure of the readiness with which such liquids will remove the dissolved oxygen from a stream into which they are discharged. For Scudder's method, see *Fowler's Sewage Works Analyses*, or Sutton's Volumetric Analysis.

Determination of carbon dioxide.—(1) The total carbonic acid is determined by completely precipitating as calcium carbonate with an excess of calcium hydroxide (a sufficient quantity of calcium chloride being added to decompose alkaline carbonates), then filtering off the precipitate, and determining the carbon dioxide in it in the usual way (Fresenius, Quant. An.; Tiemann-Gärtner, Die Untersuch. d. Wassers, 213). If the water is saturated with carbon dioxide under pressure, the above method must be preceded by *Rochleder's* process for estimating the gas which escapes on reducing the pressure to that of the atmosphere.

(2) The free and semi-combined carbon dioxide is determined by *Pettenkofer's* method, in which the water is treated with an excess of standard calcium hydroxide solution, and, after the precipitate has separated in a crystalline form, the clear liquid is decanted off, and the excess of lime ascertained in an aliquot part by titration with standard dilute oxalic acid, using phenolphthalein as indicator. If the water contains alkaline carbonates, sufficient neutral calcium chloride solution must be added to decompose them, whilst if there is a considerable proportion of magnesia salts, some ammonium chloride must also be added.

If the carbonic acid thus determined is subtracted from the total obtained according to (1), then the difference represents the combined carbonic acid. To this combined carbonic acid there corresponds, of course, an equal quantity of semi-combined, so that only an excess over and above this can be regarded as free carbonic acid. It must, however, be pointed out that the determination of total carbonic acid generally yields results which are below the truth by 1-1.5 units in 100,000 parts, in consequence of the solubility of normal calcium carbonate itself (v. Walker and Kay, J. Soc. Chem. Ind. 1912, 31, 1013).

Determination of sulphuretted hydrogen.—Colorimetrically with a solution of sodium nitroprusside, using for comparison a standard solution of sulphuretted hydrogen. The latter is standardised by taking a measured volume and adding an excess of decinormal sodium acetate; shake well, and then acidify with hydrochloric acid. After the arsenious sulphide has com-

pletely subalbed, dilute to 300 c.c., and filter through dry paper. Take 100 c.c. of the filtrate, remove acidity by means of solid sodium carbonate, add a drop of starch solution, and then run in decinormal iodine until a blue colour is obtained. This method may, of course, also be employed for the determination of the sulphuretted hydrogen in the water itself if present in sufficient quantity.

In using the colorimetric method, 300 c.c. of the water are treated with 5 c.c. sodium carbonate and 3 c.c. sodium hydroxide; allow the precipitate to subside for 1-2 hours, then decant or filter. To 250 c.c. of the filtrate in a colourless cylinder add 1 c.c. of sodium nitroprusside solution (4 grms. per litre), and for comparison take 245 c.c. distilled water, to which add 2 c.c. sodium hydroxide and as much of the standard solution of sulphuretted hydrogen as is required to produce precisely the same tint as is obtained with the water above. In this manner 0.1 part H_2S per 100,000 can be determined (Tiemann-Gärtner, Untersuch. d. Wassers, 232).

Sulphuretted hydrogen may also be accurately determined by means of centinormal iodine solution. 10 c.c. or other suitable volume of the latter are placed in a 500 c.c. flask, and the water added until the colour completely disappears; 5 c.c. of starch solution are then added, and centinormal iodine is run in until a blue colour is obtained, pure distilled water being added up to the 500 c.c. mark from a burette. On subtracting the sum of the volumes of iodine, starch solution, and distilled water added from 500 c.c., the volume of water which reacted with the iodine solution employed is ascertained. A correction should be made for the volume of iodine solution required to produce a blue colour.

BACTERIOLOGY OF WATER.

The great progress during the past half century made in our knowledge of infectious diseases and of the processes dependent on bacterial life, has necessitated that the subject of water supply should be considered from a bacteriological, as well as a chemical, point of view.

It had even previously been recognised that in making determinations of organic matter, ammonia, nitrates, &c., with a view to ascertaining the fitness or otherwise of water for drinking purposes, the concomitants of the living poisons of zymotic disease and not the morbid matters themselves, which were still more or less hypothetical entities, were being tested for, and that the living poisons themselves must be explored by biological, and not by purely chemical, methods.

Liquid and solid media.

The classical investigations on bacteria by Pasteur, Tyndall, Lister, Nägeli, Cohn, Fitz, Schloessing, Muntz, and others prior to 1880 were practically all made with liquid culture media only. Such culture media labour under several serious disadvantages:—

(1) Facility with which they become contaminated with bacteria and other organisms from the air and other surroundings;

(2) The competition which arises between

the different microbes present may lead to the entire suppression of some through the overwhelming multiplication of others;

(3) The great difficulty of obtaining pure cultivations of specific micro-organisms.

The introduction of solid culture media by Koch at the beginning of the 'eighties, in the last century, led to great developments in bacteriology. An immense variety of investigations were now rendered possible which had long been awaiting attack. These new methods of bacteriological study were at once applied to the identification of the specific micro-organisms of numerous diseases, and to the investigation of the bacteria present, in air, water, soil, and all our other surroundings.

By means of *gelatin-plate-culture* it became possible to ascertain the number and the nature of most bacteria present in any material. Thus in the case of water the number and nature of the bacteria present in any sample could be determined, and by this means it was possible to ascertain the effect of any treatment or process of purification on the bacteria present in water. Thus it was applied by the writer in 1885 to the study of the removal of bacteria from water by artificial and natural filtration, by subsidence, and by precipitation.

The results obtained in investigations of this kind led to a great modification of the opinions which had previously been entertained with regard to the value of these processes in removing the zymotic dangers of water. Thus it was found that bacteria could be almost wholly removed from water by the process of sand filtration which had a comparatively insignificant effect on the organic matter and other ingredients discoverable by chemical analysis.

Similarly these methods of bacteriological investigation enabled such processes of water purification to be readily controlled. Thus if the safety of a water-supply depends on the efficiency with which the removal of bacteria by filtration is carried out, it is obvious that this efficiency should be continually controlled by bacteriological examination, so that any defect in the working of the filters may at once be detected and rectified. The systematic control of water-works by bacteriological examination is now being very widely carried on with great benefit to the communities concerned.

With the discovery of the specific bacteria of cholera, of typhoid fever, and of many other diseases, attempts were naturally made to find these specific pathogenic bacteria in contaminated water-supplies. The chance of such discovery by the ordinary method of plate-cultivation is, of course, hopelessly remote, because a single pathogenic organism must almost inevitably be accompanied in water by a host of non-pathogenic individuals, and amongst these multitudes of harmless forms the few harmful ones will under ordinary circumstances be overlooked, whilst, in the small quantities of water operated on, the pathogenic forms may be absent, although present in a larger bulk.

To surmount these difficulties, the natural device was to provide conditions which would be favourable to the particular pathogenic form being sought for and less favourable or even antagonistic to the multitude of non-pathogenic forms with which it would be accompanied.

We may call the provision of such conditions the method of *enrichment* or *preferential culture*.

Such a method of enrichment was very satisfactorily applied by Koch to the discovery of the *cholera-bacillus* in the water of the Elbe at Hamburg during the epidemic of 1892. If 90 c.c. of the water under examination be incubated for 18 hours at 37° with 10 c.c. of a solution containing peptone 10 p.c., and sodium chloride 10 p.c., cholera bacilli will be found in the thin surface pellicle, and from this cultures are made.

Typhoid fever is, of water-borne diseases, the most important in Western Europe. An enormous amount of labour and ingenuity have been devoted in recent years to the discovery of the bacillus of this disease in water. That the problem is a very difficult one may be gathered from the fact that until recently its detection even in the discharges of typhoid patients was very frequently abortive.

The special difficulty attending the discovery of the typhoid bacillus depends on the circumstance that even in the intestine of the typhoid patient it is enormously outnumbered by other bacteria, and especially by the *Bacillus coli communis*, which, discovered by Escherich in 1886, has in recent years achieved the very greatest celebrity in the bacterial world.

Practically all conditions which are favourable to the typhoid bacillus are equally or even still more favourable to the *B. coli*, and for a long time all methods of favouring the typhoid bacillus at the expense of the *B. coli* proved futile. Much interest was, therefore, excited when in 1903 Roth announced that the *B. coli* was more disadvantageously affected than the typhoid bacillus by solutions of caffeine.

Experiments made by Kloumann¹ in 1904, however, showed that the differential effect on the two bacilli was only very slightly in favour of the typhoid bacillus.

A method of testing for typhoid bacilli in water and other liquids was elaborated by Hoffmann and Ficker in 1904; it was also based on the inhibitory action of caffeine and of crystal-violet on the *B. coli*. The method will be best understood by the following description of the manner in which it was successfully employed by Jaksch and Rau (1904) to detect typhoid bacilli in the drinking water supplied to Prague:—

900 c.c. water from a service tap were added to the Hoffmann and Ficker culture-medium, consisting of 10 grms. nutrose, 5 grms. caffeine, and 0.01 grm. crystal-violet, in 100 c.c. water.

The mixture was then incubated at 37° for 13 hours, when it was to be presumed that any typhoid bacilli originally present would have extensively multiplied. Loopfuls of this large cultivation were then withdrawn and spread on the surface of Drigalski and Conradi Plates (agar, meat extract, peptone, nutrose, lactose, sodium chloride, crystal violet and litmus), which were then incubated at 37° for 24 hours. On these plates the *B. coli* colonies are red (acid litmus) and non-transparent, whilst those of the typhoid bacillus are blue with a violet-tinge, transparent, resembling dewdrops, and smaller than the *B. coli* colonies. In the Prague experiments these plates gave only a few red

colonies, the majority being blue and transparent. The latter were sub-cultured, and, according to Jaksch and Rau, gave results in the most varied tests (including agglutination, toxicity, and immunisation) which were identical with those obtained with the true typhoid bacillus.

Other solid media which have proved of great value in distinguishing between coli-like and typhoid-like colonies are Loeffler's malachite-green agar, and McConkey's bile-salt-neutral-red agar, both of which will be referred to later.

By far the most extensive, interesting, and systematic search which has ever been made for the typhoid bacillus in natural waters is that carried out by Houston on the waters of the three rivers—Thames, Lea, and New River—from which the greater part of the London water supply is obtained. As this investigation illustrates the most approved methods which are now available to the bacteriologist, it will be considered here in some detail.

Two hundred and ninety-four experiments in 8 series were made with 156 samples of raw river water (52 Thames, 52 Lea, and 52 New River) during the 12 months ended July 31, 1908. The total volume of water dealt with was $294 \times 100 = 29,400$ c.c. The total number of bacteria in this volume of water (as ascertained by gelatin-plate cultivation for 3 days at 20°–22°) was 135,687,500. The total number of colourless (or nearly colourless) colonies sub-cultured from the Drigalski or similar plates was 7329. These 7329 selected colonies form but a small fraction of the millions of bacteria which were excluded owing to the temperature of incubation, the composition of the media employed, and the fact of their appearing on the plate-cultures as coloured colonies.

The following tabular summary indicates the method adopted in this exhaustive investigation:—

Direct Plating on Solid Media.

Series I. 100 c.c. of the sample of water were centrifuged and the resulting deposit spread over a number of plates consisting of malachite-green (1 in 5000), saccharose, dulcitol, salicin, neutral-red, bile-salt, peptone, lactose, agar. The plates were incubated at 40°–42° for 24 hours, and the colourless colonies sub-cultured into special media, as described in the next table.

Series II. Same as Series I, but the proportion of malachite-green was 1 in 10,000.

Series III. Same as Series I, but the medium used in the plates contained no malachite-green.

Series IV. Same as Series I, but the proportion of malachite-green was 1 in 20,000, 1 in 40,000, and 1 in 80,000.

Primary Liquid Cultures followed by Plating on Solid Media.

Series A. 100 c.c. of the sample of water were added to bile-salt-glucose-peptone medium containing malachite-green in proportion of 1 in 1000, 1 in 2000, 1 in 4000. This liquid was incubated at 40°–42° for 24 hours, and then plated on the same medium as was employed in Series I, 10 colourless colonies were in each case sub-cultured and tested as described.

Series B. Same as Series A, but malachite-green in the liquid medium was in proportion

¹ Kloumann, Centralbl. f. Bakteriologie, 1904, 36, 312.

of 1 in 8000, 1 in 16,000, 1 in 32,000. Subsequently plated on same medium as that used in Series II.

Series C. Same as Series A, but the liquid culture medium consisted of meat-broth only without malachite-green or any other additions. Subsequently plated on same medium as that used in Series I.

Series D. Same as Series C, but instead of cultivating 100 c.c. of water in one

portion, 10 cultures of 10 c.c. each were made.

The following table shows the behaviour of 32 strains of the typhoid bacillus, on the one hand, and of the 7329 suspicious colonies isolated from the raw waters, on the other. It will be seen that not one out of all these 7329 different microbes, although suspicious in certain features, gave reactions agreeing in their entirety with those of the typhoid bacillus.

VERIFICATION TESTS FOR TYPHOID BACILLUS.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Description of microbe.	Proskauer's and Capaldi's No. 2 medium ¹ (with inner tube).	Lactose-saccharose dulcitate-salicin-medium (with inner tube).	Proskauer's and Capaldi's No. 1 medium ² modified (with inner tube).	Glucose-neutral red broth cultures (with inner tube).	Peptone-water medium.	Gelatin sugar media:—galactose, glucose, levulose, maltose, and mannite respectively.
RESULTS CHARACTERISTIC OF TYPHOID BACILLUS.						
32 strains of typhoid bacillus from a number of different laboratories.	Acid, no gas	No visible change (No acid, no gas.)	No visible change. (No acid, no gas.)	Purplish tint. (No gas, no fluorescence.)	No indole	Acid, but no gas with all five sugars. No liquefaction.
RESULTS WHICH EXCLUDE, AS NOT TYPHOID BACILLUS, THE SUSPECTED MICROBES.						
7329 colourless (or nearly colourless) colonies, sub-cultured.	No acid, or acid and gas	Acid or gas-formation.	Acid or gas-formation, or decided growth.	Gas or fluorescence. (Absence of purplish tint.)	Indole	Gas formation in one or all of the sugar media. (Liquefaction.)

¹ Solution of peptone and mannite.

² Solution of asparagine, mannite, glucose, galactose, levulose, maltose, magnesium sulphate, sodium chloride, calcium chloride, potassium hydrogen phosphate, and litmus.

From the very nature of this investigation—the search for a specific microbe in a natural water which at some period in its history is practically certain to have received this microbe in comparatively small numbers—it is impossible to make it really exhaustive. Houston has, however, amplified his previous investigation in a very suggestive manner. Realising that the objection might be raised that the method adopted may not be capable of detecting a very small number of typhoid bacilli in the presence of a very large number of other microbes, he devised a mode of procedure which enabled him to affirm that in each particular sample of water examined there were *not more than* a certain definite number of typhoid bacilli in a given volume. The method adopted was this:—

Each sample of raw river water was divided into two equal portions of 500 c.c. (A and B). The A sample was inoculated with a very small number of typhoid bacilli. The B sample was not so infected, and was, therefore, normal raw river water. The subsequent procedure was exactly the same in each case, both samples A and B being treated exactly alike. The 500 c.c. of water were centrifuged and the resulting deposit spread over 16 plates prepared with solid medium of the following composition:

Agar, 2 grms.; peptone, 2 grms.; bile-salt, 0.5 gm.; lactose, saccharose, adenite, raffinose,

and salicin, each 0.2 grm., made up with water to 100 c.c. and tinted with 0.4 c.c. of a 1 p.c. solution of neutral red. In some of the experiments malachite-green was added to the above, in the proportion of either 1 to 10,000, or 1 to 5000 of the medium.

Of the 24 experiments, 14 were carried out with raw Lea, and 10 with raw Thames, water. These waters contained on an average 62,688 bacteria per 1 c.c. (gelatin at 20°-22°, 3 days' incubation). The worst sample contained 760,000 and the best sample 1200 bacteria per 1 c.c. Thus in the 12 litres (500 c.c. × 24) of raw water (B samples) examined for typhoid bacilli there were 752,256,000 bacteria present.

The total number of colonies selected for study was 5451 from the infected A samples, and the same number (5451) from the non-infected B samples. The average number of typhoid bacilli artificially added to the A samples was 2.242 per 1 c.c. or 1121 per 500 c.c. The average number of typhoid bacilli isolated from the A samples was 14.54 per 500 c.c. of sample. It may be argued fairly, therefore, that if only $\frac{1}{14.54}$ of the above number of typhoid bacilli had been present in the infected sample this microbe would still have been detected by the method of investigation adopted; but $\frac{1}{14.54} \times$

2.242=0.154 typhoid bacillus per 1 c.c., or 1 typhoid bacillus in 6.5 c.c. would have been detected.

From the uninfected B samples, out of the 5451 colonies selected for special study, one, and only one, consisted of bacteria which resembled the typhoid bacillus very closely.

It will be instructive to record the observations which were made on submitting this typhoid-like microbe (Lee W. 694? *B. typhosus*, Houston) to the several tests used in the diagnosis of typhoid bacilli.

Characterisation of typhoid-like bacillus from raw river water (Lee W. 694? B. typhosus, Houston).

Morphology.—A motile multiflagellate bacillus. The rods seemed shorter than in most strains of *B. typhosus*.

Gelatin and agar slope-cultures.—Possibly the growth was slightly less filmy in character than that of the true *B. typhosus*.

Glucose-bile-salt agar-slope (neutral red).—The streak somewhat brighter and cleaner red than in most strains of *B. typhosus*.

Lactose-bile-salt agar-slope (neutral red).—Colourless streak.

Potato.—No visible growth (5 days at 37°).

Nitrate-broth.—Reduces nitrates to nitrites.

Peptone-water at 55°F.—No visible growth after 5 days; on transferring tube to incubator at 37°C. growth occurred within 24 hours.

Indole test.—No indole formation (5 days at 37°).

Liquid peptone (1 p.c.) media containing separately 1 p.c. of the substances stated and tinted with litmus. Sorbite and inositol are only used in 0.2 p.c. solution. Acid but no gas in sorbite, mannite, glucose, levulose, galactose, and maltose respectively (2 days at 37°). No change in inulin, inositol, saccharose, salicin, adonite, lactose, dulcitol, and raffinose respectively (5 days at 37°).

Gelatin glucose medium tinted with litmus.—Acid but no gas formation.

Voges and Proskauer's reaction.—Negative result, 5 days.

Gelatin.—No liquefaction after one month at 20°.

Litmus milk.—Slight acid but no coagulation (5 days at 37°).

Glucose-neutral-red-broth cultures.—No gas, no fluorescence characteristic purplish tint.

Lactose-saccharose-dulcitol-salicyl-peptone medium tinted with litmus.—No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 1 (modified).—No change (2 days at 37°).

Proskauer and Capaldi's Medium No. 2.—Acid but no gas.

Agglutination experiments and tests for pathogenicity.

Anti-typhoid serum.—Microscopically, 1:200 almost instantaneous clumping, 1:800 very fair clumping, 1:2000 little or none. *B. typhosus* tested with the same serum gave very similar results but appeared to be clumped slightly more rapidly and in slightly higher dilutions. The difference, however, if any, was not well marked.

• *Serum of an animal immunised with the suspected microbe (Lee W. 694? B. typhosus, Houston).*—Microscopically, 1:200 very rapid and satisfactory clumping; 1:2000 good, but not quite complete clumping within half an hour.

B. typhosus tested with the same serum gave very similar results, but was perhaps clumped a little more slowly and in slightly lower dilutions. The difference, however, if any, was not well marked. Microscopically, the titre limit was about 1:8000 (18 hours) and was practically the same for both microbes.

Pathogenicity.—2 c.c. of a broth-culture injected subcutaneously into a guinea-pig produced a swelling and illness with recovery. A guinea-pig intraperitoneally inoculated with 5 c.c. of a broth-culture died in less than 24 hours.

On the results of this laborious investigation, which had extended over more than two years, and which had been conducted with the most meticulous care and regardless of time and money, Dr. Houston very cautiously remarks: 'If this microbe had been isolated from a case of typhoid fever (or from a suspected case) I do not think any serious hesitation would have been felt in describing it as *B. typhosus*.'

It would be impossible to produce more eloquent testimony than the above as to the enormous and almost prohibitive trouble which a systematic and conscientious search for the typhoid bacillus in natural water entails.

Comparative unimportance of searching for the typhoid bacillus in water.—The almost hopeless nature of the search for the typhoid bacillus in natural waters is of the less importance as the anxiety to detect this microbe in water is, for the most part, based upon an entire misconception of the objects of water examination. The object of a water examination is, in general, not to determine whether the particular sample of water contains typhoid bacilli and is, therefore, capable of carrying typhoid to the consumer, but to discover whether the water is likely at any time to contain such infective material.

Now any water which receives sewage matters must be regarded as a possible carrier of typhoid infection, for at any time these sewage matters may be derived from persons suffering from typhoid. Thus any sewage-contaminated water is a potential carrier of typhoid unless it has been subjected to conditions which would ensure the removal of the possibly present typhoid bacillus. Thus the all-important thing is to ascertain whether a given water has been contaminated with sewage, in what proportion such contamination has taken place, and whether the water since such contamination has been submitted to conditions which would remove or destroy typhoid bacilli should they have gained access with the sewage matters.

Firstly, as regards the detection of sewage contamination. Excremental contamination, if sufficient in amount, can be revealed with more or less certainty by chemical analysis, which can indeed even distinguish between whether such pollution is recent or remote in point of time, but in order to ascertain the fate of bacteria gaining access to water resources must be had to biological methods. If there were bacteria absolutely characteristic of sewage, the determination of their presence would be sufficient to

prove the danger of a water. Unfortunately we do not know of any bacteria which satisfy the condition of being *absolutely* characteristic of sewage, so we must be satisfied with a second best qualification for diagnostic purposes by those which are *very* characteristic of sewage.

The microbe which is most characteristic of the intestinal discharges of man and the higher animals is, as its name implies, the *B. coli communis*, and a great amount of time and ingenuity has been devoted to its accurate and expeditious discovery in water and other materials.

In identifying a particular organism, whether plant or animal, we depend on recognising in the individual a certain group of specific characters which are more or less arbitrary. The botanist at first tried to classify and distinguish bacteria by external appearances alone; he measured the length and breadth of these minute organisms; he counted the number of flagella with which some of them are provided; he was very careful to observe whether they were square or round at the ends, and so forth.

These morphological characters have, however, long been recognised as inadequate for purposes of identification, since organisms exhibiting the closest morphological similarity have been found to differ enormously in other respects.

After the introduction of Koch's methods much attention was directed to the macroscopic appearances to which the organisms give rise when grown on a variety of solid media, by which means microscopically similar bacteria can often be differentiated.

Some 35 years ago the writer commenced distinguishing bacteria, which were similar in form and in cultural appearances, by differences in the chemical changes which they could bring about in certain media. Thus he found that the capacity to reduce nitrates to nitrites was in some cases a valuable means of distinguishing between otherwise similar bacteria. This reduction of nitrates has been extensively used for diagnostic purposes, more especially by American bacteriologists. Somewhat later he devoted much attention to the fermentation of carbohydrates, polyhydric alcohols, and hydroxy-acids, by means of pure cultivations of micro-organisms, and showed how capricious is the power possessed by different bacteria in this respect. Thus perhaps one microbe will ferment glucose, mannite, and glycerol, but not dulcitol or glyceric acid, another will ferment glucose, mannite, and dulcitol, &c.

There are, however, many bacteria which more or less simulate the characters of the typhoid bacillus on the one hand, and of the *B. coli* on the other; such forms exhibit almost every degree of approximation to one or other of these two types, from which they can only be distinguished by applying a number of tests. Such forms are designated as *atypical*, and what their relationship to the typical typhoid and coli bacteria may be is a matter of uncertainty. Possibly in some cases they may have been typical forms originally, but under the particular conditions to which they have been submitted they have lost some of their characters. Thus it is often found that the *B. coli*, on prolonged

artificial culture, may lose either or both its indole-producing and milk-curdling properties.

This mode of differentiating between otherwise very similar forms of bacteria has been greatly extended within recent years. In the following table the classification of the Typhoid-coli group of bacteria into seven sub-groups has been attempted:—

TYPHOID-COLI GROUP.

Sub-groups	Glucose	Acid gas	Lactose	Acid gas	Dulcitol	Acid gas	Saccharose	Acid gas
I.								
<i>B. Typhosus</i> :	+	-	-	-	-	-	-	-
<i>B. dysenteriae</i> :	+	-	-	-	-	-	-	-
<i>B. faecalis-alcaligenes</i> :	-	-	-	-	-	-	-	-
II.								
<i>B. enteritidis</i> (Gaertner) :	+	+	-	-	+	+	-	-
<i>B. paratyph</i> :	+	+	-	-	+	+	-	-
<i>B. paracoli</i> :	+	+	-	-	+	+	-	-
III.								
Bacillus from urine :	+	+	-	-	-	-	+	+
IV.								
<i>B. acidilactici</i> (Hueppe) :	+	+	+	+	-	-	-	-
V.								
<i>B. coli</i> (Escherich) :	+	+	+	+	+	+	-	-
VI.								
<i>B. pneumonias</i> (Friedländer) :	+	+	+	+	+	+	+	+
VII.								
<i>B. capsulatus</i> (Pfeiffer) :	+	+	+	+	-	-	+	+
<i>B. lactis aerogenes</i> (Escherich) :	+	+	+	+	-	-	+	+
<i>B. cloacae</i> (Jordan) :	+	+	+	+	-	-	+	+

It is obvious that by increasing the number of biochemical tests many further variations of a given type of organism may be discovered, and, for the purpose of more precisely defining a particular microbe, bacteriologists have introduced biochemical tests involving the use of a variety of organic compounds—more especially carbohydrates, polyhydric alcohols, and glucosides. These tests generally consist in ascertaining whether an organism under investigation gives rise to acid or gas, or both, or neither, in a suitable nutritive medium containing one of these substances. The following list of substances employed in this manner will give some idea of the degree to which these biochemical tests have been complicated in recent years: adonite, asparagine, dextrin, dulcitol, erythrite, galactose, glucose, glycerol, glycol, isodulcitol, lactose, levulose, maltose, mannite, mannose, nutrose, raffinose, sucrose, salicin, sorbite, and starch. The above list by no means exhausts the number of organic substances which are acted on by bacteria, and by means of which, therefore, differences can be established.

Although such tests are extremely useful for the more precise definition of particular micro-organisms, they must be employed with discrimination, for as the writer long ago pointed out, these fermentations, as well as other characters of bacteria, are liable to be lost through conditions of environment, and he has also shown how in some cases they may be

restored by resorting to particular methods of culture and training.

It is obvious that it would be impracticable to resort to such numerous tests in the ordinary bacteriological examination of water in which we are concerned with the detection of sewage or excremental contamination, unless some very great advantage should result from such multiplication of tests, and this is not the case at present.

Quantitative determination of B. coli in water.
—If we regard the *B. coli* provisionally as the best indicator of contamination with the living bacteria of animal refuse, we shall obviously view its presence with the more suspicion the larger the numbers in which it is discovered in a given volume of water.

The numerous methods which have from time to time been devised for detecting *B. coli* will be passed over, and only the one which in this country at any rate has superseded all others will be described.

An important departure in practical bacteriology was the introduction by McConkey and Hill ('Bile-salt broth. A simple test for faecal contamination.' Thompson-Yates Laboratories Report, 1901, 4, [i.] 151) of a medium for the preferential culture of the *B. coli* and allied microbes from mixtures of micro-organisms. The essential ingredients of this medium are sodium taurocholate (bile-salt) 5 grms., glucose 5 grms., peptone 20 grms., water (tinted with litmus) 1000 c.c. Incubated in this liquid at 37°-42° bacteria of the *B. coli* group give acid and gas in 48 hours. Some bacteriologists use lactose instead of glucose, thus restricting the gas production to *B. coli* and its still closer allies. With this liquid medium in Durham fermentation-tubes cultivations of the water are made in the following quantities: 100, 10, 1, 0.1, 0.01, 0.001, 0.0001, 0.00001 c.c. The concentration of the medium should in all cases be approximately the same as that given above. In order, therefore, that the volumes of liquid incubated may not be inconveniently large, the 10 and 100 c.c. of water are introduced into correspondingly stronger McConkey media.

A positive reaction, i.e. the production of acid and gas, in any of these culture-tubes signifies that at least one coli-like microbe must have been introduced with the portion of water added. Thus, if acid and gas had been obtained, in a particular case, with all the tubes from 100 to 0.1 c.c., this would mean the 'presumptive' presence of at least one *B. coli* in 0.1 c.c., and its absence in 0.01 c.c. and smaller volumes of water.¹

¹ There is one element of uncertainty connected with such tests made in liquid media which appears to be tacitly ignored by all bacteriologists who make use of them, and that is that the particular microbe sought for may in the process of cultivation in the liquid medium become hopelessly outnumbered or even suppressed by the much more abundant proliferation of some other microbe or microbes present in the mixture.

Thus the McConkey medium may be taken as a priori favourable for the proliferation of bacteria of the *B. coli* type, but the water-bacteriologist is in general restricting his search to those bacteria which are sufficiently like typical *B. coli* as to produce acid and gas in the medium. Is it not possible that the bacteria capable of producing both acid and gas may be so greatly outnumbered by microbes not giving this reaction that the more typical *B. coli* forms may be so much kept in abeyance that no acid and gas reaction is obtained? Under these circumstances he would

• In order to ascertain whether the 'presumptive' *B. coli* is typical or not, the tube containing the smallest portion of water which has given rise to acid and gas in the McConkey medium is plated on a solid medium of the following composition: Agar 20 grms., peptone 20 grms., sodium taurocholate (bile-salt) 5 grms., lactose 10 grms., neutral red (1 p.c. solution) 4 c.c., made up to 1000 c.c. with water. After 12 hours' incubation at 37°, the colonies will be distinctly visible, and those which are most likely to be *B. coli* will have a strong red colour owing to the acid produced by this microbe in the medium. Five of the most typical red colonies are separately inoculated into 5 glucose-litmus broth tubes, which are then incubated at 37°. Any of these 5 tubes which develop acid and gas are then each further inoculated into tubes of the following media which are then incubated at 37°:—

(a) Neutral red broth to be examined for fluorescence.

(b) Litmus lactose-broth to be examined for acid and gas.

(c) Ordinary broth to be examined for indole.

(d) Litmus-milk to be examined for acid and coagulation.

(e) Gelatin to be examined for non-liquefaction.

The above glucose-tubes from which these inoculations have been made are also microscopically examined to see whether the microbe possesses the characteristic form and motility of the *B. coli*.

A microbe fulfilling these conditions has been designated by Houston as 'Flaginac' *B. coli*, from Fl—fluorescence in neutral-red broth, ag=acid and gas in lactose, in=indol in peptone broth, ac=acid and coagulation in litmus-milk.

The typical *B. coli* from human faeces gives these reactions, but, of course, it is possible to further differentiate between coli-bacteria by additional tests, such as fermentation of sucrose, dulcitol, mannitol, &c., but at present there would not appear to be any advantage in such multiplication of tests in the ordinary examination of water.

The following table summarises an interesting investigation made by Houston on the proportion of 'Flaginac' *B. coli* found amongst the coli-like microbes obtained from different sources:—

FLAGINAC *B. COLI*.

Source	Number of specimens of <i>B. coli</i> or coli-like microbes on which flaginac percentage is based	P.c. of <i>B. coli</i> .
Milk	243	61
Human faeces	101	85
Sewage	several hundreds	65-85
Oysters	464	43
Estuarial waters	183	68
Water-crees	81	40
Washings of crees	52	52
Water in which crees was grown	42	76
London filtered water	232	31

obviously draw the conclusion, and quite erroneously, that acid and gas producing microbes (and, therefore, *B. coli* amongst them) were absent. This is a matter which requires much further investigation before the conclusions as to absence of *B. coli* generally drawn can be justified.

In the following table are recorded the results of some very suggestive pioneering experiments made by McConkey (1905), undertaken with the object of ascertaining whether there is any marked difference in the types of *B. coli* found in the excreta of man and some of the common domestic animals respectively. Should it be possible to establish such a difference, an important means of distinguishing between human and animal excrementitious contamination of water would be obtained.

Such an investigation would have to be enormously extended before results capable of being used for diagnostic purposes could be obtained.

An attack on the same important problem was also made by Dr. Wm. G. Savage (1904-5) in an extremely laborious investigation, which he has summarised in the foregoing table.

The absence of streptococci in the faeces of the pig is extremely remarkable.

It is convenient to classify waters tentatively

B. COLI FROM HUMAN AND ANIMAL EXCRETA (McCONKEY).

Group	Fermentation of		Number of lactose-fermenting Coli-form microbes isolated and experimented with			Results in percentages		
	Saccharose	Dulcité	Human	Animal ¹	Total	Human	Animal	Average
I. . . .	—	—	83	37	120	34	15	25
II. . . .	—	+	93	85	178	38	36	37
III. . . .	+	+	36	74	110	15	31	23
IV. . . .	+	—	29	43	72	12	18	15
			241	239	480	100	100	100

¹ Twenty-five samples of animal excreta, of which 5 were from horses, 6 from cows, 3 from rabbits, 1 from a monkey, and 14 from a cat.

Source	Approximate number per 1 gram of excreta		
	<i>B. coli</i>	<i>Streptococci</i>	<i>B. enteritidis sporogenes</i> spores
Horse No. 1 . . .	Over 1 million	$\frac{1}{10}$ to 1 million	10 to 100
Horse No. 2 . . .	$\frac{1}{10}$ to 1 million	Over 1 million	100 to 1000
Horse No. 3 . . .	1000 to 10,000	Over 1 million	100 to 1000
Cow No. 1 . . .	$\frac{1}{10}$ to 1 million	10,000 to 100,000	100 to 1000
Cow No. 2 . . .	10,000 to 100,000	$\frac{1}{10}$ to 1 million	10 to 1000
Cow No. 3 . . .	1 to 10 millions	Over 10 millions	10 to 100
Cow No. 4 . . .	1 to 10 millions	$\frac{1}{10}$ to 1 million	100 to 1000
Pig No. 1 . . .	Over 100 millions	Absent	$\frac{1}{10}$ to million
Pig No. 2 . . .	10 to 100 millions	Absent	10,000 to 100,000
Pig No. 3 . . .	70 millions	Absent	1000 to 10,000
Sheep No. 1 . . .	10 to 100 millions	1 to 10 millions	10 to 100
Sheep No. 2 . . .	10 to 100 millions	10 to 100 millions	10 to 100

according to the results of the examination for *B. coli*, thus:—

CLASSIFICATION OF WATER BY *B. COLI* TEST.
(1 c.c. of sewage is assumed to contain 100,000 *B. coli*.)

Class	Volume of water examined	<i>B. coli</i> per 1 c.c.	Pollution in sewage
I	a.c.	0	per cent.
II	—in 100	0	—
III	+in 100	0.01	0.00001
IV	+in 10	0.1	0.0001
V	+in 1	1	0.001
VI	+in 0.1	10	0.01
VII	+in 0.01	100	0.1
VIII	+in 0.001	1,000	1
IX	+in 0.0001	10,000	10
		100,000	100 (pure sewage)

This classification must not, however, be interpreted too rigidly, as it is based on the assumption that *B. coli* is always derived from faeces and that this microbe is incapable of multiplication under any circumstances after incorporation in what is known as 'sewage.'

In the two following tables are recorded the results of the ordinary bacteriological examination of a number of typical waters. The tables sufficiently explain themselves.

Storage of water.—In 1886 (Water Purification, its Biological and Chemical Basis, Trans. Inst. Civil Engineers, 1886) the writer pointed out the great importance from a theoretical point of view of storage for the purification of surface waters. In 1892, again, he investigated the influence of storage on the bacteriological purity of the river waters abstracted for the supply of London, and showed that there is a most striking reduction in the number of

BIRMINGHAM WATER SUPPLY. (P. F. Frankland.)
Averages for 1910.

	Number of bacteria				<i>Bacillus coli</i> (typical)						
	Gelatin at 20°C.		Carbolic gelatin at 20°C.	Taurocholate agar at 37°C.	100 c.c. —	100 c.c. +	10 c.c. +	1'0 c.c. +	0'1 c.c. +	0'01 c.c. +	0'001 c.c. +
	2 days	7 days	7 days	4 days							
Whitacre ¹ —					p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.
Unfiltered .	3300	—	167	1232	—	—	—	8·3	16·7	58·3	16·7
Filtered .	12	87	0	5	75·0	25·0	—	—	—	—	—
Frankley ² —											
Inlet .	37	237	0·7	13	18·2	45·5	36·4	—	—	—	—
Reservoir .	54	258	1·6	40	41·7	33·3	25·0	—	—	—	—
Filtered .	5	38	0	3	91·7	8·3	—	—	—	—	—
City mains .	19	59	0·03	5·5	78·4	16·2	5·4	—	—	—	—

¹ Surface water from more or less cultivated land.² Moorland water from Elan Valley, Wales.

LONDON WATER SUPPLY. (Houston.)
Averages for 1908-9 and 1909-10.

		<i>Bacillus coli</i> (typical)									
	No of bacteria gelatin at 20°- 22°C 3 days	100 c.c. —	100 c.c. +	10 c.c. +	10 c.c. +	0·1 c.c. +	0·01 c.c. +	0·001 c.c. +	0·0001 c.c. +	0·00001 c.c. +	
Raw River Waters—											
Thames at Hampton, 1908-9	2558	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	
Thames at Hampton, 1909-10	5268	0·5	0·5	6·3	26·9	52·9	12·8	—	—	—	
Lea at Ponder's End, 1908-9	8794	—	0·8	5·2	34·9	38·8	15·5	3·9	0·8	—	
Lea at Ponder's End, 1909-10	37,071	—	0·5	6·3	31·4	39·7	13·2	7·3	0·5	0·5	
New River at Hornsey, 1908-9	1118	2·1	9·1	40·0	38·8	8·2	0·8	—	—	—	
New River at Hornsey, 1909-10	2801	0·9	8·3	41·7	36·8	9·8	2·4	—	—	—	
Filtered Waters—											
Thames, 1908-9	89	83·4	11·8	3·9	0·7	0·06	—	—	—	—	
" 1909-10	55	81·8	14·6	2·7	0·7	0·09	0·02	—	—	—	
Lea, 1908-9	163	85·1	10·1	4·1	0·7	—	—	—	—	—	
" 1909-10	237	88·1	8·9	2·3	0·6	—	—	—	—	—	
New River, 1908-9	7	88·3	9·4	2·0	0·07	0·07	—	—	—	—	
" " 1909-10	16	82·6	14·1	2·0	0·3	—	—	—	—	—	
Deep Wells—											
Kent, 1908-9	6	92·3	4·7	1·2	1·7	—	—	—	—	—	
" 1909-10	8	96·2	3·3	0·4	—	—	—	—	—	—	
Lea Valley, 1908-9	19	79·1	13·6	2·7	4·5	—	—	—	—	—	
" " 1909-10	16	89·0	8·8	2·1	—	—	—	—	—	—	

suspended micro-organisms during storage in large reservoirs.¹

¹ Appendixes to Minutes of Evidence, Roy. Commission on Metropolitan Water Supply, 1893, 469-475. See also "Micro-organisms in Water," P. Frankland and G. C. Frankland, London, 1894, pp. 99, 126, 131-142, 154.

The great importance of storage from the hygienic point of view was further manifest from the experiments made on the fate of pathogenic bacteria introduced into natural waters, and which showed that the duration of life of these bacteria under such conditions is generally very short.

In 1891-4 the writer had the opportunity of greatly extending his observations on this subject, as he was requested by a Committee of the Royal Society to make, in conjunction with the late Professor Marshall Ward, F.R.S., a special inquiry into the vitality of pathogenic bacteria in potable waters (see Proc. Roy. Soc.). The experiments were restricted to the study of the behaviour of the anthrax bacillus (and its spores), the typhoid bacillus, and the *B. coli communis*, and the potable waters employed were those of the Thames, Loch Katrine, and deep-well water from the chalk, these being fairly typical of the different kinds of water used for drinking purposes in this country. Experiments were made with these waters in their natural, and also in a sterilised, condition.

The results obtained may be summarised as follows:—

(1) Unsterilised water infected with anthrax bacilli containing spores was still virulent after being kept for 7 months.

(2) Anthrax bacilli taken directly from an animal dead of anthrax, and, therefore, free from spores, died rapidly (mostly in 5 days) when introduced into unsterilised water kept at low temperatures (5° and 13° in these experiments), but when introduced into the same waters and kept at 19°, the bacilli formed spores, and the latter were still present in enormous numbers even 42 days later, and doubtless for a much longer period still. This remarkable difference in behaviour is accounted for by the fact, previously discovered by Koch, that anthrax bacilli do not form spores below 16°.

The following results were obtained by introducing typhoid bacilli from one and the same cultivation and in the same numbers into each of the waters at one and the same time:—

Unsterilised water	Life of typhoid bacilli
Thames water (Oct. 19, 1893) 9°-12°	Between 0 and 13 days
Loch Katrine water (Oct. 19, 1893) 9°-12°	" 19 " 33 "
Deep well water (Oct. 10, 1893) 9°-12°	" 33 " 39 "
In two other separate experi- ments with unsterilised Thames water (May 11, 1893) and (Jan. 16, 1894) :	" 25 " 34 " " 20 " 27 "

In all these experiments only 1 c.c. of water was examined for typhoid bacilli, and the method of search, the best known at the time, was that due to Parietti, in which the water is cultivated in a phenol-broth medium at 37°, which on becoming turbid is submitted to plate-cultivation, the colonies obtained being then examined in detail for identification.

It is particularly interesting to compare with the above results those obtained by Houston in a perfectly similar inquiry and making use of all the most modern developments of bacteriological technique. Dr. Houston made 18 experiments on raw Thames, Lea, and New River waters, infecting them with typhoid bacilli (the number added being in all but three experiments very large, see table below). The presence of the bacillus was tested for at weekly intervals in 1 c.c. by means of a medium con-

taining *Agar-bile-salt-dulcitol-lactose-saccharose-saline-peptone-neutral-red-malachite-green*, and which is specially designed to favour the growth of this microbe whilst repressing that of most others. The results may be summarised in the following statement:—

In 3 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 1 week.

In 10 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 3 weeks.

In 16 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 4 weeks.

In 18 experiments the typhoid bacillus was undiscoverable in 1 c.c. in 5 weeks.

Thus, notwithstanding the great advances made in the technique of testing for the typhoid bacillus, the results obtained by Houston are essentially similar to those obtained by the writer 15 years previously. Houston has, however, extended the investigation in an interesting manner by ascertaining the length of time required before even 100 c.c. of the infected water gave a negative result on being tested by the most modern methods for the presence of the typhoid bacillus. The whole of Houston's investigations (both for 1 c.c. and for 100 c.c. of water tested) is instructively summarised in the table on p. 414.

This table shows, on the one hand, that whilst in each case nearly all the typhoid bacilli are destroyed by a single week's residence in these raw river waters, a few individuals persist for a much longer period of time. This illustrates in a very interesting and instructive manner a principle emphasised by the writer some 16 years before, 'that one of the factors determining the longevity of pathogenic bacteria placed in water, or for the matter of that placed in any unfavourable surroundings, is the absolute number in which they are present. In other words, amongst, for instance, 1000 bacteria taken from a given source there may be some individuals which will resist a particular reverse influence, whilst amongst 10 bacteria taken from the same source there may be none capable of resisting the adverse influence in question' (P. F. Frankland, Proc. Roy. Soc. 1894, 56, 486).

Before leaving the subject of the behaviour of the typhoid bacillus in water, mention must be made of some extremely interesting and ingenious experiments by the American bacteriologists, Jordan, Russel, and Zeit, in 1903. These investigators endeavoured to imitate natural conditions more closely than has been done in any other experiments by placing the typhoid-infected waters in permeable sacs made of celloidin and parchment, and then by submerging these in river, canal, or lake water, their contents were exposed to the influence of the dialysable substances present in the water under natural conditions.

Zeit experimented with Lake Michigan water and Chicago river water, the natural bacterial content of which varies between 68 and 2000 microbes per 1 c.c. in the case of the Lake, and between 80,000 and 1,500,000 microbes per 1 c.c. in that of the river water. Parallel experiments were made with infected water placed in ordinary bottles and in permeable sacs respectively. The typhoid bacilli introduced varied between 500 and 2,000,000 per 1 c.c. The destruction of the typhoid bacillus

was taken as complete when negative results were obtained on cultivating 5 c.c. of the water, the death of the typhoid bacillus being generally confirmed by the subsequent cultivation, a few days later, of much larger volumes, sometimes as much as 800 c.c. of the water. Nine experiments were made with the Michigan Lake water, the typhoid bacillus being never found after the eighth day. Five experiments were made with the Chicago River water, the typhoid bacillus being never found after the third day.

Jordan experimented with the water of the Chicago Drainage Canal, which usually contains from 100,000 to 400,000 bacteria per 1 c.c. This water was infected with from 180 to 857,000 typhoid bacilli per 1 c.c. In these experiments, however, the maximum volume

submitted to cultivation appears to have been only 1 c.c., and from negative results with even smaller volumes the death of the typhoid bacillus seems to have been concluded. Twenty-eight experiments were made in permeable sacs submerged in the canal, the typhoid bacillus being never detected after the second day, excepting in one experiment in which it was still found on the tenth day.

Russel's experiments were made with the Illinois River water, which contains from 1800 to 4000 bacteria per 1 c.c. This water was infected with 540 to 20,000 typhoid bacilli per 1 c.c. However, in these experiments, again, 1 c.c. appears to have been the maximum volume of water cultivated for the detection of the typhoid bacillus. Fourteen experiments

Description of water	Initial No. of typhoid bacilli in 1 c.c. of infected water	Number of typhoid bacilli in 1 c.c. of infected water after					Number of weeks required for destruction of typhoid bacillus in 100 c.c. of infected water
		1 week	2 weeks	3 weeks	4 weeks	5 weeks	
Thames (I) . . .	40	0 100	—	—	—	—	5
Lea (I) . . .	40	0 100	—	—	—	—	5
New River (I) . .	40	0 100	—	—	—	—	6
Thames (II) . . .	170,000	9 99.9	2	0	—	—	6
Lea (II) . . .	170,000	53 99.9	2	0	—	—	5
New River (II) . .	170,000	40 99.9	2	0	—	—	6
Thames (III) . . .	470,000	480 99.9	31	5	0	—	8
Lea (III) . . .	470,000	850 99.8	11	7	2	0	7
New River (III) . .	470,000	1430 99.7	14	7	0	—	7
Thames (IV) . . .	8,000,000	3000 99.9	30	4	0	—	8
Lea (IV) . . .	8,000,000	2900 99.9	29	5	0	—	8
New River (IV) . .	8,000,000	400 99.9	22	2	0	—	9
Thames (V) . . .	525,000	12 99.9	1	0	—	—	8
Lea (V) . . .	525,000	32 99.9	2	0	—	—	7
New River (V) . .	525,000	29 99.9	3	0	—	—	5
Thames (VI) . . .	475,000	210 99.9	12	2	1	0	9
Lea (VI) . . .	475,000	80 99.9	11	2	0	—	8
New River (VI) . .	475,000	30 99.9	3	0	—	—	7

were made in permeable sacs submerged in the Illinois River, the typhoid bacillus being never found after the third day, excepting in one case in which it was detected on the ninth day.

More recently, again, Houston has taken typhoid bacilli not from cultivations but from the human subject and introduced them into raw Thames water. He found that such bacilli perished very rapidly—much more quickly in fact than had been his experience with cultivated strains of the microbe.

The uncultivated typhoid bacteria were obtained from the urine of a 'typhoid carrier,' and on Aug. 9, 1910, the centrifuged deposit (3.5 c.c.) from 389 c.c. of urine was added to 8000 c.c. of raw Thames water; the number of typhoid bacilli was determined as follows:—

At time of mixture, 770,000 typhoid bacilli per 1 c.c. of river water.

After 1 week, 4 typhoid bacilli per 1 c.c. of river water.

After 2 weeks, 0 typhoid bacilli in 100 c.c.

On the 24th day from the commencement of the experiment half-a-pint (about 284 c.c.) of the infected water was drunk, this quantity of water having originally contained 218,680,000 typhoid bacilli. Similar amounts were drunk with impunity on the 25th, 26th, 27th, and 28th days after the beginning of the experiment.

On Aug. 19, 1910, the experiment was repeated with a fresh sample of urine, the number of typhoid bacilli per 1 c.c. of river water being 1650. A week later no typhoid bacilli could be found, and on the 23rd, 24th, 25th, 26th, and 27th day from the beginning half-a-pint of the infected water was drunk each day without any ill-effect (Sixth Research Report, Metrop. Water Board, Nov. 1910, p. 7).

If this drinking part of the experiment is to prove anything it would be necessary for Dr. Houston to follow it up by drinking a similar number of fresh typhoid bacilli from the same

patient and contracting the disease, for without this last act we have no certainty that Dr. Houston is susceptible to this malady, and, therefore, a fit *corpus vile* on which to make this crucial test.

Vitality of the Spirillum of Asiatic cholera in potable water.—Experiments were made by Houston with the cholera spirillum on exactly the same lines as those which he had previously adopted in the case of the typhoid bacillus in raw Thames, Lea, and New River water. The principal conclusions arrived at may be summarised as follows (4th Report on Research Work, Metrop. Water Board, June, 1909):—

(1) Cholera vibrios die very rapidly in raw Thames, Lea, and New River water as the result of storage in the laboratory. At least 99·9 p.c. perished within one week, and in none of the experiments could any cholera vibrios (recognisable as such) be found even in 100 c.c. of water 3 weeks after its infection. In more than half the experiments the results were negative by the second week.

(2) The isolation of cholera vibrios from artificially infected raw river water presents no insuperable difficulties even when the number artificially added is very small, both actually and relatively to the bacteria nominally present in the river water.

(3) On the other hand, microbes liable (after careful study) to be mistaken for true cholera vibrios were not found in comparable, but non-infected, river water samples examined under precisely similar conditions.

Thus the cholera vibrios are much more perishable in these raw river waters than are the typhoid bacilli under similar conditions.

The comparatively short duration of life of pathogenic bacteria when introduced into natural waters and more especially into surface waters, which these numerous and independent investigations establish, clearly show that the process of storage in large reservoirs must form a very important safeguard against the water-carriage of zymotic diseases. This safeguard, which is supplementary to and quite independent of that of filtration, has the great advantage of being under perfect control and much less liable to accidental disturbances than are most other methods of water-purification. It is, however, unfortunate that many reservoirs attached to water works have not been designed so as to secure the maximum advantages of storage, and their rearrangement with this object in view is generally a matter of great expense and sometimes impracticable. It is to be hoped that in future engineers will be more careful to arrange for such a circulation of the water that each particle of water entering shall remain as long as possible in the reservoir before passing out.

The influence of storage on the bacteriology of surface waters has recently been made the subject of very extended and interesting investigations by Houston in connection with the London water supply. There can be no doubt that adequate storage brings about the following beneficial changes:—

(1) Reduces the number of bacteria of all sorts.

(2) Reduces the number of bacteria capable of growing on agar at blood heat.

(3) Reduces the number of bacteria capable of growing in a bile-salt medium at blood heat.

(4) Reduces the number of coli-like microbes.

(5) Reduces the number of typical *B. coli*.

(6) Alters certain bacteriological ratios for river-waters, e.g. it reduces the number of typical *B. coli* to a proportionately greater extent than it reduces the number of bacteria of all sorts.

(7) If sufficiently prolonged, it devitalises the microbes of water-borne disease (e.g. the typhoid bacillus and the cholera vibrio).

(8) Reduces the amount of suspended matter.

(9) Reduces the amount of colour.

(10) Reduces the amount of ammoniacal nitrogen.

(11) Reduces the amount of oxygen absorbed from permanganate.

(12) Usually reduces the hardness and may reduce (or alter the quality of) the albuminoid nitrogen.

(13) Alters certain chemical ratios for river-waters; e.g. the colour results improve more than the results yielded by the permanganate test.

(14) Has a marked 'levelling' effect on the totality of water delivered to the filter-beds.

(15) Tends generally to lengthen the life of the filters (only under exceptional conditions is the contrary true).

(16) An adequately stored water is to be regarded as a 'safe' water, and the 'safety change' which has occurred in a stored water can be recognised by appropriate tests.

(17) The use of adequately stored waters renders any accidental breakdown in the filtering arrangements much less serious than might otherwise be the case.

The experimental basis for many of the above statements with regard to the benefits of storage will be found in the table on p. 416 (Houston, Annual Report, March 31, 1910, p. 52):—

Fæcal streptococci in water.—Attempts have been made to supplement the indications of faecal contamination yielded by the presence of *B. coli*. The most recent and noteworthy of these is the examination of water for the presence of certain streptococci which are usually very abundant, sometimes even more abundant, in human faeces than is the *B. coli*. This matter has been engaging the attention of Dr. Houston since 1898, and he has (June, 1910) given a special account of the results which he has obtained.

At the outset it should be pointed out that these streptococci are not peculiar to human excreta, but are also abundantly present in those of the higher animals, many of Houston's experiments having been made with streptococci obtained from cow-dung. The study of these micro-organisms does not, therefore, at present put us in possession of that all important desideratum—a means of distinguishing between contamination due to the excrement of man and that which is due to the lower animals.

According to Houston, human faeces contain, roughly, 100,000 streptococci per 1 grm. On the other hand, in some stools streptococci are either absent or present in such small numbers relatively to those of other bacteria that search

for them is useless. Their presence in water has hitherto been ascertained by spreading 1 c.c. of the water on a Drigalski-Conradi plate, on which medium, after incubation at 37°, the streptococci give rise to very minute colonies, which can then be sub-cultivated for determination of their biochemical characters.

Of 100 different cultures of streptococci

obtained by Houston from sewage works faeces: (a) 100 produced acid in lactose and in raffinose media, and all of them clotted milk. (b) None reduced nitrates to nitrites. (c) Only four produced acid in a mannite medium. (d) 97 produced acid in a salicin medium. (e) 49 produced acid in a saccharose medium.

The grouping of these properties is best

LONDON WATER SUPPLY.

Influence of storage shown by samples collected during 12 months ending March 31, 1910 (Houston).

		No of bacteria per 1 c c			B. coli (typical)												
		Gelatin 20°- 22°C 3 days	Agar 37°C Agar 37°C 2 days	Tauro Agar 37°C 2 days	c.c. 100	c.c. 100	c.c. 100	c.c. 10	c.c. 10	c.c. 0.1	c.c. 0.01	c.c. 0.001	c.c. 0.0001	c.c. 0.00001	c.c. 0.000001		
					-	+	+	+	+	+	+	+	+	+	+		
					p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.	p.c.		
Raw Thames water before storage	5,208	495	63		0.5	0.5	6.3	26.9	52.9	12.8				-	-		
Thames water after storage at Staines Reservoirs	240	88	3		21.4	17.1	25.7	4.3	1.4					-	-		
Thames water after storage at Chelsea Reservoirs	442	61	8		11.3	28.0	21.3	9.3						-	-		
Thames water after storage at Lambeth Reservoirs	354	54	8		20.8	43.0	31.0	4.2						-	-		
Raw Lea water before storage	37,071	837	86		0.0	0.5	6.3	31.4	30.7	13.2	7.8	0.5	0.5		0.5		
Lea water after storage at Walthamstow Reservoirs	121	21	4		60.0	30.6	8.0	1.3						-	-		

indicated by means of a convention similar to that employed in the case of *B. coli*, in which syllables are made to represent definite biochemical reactions, thus:—

la = acid in a lactose medium.
ma = " " mannite "
mi = clot " milk "
ra = acid " raffinose "
sac = " " saccharose "
sal = " " salicin "

The 100 streptococci examined may then be thus classified:—

la-mi-ra-sal . 49 la-ma-mi-ra-sac-sal 4
la-mi-ra-sac-sal . 44 la-mi-ra-sac . 1
 la-mi-ra . 2

Thus 97 p.c. clotted milk, and produced acid in lactose, raffinose, and salicin media, and of these 48 produced acid and 49 no appreciable acidity in a saccharose medium.

During the year 1909 Houston examined the raw (unfiltered and unstored) Thames, Lea, and New River waters for streptococci, employing 1 c.c. of each sample on Drigalski plates as above, with the following results:—

No of times streptococci were found in 1 c.c.
53 weekly samples of Thames water . 13
52 weekly samples of Lea water . 13
53 weekly samples of New River water . 2

As regards the types of streptococci found in the above 28 samples of the 71 sub-cultures of

streptococci examined the following combinations were found:—

	Thames	Lea	New River
La-ma-mi-ra-sac-sal.	1	2	0
La-ma-mi-sac-sal	1	3	0
La-mi-ra-sac-sal	9	17	0
La-ma-sac-sal	0	1	0
La-ma-mi-sac	0	3	0
La-mi-sac-sal	4	9	0
La-mi-ra-sac	2	10	0
La-sac-sal	0	1	2
La-mi-sal	0	1	0
La-mi-sac	2	0	0
La-ra-sac	0	3	0
Total	19	50	2

The above results are especially interesting as showing that the two impurer waters (Thames and Lea) contained streptococci much more frequently than the far purer water (New River), and further, that the streptococci actually discovered in the latter were of a type more remote from that of those which are usually discovered in faeces.

Bearing in mind that, on an average, upwards of 90 p.c. of the raw Thames and Lea samples, and about 50 p.c. of the raw New River samples contain typical *B. coli* in 1 c.c. or under, whilst in only 25 p.c. of the raw Thames and Lea samples, and in only 3.8 p.c. of the raw New River samples were streptococci found, it follows that the streptococci are a far less delicate index of contamination than is the *B. coli*. The absence of streptococci in 1 c.c. of a water

cannot, therefore, be regarded as any criterion of its purity. The relative scarcity of streptococci in waters which have undoubtedly received a considerable amount of sewage matters is accounted for by the fact, established by Hous-ton, that streptococci very rapidly die off when placed in water. This circumstance points, of course, to the presence of streptococci serving as an indication of very recent contamination.

Recent bacteriological methods applied to other processes of water purification.—From the evidence already brought forward it appears that confidence in the purification which can be effected by storage and sand-filtration, under favourable conditions, has been distinctly strengthened by the application of the more recent developments of bacteriological water examination—search for *B. coli* and other microbes more or less connected with sewage contamination.

Certain other processes of water-purification which are employed on the large scale may now be briefly considered.

Mechanical filters.—The use of mechanical filters originated in America, and their employment in our own country is becoming more and more common. Such filters are in use at Bolton, Burnley, Heywood, Edinburgh, Crewe, Gloucester, Shrewsbury, and other places in Great Britain, whilst they have also been installed in India, Japan, and some of the colonies. Space does not permit the discussion of the relative merits of the two different processes of filtration. They each possess their advantages and disadvantages; they can each be made to yield good and bad results according to the manner in which they are employed. The following results may serve as an illustration of the very high degree of purification which can be secured

PURIFICATION OF RIVER WATER BY MECHANICAL FILTERS.

	Number of bacteria in 1 c.c.				<i>B. coli</i> (typical) in			
	Gelatin at 20° C.		Carbolic gelatin at 20° C. 7 days	Bile-salt agar at 37° C. 4 days	100 c.c.	10 c.c.	1'0 c.c.	0'1 c.c.
	2 days	7 days						
Raw river water	3700	—	35	19	+	+	+	+
Ditto after passing sand filters	130	405	2	2	+	+	0	0
Ditto after further passing mechanical filters	8	33	0	0	0	0	0	0

by means of mechanical filters, which, in this instance, were employed to further purify a river water, which was being very imperfectly purified by some defective sand-filters.

Clark's process of softening.—Already in 1885 the writer showed that in softening water with lime, a very large proportion of the bacteria are carried down with the precipitated chalk, but that if the latter is allowed to stand in contact with the softened water bacteria again pass from the precipitate into the water. In the softening process this removal of bacteria may, under favourable conditions, amount to upwards of 90 p.c.

Recently the writer had occasion to deal with a chalk well water, which was causing anxiety in consequence of its frequently containing *B. coli* in rather small volumes. The most obvious and unobjectionable method of purification which suggested itself was softening with lime, inasmuch as the water contained plenty of calcium bicarbonate in solution. The following table shows the results obtained in a number of small-scale experiments in which this water was treated with lime, and sometimes with aluminoferric, and in which the softened water was sometimes decanted, sometimes filtered through paper without disturbing the precipitate ('clear filtration' in the table), and sometimes filtered after deliberately disturbing the precipitate ('turbid filtration' in the table).

A great many experiments were made in addition to those recorded below, but always with the same disappointing result, that not-

withstanding a large percentage reduction in the total number of bacteria taking place, it was only in rare cases that the *B. coli* was banished from 100 c.c. of the water by the precipitation process. It must be remembered that the demands now commonly made on a purification process with regard to the removal of *B. coli* are much more stringent than with regard to the removal of bacteria in general. Thus, should an untreated water contain 1000 bacteria per 1 c.c., if by treatment the number were reduced to 50 per 1 c.c., this would represent a purification of 95 p.c., and the water would be regarded as quite satisfactory from the point of view of the total number of bacteria present. But, if an untreated water contained the *B. coli* in 0'1 c.c., and after treatment this microbe were not present in less than 10 c.c., this would signify a removal of 99 p.c. of the *B. coli* present in the original water. But so high is the standard of purity at present often demanded in respect to freedom from *B. coli*, that the water which had thus been purified to the extent of 99 p.c. might still be regarded as of a questionable degree of purity.

Ozone treatment.—The bactericidal properties of ozone have long been demonstrated,¹ but it is only in quite recent years that it has been used on a large scale for the sterilisation of town water-supplies. In France the drinking waters

¹ Ohlmüller, *Arbeiten a. d. Kaiserl. Gesundheits-amte*, 1892, 229; van Ermengen, *Ann. de l'Inst. Pasteur*, 1896, 673; Ohlmüller and Fraß, *loc. cit.* 1900, 417; Proskauer and Schöller, *Zeitsch. Hygiene und Infektionskrankheiten*, 41, 227, 243; 42, 269; *Chimie des Ann. de l'Inst. Pasteur*, 1899, 13, 244.

PURIFICATION OF WATER BY LIME AND ALUMINOFERRIC.

	Gelatin		B. coli in				
	No. of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1° c.c.	0·1 c.c.
Raw well water	10 259	2 7	+	+	+	0	0
Ditto after filtration through sterile paper	7 236	2 7	+	+	+	0	0
Ditto+lime water, filtered through sterile paper after 1 hour's subsidence	0 90	2 7	+	+	0	0	0
Ditto+lime water and aluminoferric, filtered after 1 hour	0 39	2 7	+	0	0	0	0
Ditto+lime water; clear filtration after 3 hours	1 74	2 7	+	0	0	0	0
Ditto+lime water and aluminoferric; clear filtration after 3 hours	1 44	2 7	+	+	0	0	0
Ditto+lime water; turbid filtration after 3 hours	0 41	2 7	+	+	0	0	0
Ditto+lime water and aluminoferric; turbid filtration after 3 hours	0 41	2 7	0	0	0	0	0
Ditto+lime water; clear filtration after 25 hours	3 96	2 6	+	+	+	0	0
Ditto+lime water and aluminoferric; clear filtration after 25 hours	0 14	2 6		0	0	0	0

of the towns of Nice, Chartres, and Cosne are being subjected to ozone treatment, whilst a plant for the treatment of 10 million gallons of water was projected in connection with the Paris waterworks. In Germany there are installations at Paderborn, Schierstein, and Hermannstadt.

The writer has made experiments with ozone in connection with the practicability of purifying the chalk well-water to which reference has just been made above. The extraordinary efficacy of this agent will be apparent from the foregoing results obtained in experiments in which the impurities of the chalk

OZONE TREATMENT OF WATER.

	Gelatin		B. coli in					
	No. of bacteria per 1 c.c.	Days incubated at 20° C.	100 c.c.	50 c.c.	10 c.c.	1° c.c.	0·1 c.c.	0·001 c.c.
Chalk well-water	7,000	2	+	+	+	+	+	+
+4 p.c. polluted canal-water	10,000	7						
Ditto after treatment with 5 times its volume of ozonised air during 2 hours; cultivations made 2 hours later	0 0	2 7	0	0	0	0	0	0
Chalk well-water	4,000	2	+	+	+	+	+	+
+4 p.c. polluted canal-water	7,000	7						
Ditto after treatment with its own volume of ozonised air during 24 minutes; cultivations made 1 hour later. (The ozonised air contained 0·23 p.c. ozone)	0 3	2 7	0	0	0	0	0	0

well-water were enormously exaggerated by the addition of 4 p.c. of polluted canal-water.

Bleaching-powder treatment.—The bactericidal action of hypochlorites, again, has been long known, and bleaching powder is one of the

oldest and commonest of disinfectants. The use of hypochlorites for the sterilisation of water-supplies was first brought into prominence in this country by Houston, who used 'Chlorox' which is an electrolysed solution of common

PURIFICATION OF WATER BY TREATMENT WITH BLEACHING POWDER.

Untreated chalk well-water						Chalk well-water after treatment with bleaching-powder						Millions of parts of water treated per 1 part of available chlorine used	
No. of bacteria gelatin at 30°C.		B. coli in					No. of bacteria gelatin at 20°C.		B. coli in				
		+	+	+	+	+			+	+	+		+
2 days	7 days	100 c.c.	50 c.c.	10 c.c.	1'0 c.c.	0'1 c.c.	2 days	7 days	100 c.c.	50 c.c.	10 c.c.	1'0 c.c.	
First series of experiments													
98	640	+	+	+	0	0	17	83	+	+	0	0	1 part chlorine per 1 million
13	260	+	0	0	0	0	0	5	0 ¹	0	0	0	1 part chlorine per 1 million
20	356	+	+	+	0	0	0	33	0 ¹	0	0	0	1 part chlorine per 2 million
22	202	+	+	+	0	0	0	1	0	0	0	0	1 part chlorine per 2 million
13	539	+	+	+	0	0	0	9	0	0	0	0	1 part chlorine per 2 million
18	528	+	+	+	0	0	0	1	0	0	0	0	1 part chlorine per 2 million
9	315	+	+	+	+	0	0	4	0	0	0	0	1 part chlorine per 2 million
16	794	+	+	0	0	0	0	5	0	0	0	0	1 part chlorine per 4 million
9	152	+	+	0	0	0	0	2	0	0	0	0	1 part chlorine per 4 million
12	80	+	+	0	0	0	0	9	0	0	0	0	1 part chlorine per 4 million
14	115	+	+	0	0	0	0	10	0	0	0	0	1 part chlorine per 4 million
54	350	+	+	+	0	0	9	63	0	0	0	0	1 part chlorine per 8 million
17	116	+	+	+	0	0	12	37	0	0	0	0	1 part chlorine per 8 million
17	507	+	+	+	0	0	10	22	0	0	0	0	1 part chlorine per 8 million
—	—	—	—	—	—	—	8	38	0	0	0	0	1 part chlorine per 8 million
Av. 24	358						Av. 4	21					
Second series of experiments													
6	76	+	+	0	0	0	1	4	+	+	0	0	1 part chlorine per 1 million
1	105	+	0	0	0	0	0	3	0 ¹	0	0	0	1 part chlorine per 2 million
6	353	+	0	0	0	0	0	0	0	0	0	0	1 part chlorine per 4 million
3	305	+	0	0	0	0	0	1	0	0	0	0	1 part chlorine per 4 million
1	129	+	+	0	0	0	0	3	0	0	0	0	1 part chlorine per 4 million
4	181	0	0	0	0	0	1	1	0	0	0	0	1 part chlorine per 4 million
5	244	+	+	0	0	0	0	0	0 ¹	0	0	0	1 part chlorine per 4 million
0	111	+	+	0	0	0	0	9	0	0	0	0	1 part chlorine per 8 million
5	102	+	+	+	0	0	0	3	0	0	0	0	1 part chlorine per 8 million
1	181	+	+	0	0	0	0	15	0	0	0	0	1 part chlorine per 8 million
2	157	+	+	0	0	0	—	—	—	—	—	—	
9	289	+	+	0	0	0	0	1	0	0	0	0	1 part chlorine per 8 million
0	316	+	+	0	0	0	0	0	0	0	0	0	1 part chlorine per 8 million
1	120	+	0	0	0	0	0	6	0	0	0	0	1 part chlorine per 8 million
2	80	+	0	0	0	0	0	0	0	0	0	0	1 part chlorine per 8 million
Av. 3	183						Av. 0	3					

¹ B. coli found absent even in 500 c.c.

salt, for the treatment of the Lincoln water-supply during the memorable epidemic of typhoid which occurred in that city in 1904-5.¹

The writer had occasion some years ago to investigate the efficiency of the bleaching-powder treatment on a chalk well-water, the experiment being made with a large experimental plant.

From the results given above it will be seen what a high degree of purification is obtained by this simple and inexpensive method of treatment, even when extremely small quantities of bleaching-powder are added to the water.

¹ In that epidemic there were as many deaths (119) from typhoid in six months as had occurred from the same cause during the previous eighteen years.

Thus the only occasions on which *B. coli* was found even in 100 c.c. of the treated water was on the first day of each of the two series of experiments and thus when the apparatus had presumably not yet been completely washed out with treated water. On several occasions even 500 c.c. of treated water was examined for *B. coli*, and this microbe was on each such occasion found to be absent even in that large volume.

Similar results have been obtained by Sims Woodhead, Thresh, Hehner, Rideal, and others.

For the more recent experience in the chlorination of drinking water, and for a summary of many other important points, the reader

should consult Houston, Progress in Water Purification, Trans. Inst. of Water Engineers, 27, 1922, p. 117.

Treatment with ultra-violet light.—The known bactericidal action of the ultra-violet rays has been applied by Victor Henri to the sterilisation of water on a large scale. The rays are supplied by a Cooper-Hewitt mercury lamp. The lamp is worked with 3 amperes at 220 volts, and is placed in the bend of a semicircular trough through which the water is passed. At Marseilles the process has been tried with a plant yielding 130,000 gallons per 24 hours, and using 120 watts per 1000 gallons. The crude water always contained some *B. coli*, and the total number of bacteria varied between 30 and 300 per 1 c.c., whilst, in the treated water, *B. coli* was absent and the total number of bacteria was reduced to an average of 1 per 1 c.c. (Modern Methods of Water Purification, Don and Chisholm, London, 1911). See also W. Clemence, Engineering, Jan. 27 and Feb. 3, 1911.

Conclusions.—During the nearly 40 years that the systematic bacteriological examination of water has been practised an enormous amount of work has been carried out by a large number of investigators, but notwithstanding the immense multiplication of results it must be admitted that no very surprising novelties have been brought to light since the year 1895. By then all the salient features in the bacteriology of water had been mapped out, and the past 30 years have more especially been occupied in filling in countless details and in confirming over and over again what had already been broadly established.

Thus, already in the earlier period, the methods of bacteriology had been successfully applied to a determination of the value of the most varied processes of water purification natural and artificial, filtration, storage, precipitation, sedimentation, &c. It had been shown how such processes should, in the interests of public health, be continuously watched over and controlled by bacteriological examinations made at frequent intervals. Again, the vitality in water of the principal bacteria associated with water-borne zymotic disease had been investigated, and the results then obtained were substantially the same as those which have been arrived at by the most recent developments in bacteriological technique. In a word, these most recent developments in the methods of bacteriology have served to confirm and emphasise the conclusions which had been generally arrived at by the less perfect methods of the earlier period.

The all-important questions which the water-examiner has to answer are the same to-day as they have been all along: (a) has the water been contaminated with the excreta of man?; and (b) if such contamination has taken place, has the water in its subsequent history been subject to conditions which would ensure the destruction or removal of the pathogenic bacteria which may at any time be present in such human refuse?

To the first of these questions bacteriology cannot give a categorical answer even to-day, because we are not acquainted with any microbes which are absolutely characteristic of human excreta. The greatly increased facilities for the

detection and quantitative determination of the *B. coli*, however, have undoubtedly placed us in a position to ascertain readily whether and to what extent a water has been contaminated with excremental matter irrespectively of whether the latter is of human or animal origin, but it is obvious that this will not, in general, carry us very far, inasmuch as practically all surface water must be more or less so contaminated.

To the second question a similarly qualified answer, again, can be readily given. If the water is free from *B. coli* in a large volume, it may safely be concluded that *a fortiori* it is free from the typhoid bacillus in a similar volume. But should the *B. coli* be found in a small volume, it does not follow that the water may at any time be liable to contain typhoid bacilli, because the discovery of the *B. coli* does not prove that the water has been contaminated by man at all.

Thus with regard to both questions, it is obvious that we are in a much stronger position in the matter of exculpating than in that of incriminating a water. However, the inference that a water free from *B. coli* in a large volume is, therefore, necessarily a safe one, requires a slight qualification in view of the remarkable and interesting revelations which have in recent years been made with regard to what are known as 'typhoid carriers.' Some of these persons suffering from 'ambulatory typhoid' discharge typhoid bacilli in the urine, and it is thus possible that water may actually become contaminated with typhoid bacilli without at the same time receiving any *B. coli*. Although this is not likely to be of frequent occurrence, still its possibility, especially in the case of men working in wells, filter-beds, and service reservoirs, should on no account be disregarded.

Certainly one of the most important advances made in bacteriology during recent years is the careful characterisation of bacteria by means of biochemical tests, and the isolation of particular types of bacteria from such mixtures as are present in water by means of special culture-media, liquid and solid. However, until bacteriologists have agreed upon uniform tests for each particular microbe it is unavoidable that there should be much confusion and that the results obtained by different observers should be difficult to compare. Under these circumstances the interpretation of results by the individual observer is a matter of the greatest importance, and it is needless to say that unless the individual observer has a wide personal experience and a thorough knowledge of the factors affecting the purity of water-supplies of different kinds his interpretation of the results obtained will not only have little practical value but may easily lead to very serious mistakes.

Thus, whilst the outstanding achievement in bacteriological water examination during the past 25 years is the systematisation of tests for detecting the presence in water of specific bacteria, especially *B. coli*, Streptococci, and the spores of *B. enteritidis sporogenes*, the different possible sources of these bacteria, and their different hygienic significance according to source, render any hard and fast application of standards based on the presence of these microbes impossible without liability to serious errors of judgment being committed.

Space has not permitted reference in detail to the spores of *B. enteritidis sporogenes*¹ as an index of faecal contamination. The figures on p. 411 show how much less abundant in faeces are these spores than is the *B. coli communis*. They do not, therefore, form such a delicate test for sewage contamination as does the *B. coli*, and their final identification is much less certain. The water-bacteriologist should, however, not neglect a search for these spores, but should regard the evidence which their presence or absence affords as supplementary to that which is furnished by the *B. coli* results.

In conclusion a word may be said with regard to the relative value of the chemical and bacteriological examination of water. At the present time it is often supposed that the chemical has been entirely superseded by the bacteriological examination, and that the chemical analysis of drinking water can be dispensed with. In reality the two methods of examination supplement each other. In those cases in which the source and general characters of a water supply are well known, the variations in purity from day to day or from week to week can undoubtedly be more satisfactorily watched by means of bacteriological examination. On the other hand, it is often desired by means of a single examination to ascertain the fitness or otherwise of a water for domestic use, and in such cases the omission of a chemical analysis may lead to an entirely erroneous opinion being formed. The ingredients detected by chemical analysis—organic matter, ammonia, nitrates, chlorides, &c.—on which an opinion as to hygienic quality is based, are all much more permanent and uniform features in the composition of the water than are the amount and the nature of the bacterial life which it may contain. The chemical analysis will, therefore, if skilfully interpreted, enable a much better idea of the potability of the water to be obtained than would be possible from a single bacteriological examination.

There are so many factors and considerations which have to be taken into account if an opinion of any real value as to the hygienic quality of water is to be formed, that no knowledge or information which can be gained either by chemical, or by bacteriological examination, or by inspection of source, or by any other available means whatsoever should be neglected.

P. F. F.

WATER-GAS v. GAS, WATER.

WATER-GLASS. *Soluble glass v. GLASS.*

WATER-OF-AYR STONE v. WHETSTONE.

WATER-SOFTENING. Some natural waters require the use of a relatively large amount of soap to form a lather, and are characterised as 'hard' waters. They contain impurities which react with and destroy soap forming a curdy precipitate, and the generic term 'water softening' comprises all processes which remove these impurities, wholly or in part. Certain processes of water purification or treatment not falling strictly within this definition, are nevertheless so related to true water-softening processes that they are most conveniently considered here.

Effects of hardness.—Hardness renders water unsuitable for many domestic and industrial uses. In washing and scouring, hard water wastes soap and discolours fabrics by the deposition of insoluble salts; in the manufacture of worsteds and woollens it decreases the pliancy of the fabric; in tanning it deposits lime in the hides; when heated or evaporated in kettles, calorifiers, boilers, &c., it deposits scale which impairs heat transmission and increases charges for maintenance and depreciation. Bicarbonate hardness hinders the uniform dyeing of fabrics. Even ice prepared by freezing hard water is unsatisfactory, being opaque, or coloured if iron is present, and leaving a dirty sediment on melting (Behrman, *J. Ind. Eng. Chem.*, 1921, 13, 235).

Nature of hardness.—Hardness may be caused by the presence in water of soluble salts of most metals other than the alkali metals; for example, barium chloride is occasionally found as a major impurity causing hardness. But in the great majority of cases hardness is due mainly to salts of calcium and magnesium, and to a lesser degree to salts of iron and manganese.

It is usual to recognise two types of hardness, temporary and permanent.

Temporary hardness due to bases, usually calcium but occasionally iron, present as bicarbonates, is so called because it is removed by boiling the water, whereby excess carbon dioxide is gradually expelled and the less soluble normal carbonate is precipitated. With regard to certain softening processes which depend entirely on this reaction, it is important to observe that at temperatures below 100°C. but little carbon dioxide is removed unless the water be violently agitated, and that even at 100° some 10 minutes' boiling is necessary for its complete expulsion (Paul, *Boiler Chemistry*, Longmans, p. 94).

Hardness due to magnesium bicarbonate, often regarded as temporary, is less affected by boiling than that due to calcium bicarbonate, normal magnesium carbonate being more soluble than calcium carbonate. On the other hand, at the temperatures attained in boilers, magnesium carbonate is hydrolysed to magnesium hydroxide, which is precipitated and may even be dehydrated to the oxide.

Permanent hardness is that which persists after boiling; it is due to the combined effect of a small quantity of residual normal carbonates and of other salts, chiefly sulphates, nitrates, and chlorides, of calcium and magnesium.

Quantitative estimate of hardness.—Originally hardness was measured and stated in terms of the number of grains of calcium carbonate per gallon of a solution equivalent to the water under test in respect of the quantity of soap required to produce a lather. Hardness corresponding to 1 grain CaCO_3 per gallon (1 part CaCO_3 in 70,000 parts of water) is described as 1 degree (Clark) of hardness. Hardness is now frequently expressed in terms of parts of CaCO_3 per 100,000 parts of water; a quantity evidently equal to $10/7 \times$ the hardness expressed in Clark degrees.

It is convenient to give here a statement (Table I) of the solubilities at about 15°C. of the chief hardening impurities, together with the equivalent concentration of calcium carbonate.

¹ Klein, Local Government Board; Medical Officer's Reports, 1897-8, 1898-9, 1901-2; Klein and Houston, *ibid.* 1899-1900; Hewitt, Trans. Jenner Institute, vol. 11, 76; *Ann. State Medicine*, 1904, 12, 158.

in grains per gallon and parts per 100,000, which, evidently, represent the maximum hardness of water which can be caused by each impurity at the ordinary temperature.

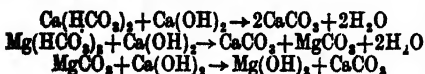
TABLE I

Impurity	Solubility. Parts per 100,000	Equivalent hardness.	
		Parts per 100,000	Degrees (Clark)
CaCO ₃ } Dissolved	118	118	82.6
MgCO ₃ } as bi-	3100	3675	2570
FeCO ₃ } carbonates	abt. 400	345	240
CaCO ₃	6.8	6.8	4.8
MgCO ₃	abt. 70 ¹	83	58
CaSO ₄	198.3	145.5	101.8
Ca(OH) ₂	170	230	161
Mg(OH) ₂	0.9	1.54	1.08

¹ The solubility of magnesium carbonate varies greatly with the pressure of carbon dioxide; the figure given is for a solution in equilibrium with carbon dioxide at about the partial pressure normally existing in the atmosphere.

Some of the solubility data are uncertain, but the table will serve to give a useful indication of the softening effect of the reactions under consideration. Thus, hardness due to calcium bicarbonate alone, which may in equilibrium with carbon dioxide at atmospheric pressure attain a maximum of 82.6 degrees, can be reduced by boiling to that due to calcium carbonate alone, viz. 4.8 degrees; whilst that due to magnesium bicarbonate which may reach a maximum of 2500 degrees under the above conditions, is, by boiling, reduced only to 58 degrees, equivalent to the solubility of magnesium carbonate.

Water softening reactions.—Temporary hardness is usually removed by the addition of lime, as originally advocated by Clark in 1841, and applied by J. H. Porter in the 'Porter-Clark' process (J. Soc. Chem. Ind. 1884, 3, 51). The chief reactions involved are:



From Table I it appears that the residual hardness in a solution saturated at 15° with calcium carbonate and magnesium hydroxide would be 5.9 degrees. In practice the reactions are not complete and it is difficult to avoid a slight excess or deficit of lime, but the minimum hardness actually attained at 15° is about 3.5 degrees.

Lime precipitates as hydroxide any magnesium present as sulphate, chloride, &c., but an equivalent amount of calcium remains in solution; lime does not, of course, react with calcium salts: hence permanent hardness is unaffected by the lime treatment.

Permanent hardness due to calcium salts may be treated by addition of sodium carbonate (soda ash), which precipitates calcium as carbonate, leaving in solution sodium salts of the acidic radicals with which it was combined; thus, e.g.



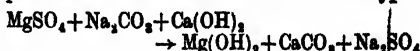
The origin of this use of soda ash is obscure, but it is clear that P. A. Maignen was one of the first to employ it, as a powder with lime and steam (J. Soc. Chem. Ind. 1893, 5, 22). Sodium

carbonate also removes temporary hardness due to calcium bicarbonate:

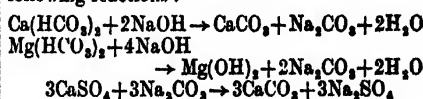


but the method has the disadvantage of leaving sodium bicarbonate in solution and is relatively costly.

Reference to Table I shows that addition of sodium carbonate cannot reduce permanent hardness due to magnesium below the 58 degrees, due to the solubility of magnesium carbonate. Such hardness is best removed by the addition of caustic alkali, or, what is equivalent and cheaper, lime and soda ash in equivalent proportions. The reaction involved is of the type:



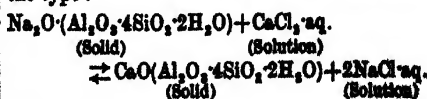
Should a water have only permanent hardness due to magnesium salts the use of caustic soda has the advantage of leaving no residual hardness due to calcium carbonate. In the equally unusual case where the bicarbonate hardness is exactly two-fifths of the total hardness, caustic soda alone will soften the water according to the following reactions:



Certain other reagents merit brief mention. Borax, sodium silicate, and sodium phosphate can precipitate calcium and magnesium as the relatively insoluble borates, silicates, and phosphates; the two former are common ingredients in washing powders, but none of the three is used in industrial water-softening. Barium hydroxide is an effective softening reagent, especially if the impurity in water is chiefly sulphate, but its high cost and poisonous character hinder its general use.

A suspension of barium carbonate in milk of lime has been patented as a softening reagent (H. Reiser, D. R. P. 333994, 1916) and is used in certain plants by Royle; it has the advantage of yielding a water of minimum hardness even where precise adjustment of the quantity of reagent is not attained, but is liable to acquire a coating of barium sulphate, rendering it inactive.

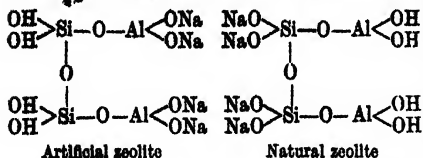
Permutite, or artificial zeolites, form a distinct class of water-softening reagents. They are hydrated aluminosilicates of soda, similar in composition to naturally occurring zeolites, e.g. *analcite*, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Such compounds, in contact with aqueous solutions of metallic salts, enter into reversible reactions of the type:



With dilute solutions of salts of the heavier metals, such as hard water, the reaction is almost complete toward the right; with concentrated solutions of sodium salts, e.g. brine, the reverse reaction largely preponderates. The utility of such reactions in water-softening is obvious, and their application is discussed below.

Though some waters are naturally softened by percolation through strata containing

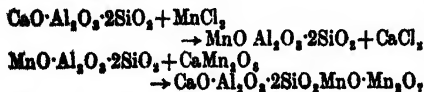
zeolites, these minerals undergo base-exchange but slowly and to a small extent. The artificial zeolites, on the other hand, undergo base-exchange readily and to a large extent, and this has been attributed by Gans to a difference in constitution of the kind indicated by the following formulae:—



Permutit was first prepared by Gans (D. R. P. 174097, 1905) by allowing alkali aluminate free from uncombined alkali to act on hydrated silicic acid, employing heat to complete the reaction. Calcium permutit is formed by treating the product with calcium chloride solution to replace soda by lime.

Numerous methods for preparing similar reagents have since been described, for details of which the patent literature must be consulted. The more important methods consist (a) in fusing together convenient ingredients to yield the desired composition, e.g. 3 kaolin, 6 quartz, and 12 soda-ash (J. D. Reidel, D. R. P. 186630, 1906; see also D. R. P. 200931, 1907); or (b) in hydrating by high pressure steam, with or without the addition of alkali, natural minerals of appropriate composition such as trass, phonolite, leucite, sodalite, &c. (Permutit Filter Co., Eng. Pat. 26094, 1910; see also, re similar hydration of Portland cement, Snelling, U.S. Pat. 1325213, 1919); or (c) in effecting base-exchange by the action of metallic salt solutions upon primary products obtained as above.

Some other base-exchange reactions deserve mention. Sodium permutit removes ammonia from water; if sodium permutit be treated with dilute acid it becomes an acid permutit, which will remove soda and produce an acid water; calcium permutit removes manganese from water. If calcium permutit be treated with a solution of a manganese salt and the resulting manganese permutit be acted upon by a solution of calcium permanganate, reactions of the following type occur:



producing a dark-coloured mass containing both lime and a highly oxidised manganese group. This is, in effect, an insoluble permanganate and can serve either to sterilise water or to eliminate any iron it may contain by precipitation as ferric hydroxide which is retained upon the surface of the filter-bed (J. D. Reidel, A.-G., Fr. Pat. 405900, 1909; R. Gans, Eng. Pat. 21184, 1909). A zeolite in which soda has been substituted by stannous oxide will reduce gold from solutions of its salts and retain it as purple of Cassius. Thus it is evident that base-exchanging reactions are known of the most diverse character and applicable to many purposes.

A number of processes have been described

in which iron is removed from water by aeration effected by allowing the water to flow down towers packed with coke, or by spraying it through nozzles. In this way the iron is oxidised to the hydroxide, which remains in colloidal solution until it is coagulated and removed by the action of the material forming the filter bed. Too much aeration is to be avoided if the water contains a relatively large proportion of lime and carbon dioxide, or the latter may be driven out of the water leaving insufficient to hold the lime in solution as bicarbonate, with the result that calcium carbonate is precipitated and blocks the pipes (Kisskalt. Gas- u. Wasserfach, 1924, 67, 3; J. Soc. Chem. Ind. 1924, 43 B. 230).

Treatment of alkaline and acid waters may be briefly considered. There is no practicable method for the removal of alkali, but various reactions, e.g. addition of calcium chloride or sulphate in the form of a strong solution or as water containing permanent hardness, will serve to convert alkali carbonate or bicarbonate to a neutral salt, but the resultant water will evidently be undesirable as a boiler feed water.

Acid waters derived from moorland catchments may dissolve lead; this tendency may be corrected either by hardening the water with lime or, better, by Thresh's method of adding sodium silicate, which removes plumbo-solvency without increasing hardness.

Artificial hardening, by addition of calcium sulphate, is practised in some cases to render a soft water supply more suitable for use in brewing.

Boiler compositions contain either or both (a) ordinary softening reagents such as lime, soda-ash, and caustic soda, and (b) organic matter, e.g. tan bark, which serves, by mere mechanical action, to prevent the formation of hard scale. Reagents of class (a) may be dismissed with the comment that they are usually dearly bought in the form of boiler compositions and that, in any case, it is unsound to perform water-softening reactions within a boiler. Materials of class (b) are evidently the lineal descendants of the dead pigs our forefathers are reputed to have put in boilers to prevent scale formation (P. G. Jackson, Boiler Feed Water, Griffin, 1919, p. 28).

If a mechanical preventive of scale is desired, undoubtedly the best is pure graphite applied as a cream with water to the clean internal surface of the boiler and subsequently introduced with the feed water at the rate of about $\frac{1}{2}$ lb. per day (Hinchley, Notes on the Economical Management of Small Boiler Plants, Proc. Chem. Eng. Group, (Soc. Chem. Ind.), 1919; but see, for a scientific investigation of the mechanical effect of linseed, Brun, J. Soc. Chem. Ind. 1919, 22, 76; R. Heuss, Zeitsch. ges. Brauw, 1918, 41, 200).

Proportions of reagents.—In the great majority of cases water is treated with a mixture of lime and soda-ash in such proportion that hardness due to bicarbonates and to magnesium is completely removed by lime, and the hardness then remaining by soda-ash. The amount of reagent required for 1000 gallons of water for each grain per gallon of the various impurities is given in Table II (Paul, Boiler Chemistry, p. 99).

If magnesium salts are to be removed as hydroxide the appropriate quantities of both lime and soda-ash should be used. Quantities of reagent calculated from the table are evidently minima, and in practice a slight excess, about 5-10 p.c., should be used, and the treated water should be faintly alkaline to phenolphthalein.

TABLE II.

Impurity (Present in a concentration of 1 grm. per gallon)	Calcium hydroxide required; lbs. per 1000 gallons	Soda-ash (Na_2CO_3) re- quired; lbs. per 1000 gallons
Free carbon dioxide.	0.260	—
CaSO_4	—	0.111
$\text{Ca(NO}_3)_2$	—	0.092
CaCl_2	—	0.136
MgSO_4	0.095	0.126
$\text{Mg(NO}_3)_2$	0.077	0.102
MgCl_2	0.120	0.159

Emphasis should be laid on the conclusion, following necessarily from the preceding discussion, that the nature and proportions of water-softening reagents cannot be determined simply upon data of temporary and permanent hardness; for the best results it is necessary to have a complete analysis of the water.

Purity of reagents is desirable in all water-softening processes and essential where the proportion of reagents is adjusted directly or indirectly by weighing.

Commercial caustic lime may be of almost any degree of purity. Some samples contain magnesia, some silica and alumina, and in all the content of real lime may vary from 100 p.c. to 70 p.c. or less by absorption of moisture. A much more reliable reagent is calcium 'hydrate,' slaked lime, which, when obtained from trustworthy sources, always contains about 70 p.c. of CaO , will not easily absorb more water, and is a fine powder, convenient for storage and use. If raw quicklime is used, each batch should be tested.

Sodium carbonate is obtainable commercially as the anhydrous salt, soda-ash, and as various hydrates, and may contain impurities such as sodium sulphate or chloride, detrimental to its use in water softening. It should be bought under guarantee or be subject to test before use.

Similarly, caustic soda is easily procured in a state of sufficient purity for water-softening; but it should preferably be in the form of 'flake' or powder for convenience in handling, storage, and measurement.

[In the succeeding paragraphs names given in italics in brackets, thus (*Paterson*), are those of plants or processes which embody the feature under discussion.]

Municipal and domestic water softening and filtration is directed to the production of water free from bacterial contamination and suspended matter, free from colour and from excessive hardness. Owing to its cost, water softening of municipal supplies is practised only in exceptional cases, e.g. with Kentish waters of extreme hardness, derived from the chalk. It is usually effected by an intermittent process in which softening reagents are added to and mixed with a large bulk of water, the precipitate being separated by settlement and decantation; but some small municipal supplies are softened in

large continuous automatic plants of the usual industrial type described below.

Conversely, some large industrial supplies are treated by the intermittent process, using steam to assist solution of reagents and compressed air agitation to ensure their uniform admixture with the water under treatment (*Archbutt and Deeley*). After settlement, the treated water is drawn off by a floating syphon and carbonated by a counter-current of carbon dioxide passed through the outflow pipe (*Proc. Inst. Civ. Eng. 1898, Part 3, p. 404*). Such intermittent systems when properly controlled are probably the most accurate means available for water softening (*E. V. Chambers, J. Soc. Dyers and Colourists, 1918, 34, 240*). They necessitate considerable attention in working and require large tank space, and thus are costly, unless, as in municipal processes, large quantities of water are treated and existing reservoirs can be used.

Domestic water softening is quite commonly practised, and, unless on an unusually large scale appropriate to automatic continuous plant, is also best effected intermittently. Measured bulks of reagent powder are mixed by hand with 5-10 gallon lots of water, the precipitate is allowed to settle and the softened water is withdrawn through a filter (*Maignes*) or by slow decantation (*Wilson-Perrett 'Pukka'*).

One small plant, which may be mentioned here, softens water by heating to about 80°-90°, partly by heat-exchange with treated water, partly by direct heat, the scale being deposited in a tower upon plates removable for cleaning (*Lawrence*). This treatment effectively sterilises water (*Hatch, Proc. Inst. Civ. Eng. 1906*).

Bacteria and suspended impurities are usually removed by filtration. For small domestic supplies this is sometimes effected through porous earthenware filters under pressure, and it is clear that the 'stream-line' filter, which is capable of removing bacteria and even colour from water, could be applied to the purpose (*Hole-Shaw, Proc. Roy. Soc. 1923, 103A, 556*). Wood wool, prepared asbestos wool, cloth and sponges are sometimes employed as filtering media, but practically all large-scale water filtration is effected by beds of sand, preferably quartz sand, carefully graded and supported by a layer of gravel. Filtered water is drawn off either by supporting the gravel layer upon a perforated metal plate or by providing in that layer an effluent pipe system, provided with numerous screened orifices. Wood wool filters are cheaper to install, but the difficulty of cleaning them satisfactorily necessitates periodical renewal, the cost of which must be taken into account.

Large slow sand filters are usually cleaned by laying off units of the filter periodically and removing by hand the top layer of sand. This is continued until the sand bed is so diminished as to require renewal. Rapid sand filters of the gravity or pressure type can easily be cleaned by reversing the flow of water and agitating the sand violently. Agitation is effected in some small plants by hand, in the larger plants by compressed air or by the stream of wash-water itself. A typical illustration is the *Paterson* gravity filter, shown in Fig. 1, in which the steam-jet air-injector is shown as

stream of compressed air through the manifold strainer system *ss*, thus agitating and cleansing

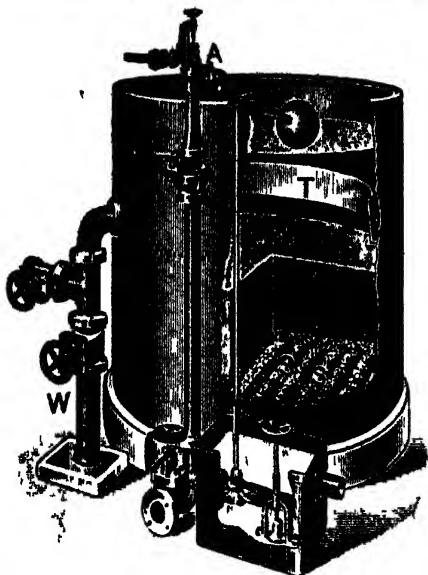


Fig. 1.

the filter bed, whilst the dirty water is drawn off by the annular trough *r* to the water outlet *w*.

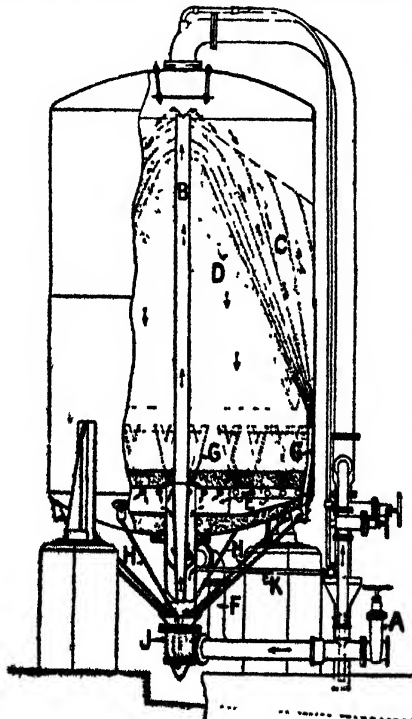


Fig. 2.

The Vickers' drifting sand filter very ingeniously effects a partial cleansing of the sand-bed while in operation, and is adaptable to

gravity or pressure filtration on any scale. Fig. 2 illustrates a single unit pressure-filter. In normal operation raw water admitted by the valve *A* enters the filter at *B* and passes first through the loose mass of slowly drifting sand *C*, and then through the stationary sand-bed *D*, to the manifold *M*, and the filtered water outlet *X*. Sand is continuously extracted by the pipe system *G*, and conveyed by the pipes *HH* to the sand-washer *J*, where it is washed by the incoming raw water and a small quantity of dirty water passes away by the outlet *K*, whilst the main flow of raw water carries the cleaned sand back to the filter at *B*. Valves are provided to permit agitation and washing of the whole filter bed when necessary, the advantage of this type of filter being that, under any given conditions, the interval between such washings is much greater than with ordinary filters.

Efficient working of sand-filters depends upon the formation of a superficial film, composed of the suspended matter derived from the water, which is the effective filtering medium. Where the impurities in water are so small in amount, or of such a nature, that this film is not easily formed, filtration is frequently assisted by the previous addition of 'coagulants,' such

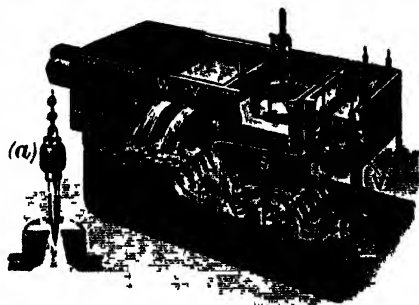


Fig. 3.

as aluminium sulphate. This salt, usually used in the crude form, known commercially as 'alumino-ferrie,' is hydrolysed in dilute solution, especially in the presence of bicarbonates, forming aluminium hydroxide, which rapidly coagulates and carries down suspended matter otherwise unfilterable, and also, by adsorption, removes colouring matter present in the water. Precipitation is best effected in a neutral solution (hydrogen ion concentration $P_H 7$), but is not complete even with the addition of an amount of lime equivalent to the aluminium sulphate (Hannan, Chem. Met. Eng. 1921, 24, 728; 25, 502). Similar results may be attained by the use of the clear 'aluminium hydroxide solution' produced by mixing aqueous solutions of aluminium sulphate (40 grm. in 80 c.c.) and sodium carbonate (10 grm. in 40 c.c.), which, on dilution, precipitates the hydroxide in a form which settles readily (J. W. Coxe, Met. & Chem. Eng. 1923, 29, 379).

Adjustment of the supply of coagulant is effected in pressure filtration by control of the small acid-resisting pump which delivers it into the plant, and in gravity filtration by float-controlled valves. A typical coagulant supply gear of the latter type is illustrated in Fig. 3 (Paterson), the float *v* controlled by the head of

water at the weirs *w* actuating taper valves *vv* (shown enlarged at (a)) so contoured as to permit, for any flow of water, a corresponding flow of coagulant by the *ss* pipes to the trough where baffles *b* cause intimate admixture with the water.

Automatic water-softening plants.—Many types of these plants are in use, differing in the means employed to effect the fundamental operations into which water softening processes are divisible, viz. (1) preparation of reagents, (2) apportionment of reagents to water, (3) mixing, and (4) settlement and filtration to remove precipitated impurities. For the better consideration of the methods to be described, it is desirable to bear in mind the following essential features of an ideal lime-soda softening plant. Preparation of reagents must be conveniently effected, preferably by automatic means, and should be so made and used that they remain of precisely the same concentration until wholly consumed. Measurement of reagents in relation to water must be accurate over long periods and at all rates of flow, and must yet permit of ready and precise adjustment. Mixing must be speedy and thorough. The reaction tanks must be of such capacity that ample time (preferably at least 2 hours) is allowed for completion of the softening reactions before the water leaves the settling tank, and of sufficiently large cross-section to permit proper settling of the precipitate. The filter should be efficient and readily cleansed, but should only be supplementary to efficient sedimentation.

(1) *Preparation of reagents.*—Occasionally reagents are used in the form of a dry powder, usually purchased ready mixed from the manufacturers of the plant or from a firm specialising in the supply of such prepared reagents. In the great majority of cases they are applied as solutions or suspensions in water, which are commonly made by direct weighing and measurement, mixing or solution being effected, in the smaller plants by hand, and in the larger plants by mechanical stirrers or injector agitators, in a tank at ground level (see Figs. 14 and 15), from which they are pumped to a supply tank above the plant.

Sometimes lime is used in the form of clear lime-water prepared in an automatic solutioner, consisting essentially of a vertical tank, having for the whole (*Boyle*) or part (*Harris-Anderson*) of its height the form of an inverted cone (Figs. 16 and 17). By means of a pipe leading nearly to the bottom, the tank is charged from time to time with a sufficient excess of a cream of slaked lime and water, and a stream of water admitted at the apex of the cone flows upward, first agitating and dissolving the lime, and later, as the cross section of the tank increases, depositing excess lime and all impurities, so that clear saturated lime-water overflows at the top. Accumulated impurities are removed from time to time by a sludge cock. The use of saturated lime-water is attended by certain difficulties which must be recognised in order to attain good results. Owing to the small solubility of lime, a considerable proportion of the raw water, sometimes 15-25 p.c., must be by-passed to the lime solutioner, which is, therefore, of considerable capacity. Sometimes the lime, probably because it is of a lumpy character

and unsuited to the process, becomes 'coated' with carbonate and fails to maintain saturation. Lastly, in cases where the temperature of the raw water varies, care must be taken to adjust the proportion flowing to the lime solutioner, so as to compensate for the considerable variation of solubility of lime shown in Table III (Paul, *l.c.* p. 96).

TABLE III

Temperature, Fahrenheit	Calcium hydrate $\text{Ca}(\text{OH})_2$, grains per gallon
32°	132.1
40°	128.0
50°	121.7
60°	115.5
70°	110.9
80°	107.7
90°	103.6
100°	100.0

(These figures do not agree with the absolute solubility given in Tables I and II, but probably correctly represent the variation of solubility with temperature.)

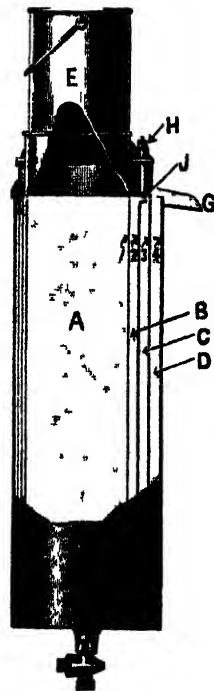


Fig. 4.

One type of plant has a very ingenious solutioner to prepare automatically from solid soluble salts unsaturated solutions of any desired density (*Harris-Anderson*). It consists essentially of three coaxial tubes, 1, 2, and 3 (Fig. 4), contained in a cylindrical tank 4, forming a central chamber *A*, and three annular spaces *B*, *C*, and *D*, all intercommunicating at the bottom. Solid contained in the bucket *D*, having a gauze bottom, dissolves readily in the water in *A*, owing to gravitational convection. Fresh water, introduced at the top of the annular space *B*, rises at the bottom

with strong solution from A, and flows up the outer space D, to the outlet C. The relatively heavy solution in D balances a greater height of water in A, and the tube 2 is set, by means of the screw and nut H, at such a height that when the density of the solution in D reaches the desired value, water begins to overflow the lip J on tube 2, and, passing down the space C, mixes with the effluent solution and maintains the desired concentration in D.

(2) *Measurement of reagents.*—The numerous methods employed fall into two broad classes.

Of the plants using clear solutions of lime and soda, some prepare either or both of these as described above, whilst some rely on the displacement of the proper amount of a previously prepared soda solution by the quiet inflow of a corresponding amount of water at the top of a

water required to make saturated lime-water, whilst a small cup L, of fixed size, withdraws a smaller proportion of the water to the soda solutioner, the proportion of soda added to the water being controlled by adjustment of the density of the solution as described above.

In plants using lime suspensions, with or without the addition of soda, the commonest

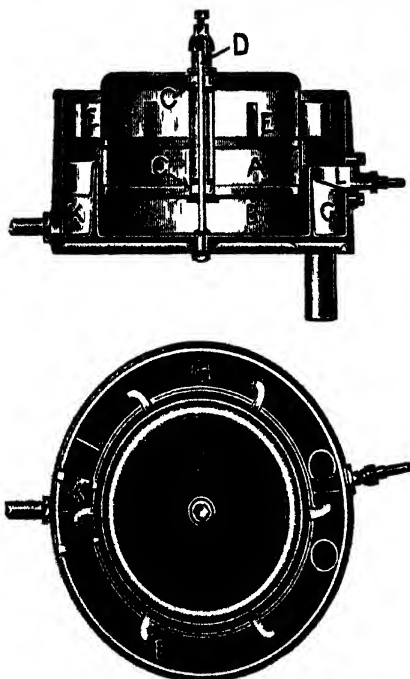


FIG. 5.

'displacement tank,' from the bottom of which a pipe conducts the soda solution to mix with the water under treatment (Figs. 16 and 18). In either case the raw water is divided into one large stream and two smaller streams, of the proper size to make or displace the required quantities of lime and soda solutions. This division is effected by micrometer valves in the base of a common supply tank (Boyle, Fig. 16) or by a turbo-distributor (Harris-Anderson). In this distributor (Fig. 5) a circular tank A, floating on water in B, and free to rotate under guidance by the roller bearings C on the shaft D, receives the whole supply of raw water which flows out tangentially by the orifices E, F, causing A to rotate: the water is thus distributed evenly over the annular trough G at all rates of flow. Radial partitions, one of which is adjustable, divide off a sector of the annulus, of such size as to separate precisely the fraction of the

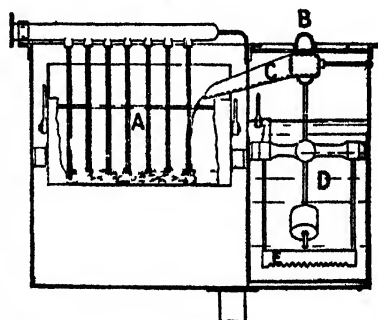
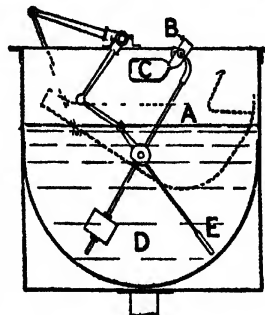


FIG. 6.

measuring device is some form of tipping bucket, actuated by the main flow of water, and actuating cups or scoops which supply a definite quantity of reagent to each charge of water passing. Typical examples of this device in its simplest form occur in the Boby and Becco-Legg plants, the latter being illustrated in Fig. 6, where A is the tipping bucket which, after emptying, returns to the normal position

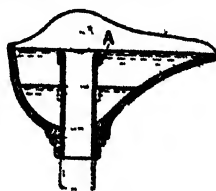


FIG. 7.

shown, and in so doing actuates the arm carrying the chemical scoop B, which discharges into A by a channel C, and agitates the suspension in the chemical tank D by means of the stirrer E. In the Boby plant the contents of the chemical cup (Fig. 7) are variable by vertical screw adjustment of the overflow tube A. Some plants (Lassen-Hart, Paterson, Wilson-Parsons) use double tipping buckets, illustrated by the

Peterson 'Oslameter,' Fig. 8. In the Lassen-Hjort plant the tipping bucket actuates a piston valve supplying reagent.

Special devices are employed in most cases to increase accuracy and decrease wear and tear;

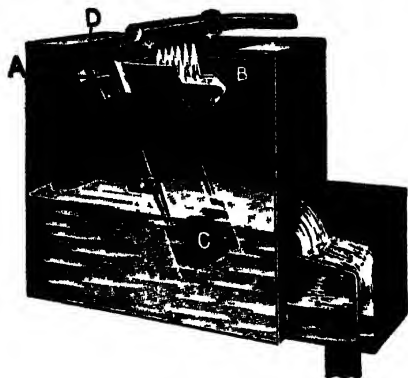


FIG. 8.

thus in Fig. 8, it is seen that the tank has some freedom of movement before it touches the arm A operating the chemical supply gear, whilst an extension lip B on the bucket enables a small addition of water finally to overturn it; and the resulting shock is diminished by the brake paddle C, and absorbed by the rubber buffer D. The Lassen-Hjort tipper has a lock, actuated by

a float in the bucket, which releases the latter when it has a definite content of water; and is buffered by a brake-paddle and springs.

Despite such devices, all tipping buckets are noisy, and in large sizes are impracticable owing to heavy wear and tear. Therefore it is

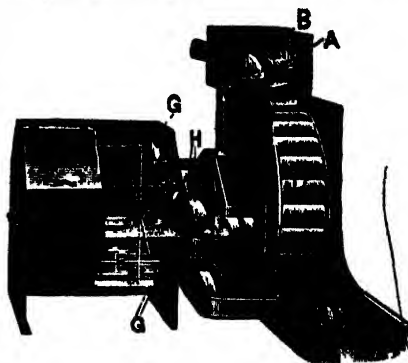


FIG. 9.

customary in the larger plants to sub-divide the main flow of water so that the measuring gear passes but a fraction of the water, whilst the remainder operates stirring gear in the reagent tank. Fig. 9 shows the Peterson bye-pass Oslameter; a dividing plate A at the weir B takes a small fraction of the water to the tipping bucket C, and sends the remainder over the

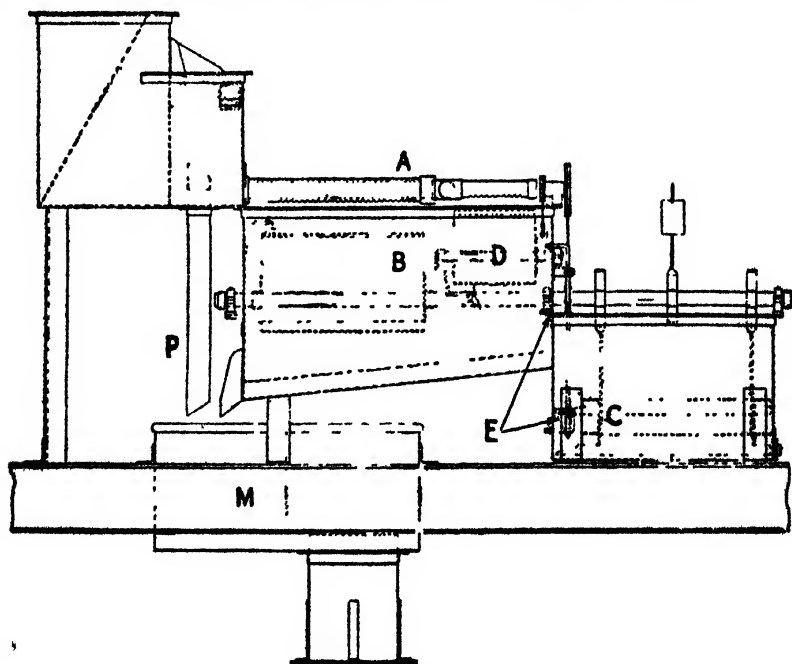


FIG. 10.

wheel D, driving the stirrers E carrying cups F, which maintain a supply of reagent to the actual measuring cups G. The Wilson-Farnett plant, shown in Fig. 10, passes a large part of the raw water direct to the mixer H

by the main F, and divides the residual flow from the perforated pipes A, between a larger tipping bucket I, driving the paddles J, and a smaller bucket K actuating by wheel and chain the chemical cups L.

A plant made by Wright's Forge and Engineering Co., Ltd. (Fig. 11), passes part of the water from a dividing box A through a bucket wheel B, driving a chain elevator C, carrying chemical scoops D, dipping into the reagent tank E. Another by the same maker (Fig. 12) uses the wheel B to drive by chain and bevel gearing, C, D, a screw X working in an oil-bath which lowers the discharge pipe G in the chemical tank, and so delivers reagent in proportion to the water passing. The Kennicott proportioning gear (Fig. 13) uses a small definite proportion of the raw water to lift the float F in the regulating tank T, whereby the cord C lowers a

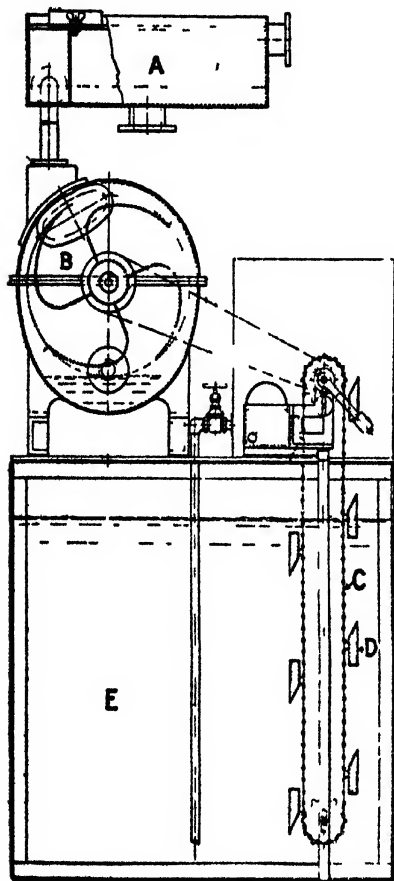


FIG. 11.

slotted discharge pipe F in the chemical tank, the contents of which are agitated by means of a separate water wheel.

In the foregoing plants the proportion of reagent is adjusted by altering the proportion of water passing to the measuring gear, by changing the volume of reagent added or by varying the concentration of the reagent suspension.

Certain plants use a tipping bucket or water-wheel to deliver reagent in the form of dry powder, either from a hopper (Becco-Legg, Maignens, Selys) or by continuous rise of a piston in a

vertical cylinder, having a scraper to strike off the powder flush with the top (Tate and Bell).

(3) *Mixing and precipitation.*—Reagents and water usually flow together into the precipitation tank, sometimes along a channel provided with baffles (see e.g. Fig. 3), and are thereby mixed. Liquid reagent is frequently discharged into a tipping bucket as it begins to fill, and is thus agitated by and with the inflowing water, mixing being completed by the very turbulent

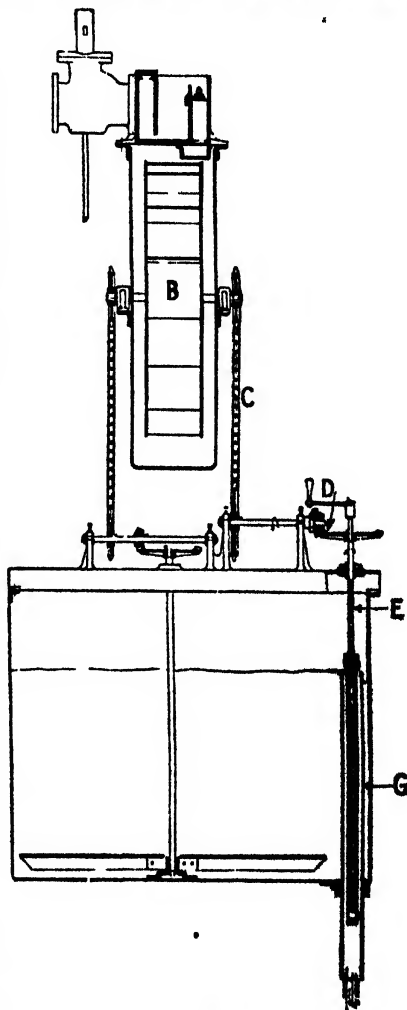


FIG. 12.

outflow when the bucket tips. Some further mixing occurs in most plants by the relatively rapid flow of the water through the channel or pipe leading it down into the settling tank.

(4) *Clarification and filtration.*—Separation of the precipitate is always chiefly effected by settlement, during the slow passage of the water up or along the settling and reaction tank, and completed by filters. These tanks and filters determine the general form and disposition of the plant in one of two commonly occurring types, characterized as 'horizontal' and 'vertical', respectively.

A typical example of the horizontal type, the Lassen-Hjort rectangular softener, is shown in Fig. 14. Water, carrying reagents discharged

by the proportioning gear *a* already described, passes down the reaction chamber *b*, up the first settling tank *c*, and through the first

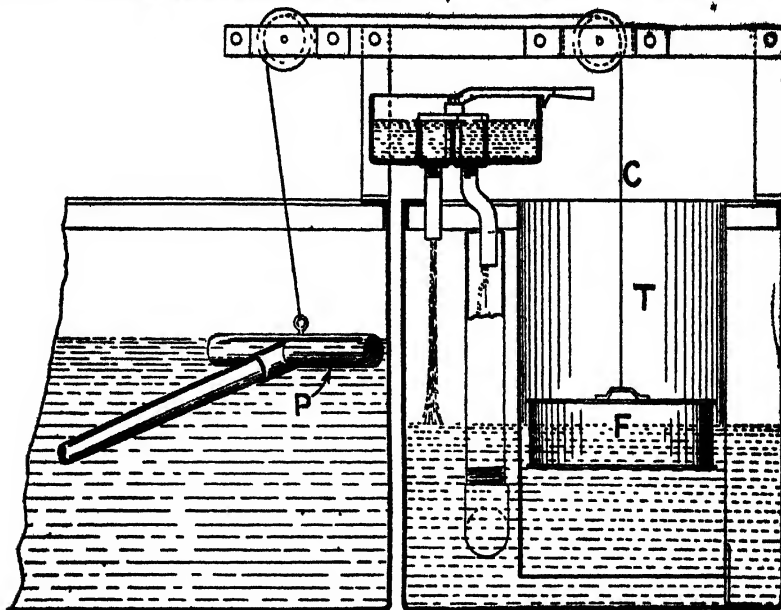


FIG. 13.

wood-wool filter *d*, overflows down channels *ee*, and passes upward through the second tank and filter, *f* and *g*, and finally overflows into

the storage tank *h*, in which a ball-cock *k* maintains a constant level by controlling the raw water supply. Sludge is removed by cocks

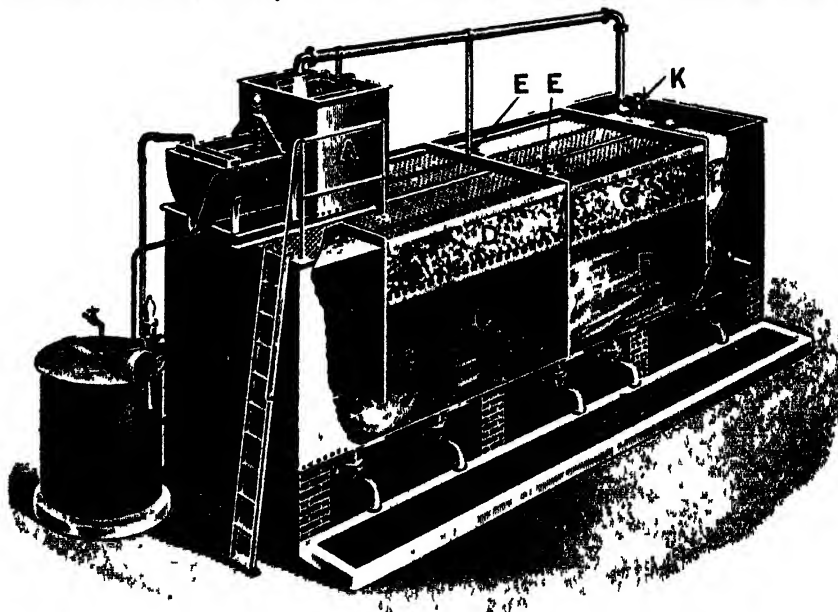


FIG. 14

is, this operation being assisted in many plants (*Boley, Paterson*) by hand agitators.

The vertical type is illustrated by the *Paterson* plant shown in Fig. 15, the mode of

operation of which is obvious from the preceding description. Here also a wood-wool filter is used.

Sand filters have the advantage that they

are more efficient and more easily cleaned than wood-wool filters. The Royle's plant, shown in

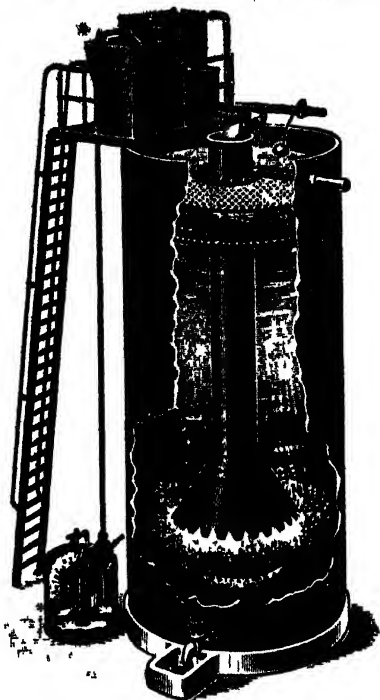


FIG 15

Fig. 16, affords an example of their incorporation in a vertical plant, and is interesting also as

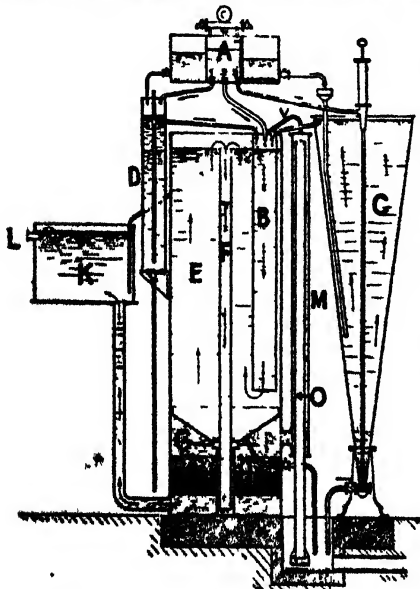


FIG. 16.

containing an automatic washing device which needs description. Raw water enters the distribution tank A, where the three micro-

meter valves, 1, 2, and 3, pass the major portion of the water to the reaction tube B, a smaller portion to the lime dissolver C, and the smallest portion to displace soda solution in the tank D. These reagents mix in B, with the water which then rises slowly, and is clarified by settlement in E, and then overflows down F to the filter chamber G, passes through the sand filter H, rises to the tank I, and overflows at L. As sediment accumulates on H, the head of water in F, necessary to maintain the required rate of filtration, increases, and the corresponding rise of water in the outer tube M finally sets the syphon O in action and causes a heavy back-stream from I to flow through the filter, thoroughly agitating and cleansing the filter bed.

External independent filters have the great advantage of ready accessibility; their use is illustrated by the Harris-Anderson plant, shown in Fig. 17, where A is the turbo-distributor,

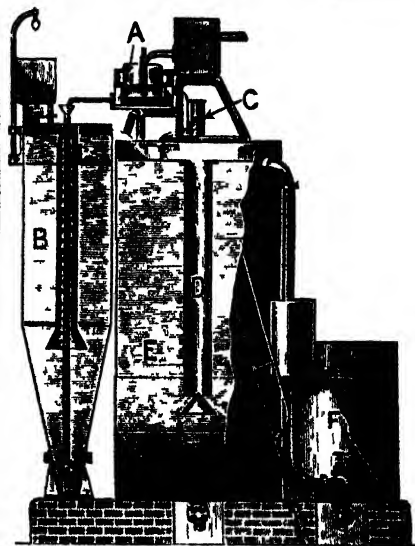


FIG. 17.

B the lime solutioner, and C the soda solutioner, already described, D is the reaction tube, E the settling tank, and F the external filter.

All the foregoing types of plant are open, and thus cannot deliver water at a pressure greater than that due to the height of the outlet above the point of application. Where it is desired to utilise a natural or forced head of water without material loss, a water-softening plant may be enclosed in the manner illustrated by the Royle's plant in Fig. 18, which differs from that of Fig. 16, in that the function of the head tank and micrometer valves in the latter is now performed by the dial cocks 1, 2, and 3, that the tops of C, D, and E are enclosed, that pumps are fitted to charge the reagents into C and D, and that the automatic washing arrangement is eliminated.

By the introduction of waste steam or hot condensates into the mixing chamber (not via the measuring gear), most of the above plants, though sometimes described as 'cold-process' plants, can be used for the hot softening of water. This is frequently advantageous, both

as a means of conserving heat and because a softener worked hot will yield water of lower hardness than one worked cold.

There are, however, a number of plants specifically designed to combine the functions of exhaust steam feed-water heating, water-softening and oil elimination, of which that

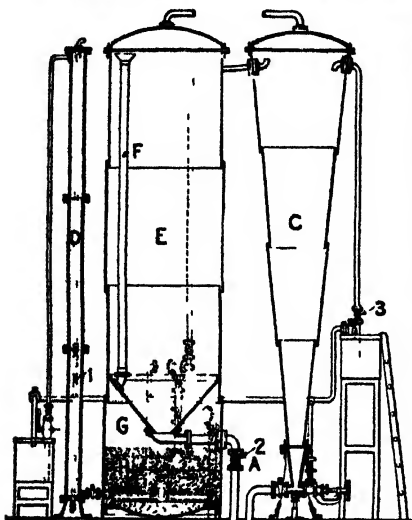


FIG. 18.

shown in Fig. 19 (Royle's) is an example. Some plants rely solely upon heating to soften the water (Lawrence, Erith's Recording Heater), but usually the water is treated also with soda or lime and soda, and if necessary with aluminium sulphate (Erith's, Wright's 'Neptune,' Royle's Type E, Kennicott, Lassen-Hjort, Harris-Anderson).

In Fig. 19 the crude water supply, controlled by the ball-cock A, is distributed in B, and part taken to displace soda and aluminium sulphate solutions in C and D respectively in the usual manner. Water and soda flows down through and over a series of dished plates EE, in parallel current with exhaust steam introduced at F, via an oil-separator G, any excess steam passing to atmosphere by the pipe H. Most of the hardening impurity is deposited on the plates EE, which are easily removable for cleaning. Aluminium sulphate is added in the mixing tube at K, and the water finally passes through a settling tank L and filter M as usual.

Brief reference may here be made to much work that has been done upon the 'degassing' of boiler feed-water, as a consequence of the general recognition of the fact that dissolved oxygen is the essential active agent in the corrosion of boilers and other steam plant. Two methods have been proposed, in various forms, for its removal; depending respectively upon boiling it out at atmospheric or reduced pressure, and upon causing it to combine with iron in the form of scrap-iron, iron-manganese alloys, or couples of iron with zinc or copper (see e.g. Warner, Eng. Pat. 7272, 1915; Wilson and Anti-Corrosive Eng. Co., U.S. Pat. 1387748, 1921; and Hall, D. R. P. 306388, 1916;

L. and C. Steinmüller, D. R. P. 320893, 1917; Hartung, D. R. P., 368645, 1918; Bailey, Morgan and Met.-Vickers' Elect. Co., Eng. Pat. 194942, 1921. For a full discussion see Kastner, Proc. Inst. Mech. Eng. 1921; J. Soc. Chem. Ind. 1921, 40, T. 67).

Zeolite water-softening plants.—These plants make provision for the filtration, or, rather, percolation, of water through a bed of granular zeolite, and for the periodic regeneration of the zeolite by means of brine; they are, therefore, essentially very simple and conform to the type (United Water Softeners, Ltd.) illustrated in Fig. 20. Water enters by a meter A, and, valves 1 and 4 only being open, passes in at the top of the closed reagent tank B, down through the

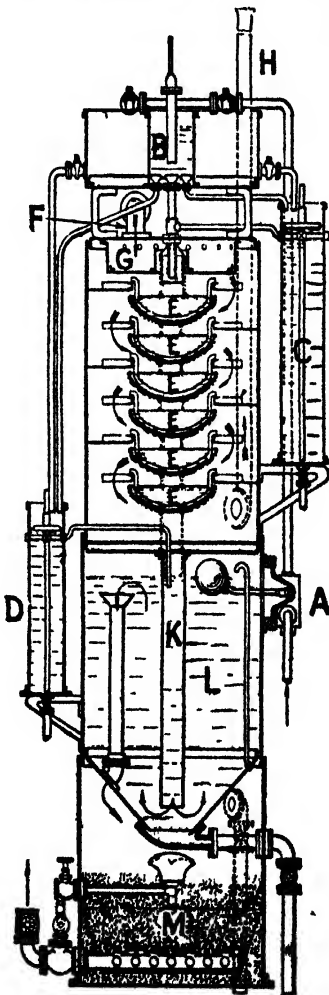


FIG. 19.

bed of zeolite, supported upon a layer of quartz sand D, and thence to the main. When the meter indicates that the apparatus has treated the maximum quantity of water (calculated with regard both to the quantity of zeolite and to the initial hardness of the water), the cocks are manipulated so as to (1) drain

the water wholly from the tank, (2) introduce, by means of the steam injector *x*, the proper charge of brine previously prepared in the wooden tank *g*, and (3) to drain and wash the salt from the zeolite bed. This done, cocks 1 and 4 are again opened, all other cocks being shut, and the plant again functions as a water-softener.

Comparison of soda-lime and zeolite processes.

—Each process has its peculiar advantages and limitations, which broadly determine its field of use and may be summarised as follows:—

With efficient plant, properly operated, the residual hardness of treated water should be 3–5 degrees for the cold soda-lime treatment, 1–3 degrees for the same process worked hot, and 0–1 degree for the zeolite process.

Dissolved solids are diminished by lime-soda treatment, but increased by zeolite softening,

owing to the substitution of sodium salts for calcium salts.

Treatment of water containing iron or sediment presents no difficulty in the lime-soda process, as these impurities are removed with the precipitate in the normal course of working. Such waters, however, must be freed from iron and sediment before entering zeolite softeners, to avoid the formation of a deleterious coating on the active material.

Cost of plant for lime-soda treatment depends only on the maximum hourly flow of water, whilst for the zeolite process it depends also on the hardness of the water. It is also affected by the fact that stoppages for regeneration of a zeolite plant are more frequent and of greater duration than those for cleaning of a lime-soda plant.

Cost of treatment is about the same for removal

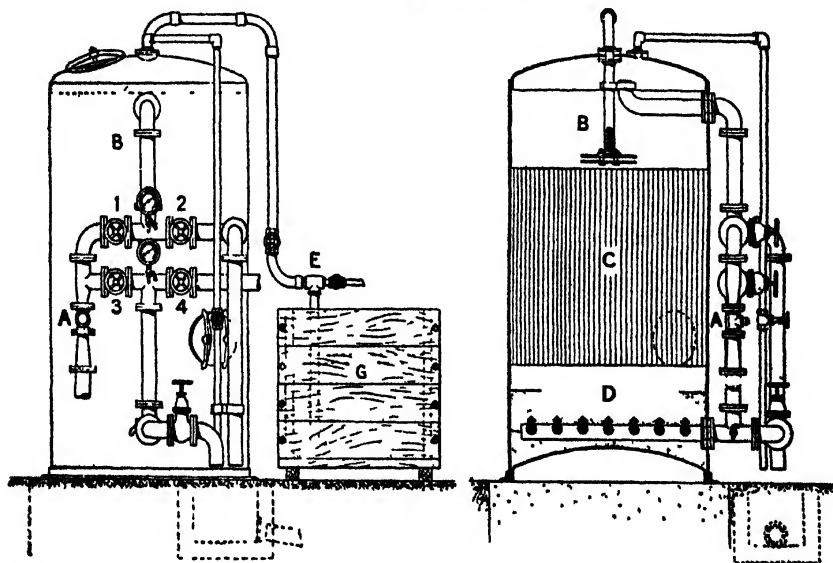


FIG. 20.

of permanent hardness by either method, but temporary hardness is removed by lime at about one quarter the cost of its removal by zeolite.

From the foregoing characteristics it appears that in the textile, dyeing, and laundry industries, where minimum hardness is the first consideration, zeolite softening is the more suitable. In many such cases, where the water contains iron or sediment, and has any considerable temporary hardness, it is advantageous to treat it first with lime in a precipitation softener and then remove residual hardness with zeolite. If this is done, ample reaction space must be provided in the lime softener, as any excess lime may hinder the operation of the zeolite softener and produce a turbid effluent.

The lime-soda process is the better for boiler-feed water, for municipal softening, and for water to be used in ice manufacture. Its suitability for municipal softening is determined by its low cost and by the possibility of applying it in existing installations. For boiler-feed and

ice manufacture reduction of dissolved solids is of primary importance, and this requirement is best met by the precipitation process. Where a raw water contains much bicarbonate hardness, the quantity of alkali bicarbonate produced by zeolite softening may cause serious alkalinity and priming in boilers. (For a fuller discussion of these matters, see Blumenthal, *Zeitsch. angew. Chem.* 1921, 34, 189; and Behrman, *J. Amer. Waterworks Assocn.* 1923, 10, 623; Memoranda by the Chief Engineer to the Manchester Steam Users' Association, 1903, and 1917–18; for a discussion with special reference to the textile industries, see King and Chambers, *J. Soc. Dyers*, 1918, 34, 240–247.)

H. V. A. B.
P. L. R.

WATER STONES v. AGATE.

WATERS, AERATED v. AERATED WATERS.

WAVELLITE. A mineral consisting of hydrous aluminium phosphate $3Al_2O_3 \cdot 2P_2O_5 \cdot 12H_2O$, forming globular or stalactitic masses with an internal radiating structure. The colour is

white, yellowish, or green; sp.gr. 2.32. The mineral usually occurs on the joint faces of slaty rock, and was first observed in the eighteenth century by Dr. W. Wavell in the slates at Fillsigh near Barnstaple in Devonshire. Good specimens have also been found in Co. Cork. In larger amounts it occurs in Arkansas and Pennsylvania. At South Mountain in Pennsylvania it has been mined for use as a fertiliser and as a source of phosphorus, used locally for making matches. L. J. S.

WAX-OPAL v. OPAL.

WAXES, ANIMAL AND VEGETABLE.

These waxes are a group of substances resembling beeswax in their physical properties; they are mixtures of compounds composed of the elements carbon, hydrogen, and oxygen. Waxes of mineral origin, such as paraffin wax, ozokerite, ceresin, and montan wax, are described elsewhere. Physically the waxes come in the series (1) fixed oils, (2) soft fats, (3) tallow-like substances and solid fats, (4) waxes, and (5) resins. The waxes all melt below 100°. The waxes differ from the fats in having little or no greasiness at ordinary temperatures. The greasiness of most of the fats is probably due to their containing some olein (glyceryl oleate) or some glyceryl esters of unsaturated fatty acids. There was an impression in the last century, doubtless produced by Chevreul's work on the fats, that whilst the fats contained glyceryl esters, the true waxes did not, but contained esters of higher members of the $C_nH_{2n}O_2$ series of acids with alcohol radicles other than glyceryl. As a result of this an unfortunate system was introduced of denying the name of 'wax' to those waxes that are largely composed of glycerides, and of calling them 'tallows.' It serves no useful purpose and has the effect of upsetting the ordinary meaning both of 'wax' and of 'tallow.' By it, on the one hand, Japan wax was to be called Japan tallow and myrtle wax was to be called myrica tallow, because they are both largely composed of glyceryl palmitate; and on the other hand, sperm oil was to be described as a liquid wax, because it was thought to contain very little glyceryl esters. Refined wool fat, a soft unctuous substance, was called wool wax. The inadvisability of attempting to alter the meaning of a word in common use to suit some special scientific classification was pointed out by Gregory in *Nature*, 1911, 87, 538.

Beeswax and most of the vegetable waxes seem to be produced by the integuments of the organisms and not internally, and their value to the plant is to repel water or resist its action and prevent its ingress or egress. Beeswax, similarly, is a very suitable material of which to form the cells for storing honey, as it does not become soft or soppy by the action of the water in the honey.

The chief proximate components of the waxes are: (1) esters of the fatty acids with alcohols containing a high number of carbon atoms; (2) esters of fatty acids with glycerol; (3) free fatty acids; (4) free alcohols containing a high number of carbon atoms; (5) hydrocarbons. With respect to the formulae of compounds containing a high number of carbon atoms, it should be borne in mind that a CH_2 , more or less makes such a small difference in the percentage com-

position that the exact formula cannot be settled by a carbon and hydrogen determination, and consequently authors differ somewhat in the formulae they assign to the components of the waxes; such formulae must therefore be regarded as scarcely fixed yet. Another point to be remembered is that authors have sometimes been careless, in that they have stated that substances found in the products of saponification of a wax were present in the wax; thus it has been stated that beeswax contains myricyl (melissyl) alcohol and ceryl alcohol, when the experiments only showed that these were found after saponification. There was no evidence to show that the free alcohols were present, and no doubt those found came from esters in the beeswax.

The waxes, like most natural products, are mixtures of several components, and the isolation of these is a difficult and lengthy task, which has been attempted by comparatively few investigators. In consequence of this and in order to meet the requirements of commerce, it is customary when examining samples of the waxes to determine what may be called their *analytical values*, and from the results to infer their quality and freedom from adulterations. These values are also called the *characteristics* of the waxes; they have been much studied and include the physical determinations of specific gravity, melting point and sometimes refractive index, and also certain chemical determinations, which are explained below under the heading 'Beeswax.'

It has been observed that Japan wax has the peculiarity of showing a lower specific gravity and a lower melting-point when it has recently solidified after having been melted, than when some time has elapsed since solidifying. Other waxes probably possess similar peculiarities.

Text-Books.—Benedikt-Ulzer, *Analyse der Fette und Wacharten*, Fünfte Auflage, 1908. Lewkowitsch and Warburton, *Chemical Technology and Analysis of Oils, Fats and Waxes*, 6th ed. 3 vols. 1921-23. Wolff, *Die Lösungsmittel der Fette, Oele, Wachse und Harze*, 1922.

Arjun wax (*White insect wax of India*). About the year 1788 a wax produced by an insect was noticed in Madras by Dr. James Anderson (Correspondence, 1788-1791) and was called by him *White Lac*. It was thought that it might resemble the Insect wax of China, but it is distinctly different. Attention has been drawn to it from time to time, but it seems never to have been utilised. The insect producing it was first named *Coccus ceriferus*, and later *Cero-plastes ceriferus*; it has been found on the arjun or kowa tree, on peplul, mango, tea bushes, and on other trees. The crude wax occurs on the twigs in small mounds of a dull buff colour; it contains some moisture and black matter from which it can be freed by melting and straining. When thus purified it is yellow like beeswax, and hard and brittle like resin. It is partially soluble in cold alcohol, and nearly all of it dissolves in boiling alcohol; when the solution cools it becomes white and opaque. In warm ether it dissolves readily, but not completely. In hot oil of turpentine it dissolves readily, but the liquid becomes white and opaque on cooling. In benzine it is easily soluble with the exception of a little brownish matter. Carbon disulphide dissolves it only partially.

Pearson (Phil. Trans. 1794, p. 383) examined the wax from Madras and found that it melted in water at 83°. He made candles of it, but found that they smoked and gave a resinous odour.

Moore (J. Agric. Hort. Soc. of India, 1874-78, 5, 78) reported on some from Chota Nagpur, that one specimen contained 11 p.c. of moisture, another 13 p.c.; that it melted at 55°; that (probably after drying and melting) the specific gravity was 1.04, and the composition corresponded to the formula $C_{11}H_{20}O$.

Holland (Indian Museum Notes, 1891-93, 2, 93) reported on some from the Central Provinces, that it (the crude material apparently) melted at 60°, and had a specific gravity of 1.04 at 29°.

Balanophore wax occurs in the parenchymatous cells of various species of Balanophoræ. These are small parasitic plants growing on the roots of various other plants and are found in abundance in Java. They are so rich in wax that they burn with a bright light, and the natives prepare candles by pounding the plants to a paste and coating thin strips of bamboo with this. The wax was named *balanophorin* by Göppert in Nova Acta Acad. Cæs. Leopoldino Carolinæ Nat. Curiosorum, 1841, 18 Suppl. 229, where a botanical account of the plants is given. The wax was examined by Poleck (*ibid.* 1847, 22, 117), who found that it was very soluble in ether and also that it dissolved when gently warmed with concentrated sulphuric acid and was precipitated again by dilution. It was examined more recently by Simon (Sitz. Ber. Kaiserl. Akad. Wissenschaften, Wien, 1910, 119 II. b, 1181). Air-dried slices of the plants (the latter had been preserved in alcohol) were reduced to a coarse powder and extracted with hot ether; they yielded about 65 p.c. of crude wax which, when melted and filtered (this took 4 months to accomplish), gave a honey-yellow wax, brittle when cold, but becoming soft when warmed in the hands and capable of being drawn out in fine threads. One part required about 140 parts of 95 p.c. alcohol for its solution, and of the product of this purification one part required about 50 parts of acetone for its solution. Balanophorin was thus obtained as a white amorphous powder. After further purification it was found to melt at 56°-57° to a colourless liquid resembling glycerin, which slowly solidified to a white wax. By analysis it was found to have a composition corresponding to $(C_{11}H_{20}O)_n$, just as Poleck had found. It gave no acid value nor saponification value. When strongly heated no acrolein was given off. Simon succeeded in decomposing it by distillation in a partial vacuum containing carbon dioxide, and also by fusion with potassium hydroxide, and in both cases obtained palmitic acid as a product. An account of other products was to be published later.

Langsdorffia hypogæa, another of the Balanophoræ, which is found near Bogota, in Colombia, yields large quantities of wax, and the stems are sold in the markets and used as candles on saints' days (Hooker, Trans. Linn. Soc. 1859 22, 41). This wax does not seem to have been chemically examined yet.

Beeswax is produced by the common bee *Apis mellifica*, and also by some allied species;

it is not collected from the flowers by the bee, but is the secretion of certain organs situated on the underside of the abdomen of the neuter or working bees, and is used by them in forming the cells of the honeycomb. They are said to consume about 10 lbs. of honey in order to secrete 1 lb. of wax. To obtain the wax the honey is allowed to run out from the comb, which is then pressed to separate as much honey as possible. The adhering honey and other impurities are next removed by melting the mass in hot water; the melted wax floats on the surface, and is strained to remove dead bees and brood. The residue is put in layers with straw, and is pressed to obtain more wax, the straw acting as a filter; this product is known as 'press wax.' The mass then remaining is sometimes extracted with benzene to obtain still more wax, the product being 'extraction wax.' The 'extraction wax' is apt to be impure from the use of artificial comb, and also from substances being extracted from the dead bees and straw; further, wax compositions and adulterated beeswax are also sold under the name of 'extraction wax' (Hirschel, Chem. Zeit. 1904, 28, 212). A common practice is to pare off the capping of the honey cells and then place the comb in a centrifugal machine, which removes the honey and leaves the comb undamaged, so that it can be replaced in the hive to be refilled by the bees, and thus save the honey that they would use to produce fresh wax. In this system the capping only is melted down for wax. Impurities may be introduced into beeswax by the use of artificial combs and foundations for combs made of materials other than beeswax. These are employed to save the honey which the bees would consume in making the wax.

Beeswax is yellow in colour and varies in tint, according to the materials employed by the bees and the care taken in its preparation; sometimes it is brownish, reddish, or greenish. It has a pleasant honey-like smell, which is made more apparent by warmth. When cold it is brittle; at ordinary temperatures it is tenacious; its fracture is dry and granular.

Solubility.—It is insoluble in water. Carbon tetrachloride is said to be the best solvent. Other solvents are: chloroform, carbon disulphide, tetralin (tetrahydronaphthalene), hexanil (hexahydrophenol), benzene, benzine, oil of turpentine, ether (not a very good solvent). The solvent is to be used hot, and in the case of some or all of these, a portion of the beeswax separates on cooling.

As regards ether, Buchner (Chem. Zeit. 1907, 31, 570) allowed beeswax to soak in ether at the ordinary temperature for some time, then filtered the resulting homogeneous paste, and washed it with ether; after getting rid of the ether he obtained from the filtrate 30 p.c. of a fairly soft, deep yellow mass, and from the insoluble residue 70 p.c. of a bright brownish wax considerably harder than the original wax. The soluble portion had an acid value of 40 and a saponification value of 83.8, whilst the insoluble portion had an acid value of 11.6 and a saponification value of 99.1; thus the part that dissolves is richer in acid and colouring matter and poorer in ester than the undissolved part.

Buchner (Chem. Zeit. 1918, 42, 373) also describes the difference in analytical values of

wax obtained from press-residues by using different solvents, namely, benzine, chloroform, and carbon tetrachloride. The esters appeared to be less easily dissolved than the other components, so that light benzine removed less of them than the other solvents, and the extraction wax, when light benzine was used, appeared abnormal.

Cold alcohol dissolves scarcely any; boiling alcohol dissolves a good deal (about 15 p.c. reckoning from the acid value), leaving an undissolved residue from which something is dissolved every time the treatment with boiling alcohol is repeated. All except about 2 p.c. is deposited when the alcohol cools.

Analytical values.—The creation of a systematic plan for examining samples of beeswax is due to Becker, Hohner, and Hübl. Becker (Dingl. poly. J. 1879, 234, 79), following Kottstorfer's plan for butter (Zeitsch. anal. Chem. 1879, 18, 199), determined the saponification value. Hohner (Analyst, 1883, 8, 16) determined the amount of potassium hydroxide required to neutralise the free acid and that required to saponify the whole wax; but he expressed his results in terms of cerotic acid and myricin. Hübl (Dingl. poly. J. 1883, 249, 338) prescribed the determination of the acid value, the ester value, the ratio value, and later for fats and oils (*ibid.* 1884, 253, 281) of the iodine value. The meaning of these terms may be briefly explained as follows:—

Acid value.—This is the number of milligrams of potassium hydroxide required to neutralise the free acids in one gram of the sample.

Saponification value.—When an oil, fat, or wax is boiled with alcoholic solution of potassium hydroxide, not only is the free acid neutralised, but the esters of the various acids are decomposed, potassium taking the place of the alcoholic radicles and forming salts (soaps) with the acids and the alcoholic radicles forming the corresponding alcohols. The number of milligrams of potassium hydroxide used in effecting these two actions for one gram of sample is called the *saponification value*.

Ester value.—If the acid value is deducted from the saponification value the remainder represents the number of milligrams of potassium hydroxide that has been used in decomposing the esters, and is called the *ester value*. Esters were formerly known as compound ethers, so the term *ether value* is sometimes found instead of *ester value*.

Ratio value.—If the ester value is divided by the acid value, the quotient is called the *ratio value*. It is useful in deciding on the purity of a sample.

Iodine value.—In most cases the oils, fats, and waxes contain unsaturated compounds; these when treated with solution of iodine and mercuric chloride under prescribed conditions combine with a certain amount of iodine. The percentage of iodine thus taken up is called the *iodine value*; it is a measure of the amount of unsaturated compounds in the sample. It differs from the other values in being a percentage and not a number of milligrams.

Total acid number.—Benedikt and Mangold (Chem. Zeit. 1891, 15, 474) proposed a determination of what they called the *total acid number*, but it has not come into general use.

Instead of 'value' the term 'number' is often used for the above results.

Although these values are a useful guide in judging the purity of a sample, they are not infallible, since it has been found possible, by a judicious mixture of ingredients, to prepare composition waxes which will give the correct analytical values for a pure beeswax.

Buchner value.—To examine samples of beeswax containing such composition waxes, Buchner (Chem. Zeit. 1895, 19, 1422, corrected by Kissling, *ibid.* p. 1682, and improved by Berg, *ibid.* 1903, 27, 753 and 754, and in Benedikt-Ulzer's Anal. Fette u. Wachsarten, 1908, p. 1095) devised a determination giving what is known as the *Buchner value*. The sample is boiled with alcohol, and then after 12 hours the acidity of the liquid is determined.

Weinwurm's test.—This is a test described by Weinwurm in Chem. Zeit. 1897, 21, 519, to detect paraffin or cerosin in beeswax. It uses glycerol and is useful, but not always reliable; see various papers in the bibliography and Benedikt-Ulzer, Anal. Fette u. Wachsarten, 5th ed. 1908, p. 1109.

Long tables giving the recorded analytical values of ordinary yellow beeswax are to be found in the text-books of Benedikt-Ulzer and of Lewkowitsch and Warburton; and Buchner in Zeitsch. öffentl. Chem. 1912, 18, 90, gave the values of some abnormal waxes. Berg (Chem. Zeit. 1903, 27, 752) gives a long table of the values of various waxes. They may be summarised as follows. Some errors have been corrected by the original sources, and 'press wax' and 'extraction wax' are excluded.

	Commonly occurring values lie between	Extreme values are	
		Minimum	Maximum
Specific gravity at 15°.	0.958 to 0.967	0.949 F. (0.941 L.)	0.972 Bt.
Melting-point	62.5° „ 66.5°	61° Bt. (60.5° L.)	68.5° Bg.
Acid value	17 „ 22	15.6 I.L.	25.7 Bch.
Ester value	70 „ 82	60.8 Bch.	84.9 Bg.
Saponification value	90 „ 103	80.8 Bch.	106.5 Bg.
Ratio value	3.2 „ 4.3	2.38 Bch.	5.0 I.L.
Buchner value	1.5 „ 6.1	1.1 M.	7.4 Bg.
Iodine value	6 „ 13	5.6 Bg.	17.12 Bg.

- Boh.—*Buchner*, Zeitsch. öffentl. Chem. 1912 18, 90.
- Bg.—*Berg*. Beeswax from many places, Chem. Zeit. 1903, 27, 755.
- Bt.—*Bertainchand and Marcille*. 'Note sur la Cire d'Abeilles en Tunisie, 1898; Extrait du Bulletin de la Direction de l'Agriculture, Tunis.' (A pamphlet.)
- F.—*Fendler*. Beeswax from German East Africa, Arbeiten Pharm. Inst. Univ. Berlin, 1904, 1, 203.
- I.I.—Beeswax from Northern Nigeria, Bull. Imperial Institute, 1911, 9, 238.
- L.—*Lidov*. Russian commercial samples, but it is not clear whether adulterated samples were excluded and in the sp.gr. the temperature is not stated, Chem. Zeit. Repert. 1905, 29, 278, from Westnik shirow. weschtsch, 1905, 6, 89.
- M.—*Mastbaum*. Portuguese beeswax, Zeitsch. angew. Chem. 1903, 16, 647.

Detailed directions for ascertaining the analytical values, for performing tests, and for interpreting the results will be found in the text-books and in the original papers; they have been subjects of much controversy especially those for the saponification value, since many of the waxes are not so readily saponified as the fats.

In deciding on the purity or otherwise of a sample, all the analytical values and the results of tests for impurities must be considered together. The text-books and various original papers and experience give guidance in forming an opinion.

Composition.—The composition of beeswax has received the attention of several investigators, and some account of the leading researches is given below.

Dr. J. F. John (Chem. Tabellen der Pflanzenanalysen, 1814, p. 42) separated beeswax by means of alcohol into a soluble and an insoluble portion. These he named *cerin* and *myricin* respectively, believing them to be the same substances that he had previously obtained from the wax of *Myrica cordifolia* from Cape Colony and had so named; thus making the common mistake of early investigators of identifying compounds from different sources on quite inadequate grounds. The *cerin* and *myricin* from beeswax and from *M. cordifolia*, however, must not now be regarded as identical. The latter wax seems not to have been examined recently and probably would be found to resemble myrtle wax in its composition. In Dr. John's time it was imagined that the number of compounds present in plants and animals was far fewer than are now known, and consequently compounds were believed to be identical if they agreed in a few simple properties. This belief has given rise to some misleading names.

Brodie (Phil. Trans. 1848, Pt. 1, 147; 1849, Pt. 1, 91), using Surrey and other beeswax, found two acids in the *cerin* or portion soluble in boiling alcohol, and named the most important of them with m.p. about 78° *cerotic acid*, giving it the formula $C_{21}H_{42}O_2$; he thought that the other acid was present in the wax in very small quantities; he estimated the wax to contain 25 p.c. of cerotic acid. In the *myricin*, or portion nearly insoluble in boiling alcohol, he found an ester of palmitic acid with a wax alcohol $C_{21}H_{42}O$ with m.p. 85°, which he named

melissin, no doubt from *melissa*, a bee. This alcohol is now called *myricyl alcohol*, or better, *melissyl alcohol*, since myricyl is a misleading name, arising from Dr. John's mistake, and very probably there is no myricyl present in the waxes of the *Myrica* group. Brodie also found in beeswax indications of other substances.

Very thorough investigations to find the components of beeswax were made by Nafziger (Annalen, 1884, 224, 225) and Schwalb (*ibid.* 1886, 235, 106); they used Württemberg country yellow wax and employed long series of fractionations. In the part soluble in hot alcohol, the *cerin*, Nafziger found principally cerotic acid with m.p. 78°, for which he favoured the formula $C_{21}H_{42}O_2$, or perhaps $C_{21}H_{40}O_2$; he found also some melissic acid $C_{20}H_{40}O_2$ with m.p. 89°–90°, and another acid of m.p. 75°–76° in small quantity. The ester portion left undissolved by the hot alcohol, the *myricin*, was saponified, and the product was extracted with hot petroleum ether to dissolve out wax alcohols, &c., thus leaving sodium salts of the fatty acids. From these latter he obtained palmitic acid $C_{16}H_{32}O_2$ with m.p. 61·5°, and satisfied himself that they included no salts of other higher fatty acids such as cerotic acid or melissic acid. Consequently no esters of such acids are present in the *myricin*, although cerotic and melissic acid are present in the wax in the free state and are found in the *cerin*. As regards acids of the oleic series: from the mother liquor of the *cerin* and from a certain mother liquor obtained in the examination of the *myricin*, he obtained similar yellow acid syrups having the characteristic odour of beeswax. These he believed to contain mixtures of acids of the oleic series, the odour being due either to these acids or to some special substance mixed with them. Thus these acids are present both free and as esters.

Schwalb completed Nafziger's work by examining the substances extracted by petroleum ether from the saponified *myricin* and so containing the wax alcohols which had existed as esters in the original wax. In this extract he found not only wax alcohols, but hydrocarbons; the presence of which in beeswax he was the first to discover. He isolated two which he believed to be normal heptacosane $C_{27}H_{54}$ with m.p. 60·5° and normal hentriacontane $C_{31}H_{62}$ with m.p. 68°; he also obtained a soft vaseline-like mass and thinks that other lower paraffins were present. He estimated the amount of the above two in beeswax (not the total hydrocarbons) to be about 5 to 6 p.c. As regards the alcohols produced by the saponification of the *myricin*, he found melissyl alcohol with m.p. 85°–85·5° and from it prepared the corresponding melissic acid with m.p. 88·5°–89°. He favoured the formula $C_{21}H_{42}O$ for the alcohol and $C_{21}H_{42}O_2$ for the acid. He also found evidence of the presence of lower alcohols in the saponification products, so to identify them he converted the mixture containing them into the corresponding acids and drew the conclusion that one was ceryl alcohol $C_{26}H_{54}O$ or $C_{27}H_{56}O$, convertible into cerotic acid by heating with soda lime and that another was $C_{25}H_{50}O$ or $C_{26}H_{52}O$. (These alcohols, doubtless, were not present free in the wax, but were produced by the saponification of their esters with palmitic acid.)

Marie (Ann. Chim. 1896 [7], 7, 145) made a close examination of the product regarded by Brodie as cerotic acid. He found that fractional solution in methyl alcohol was a much better method of separation than fractional precipitation or fractional crystallisation, and that it effected separation into pure cerotic acid and a much larger proportion of melissic acid than had previously been believed to be present. He regarded cerotic acid as being $C_{28}H_{56}O_2$ or $C_{28}H_{54}O_2$ with m.p. 77.5° , the evidence pointing to the first of these formulæ; and melissic acid as being $C_{28}H_{54}O_2$ with m.p. 90° . He obtained from beeswax about 15 p.c. of the pure mixed acids, and in this he found 30–40 p.c. of melissic acid. As regards these percentages, it should be noted that in extracting the beeswax with boiling alcohol to obtain the free cerotic and melissic acids a certain amount of myricin (melissyl palmitate, &c.) dissolves too. In the treatment adopted by Marie, namely, heating the crude mixed acids with potash-lime and potash, the alcohol radicles of the myricin are converted into melissic and cerotic acids, and these are included in his percentages, although they were not present free in the beeswax. What proportion they amounted to is not clearly stated; perhaps it was not large. His object was rather to get cerotic acid than to estimate its amount in beeswax.

Schalkef (Ber. 1876, 9, 278, and 1888; 1879, 12, 696, from Russian Phys. Chem. Soc.) thinks that cerotic acid, melissic acid, and melisin are mixtures of several substances and that in cerotic acid he found an acid with m.p. 91° and formula $C_{28}H_{56}O_2$. Lipp and Casimir (J. pr. Chem. 1919, 99, 263) found in Ghedda wax an acid with this formula, but with m.p. 94.5° – 95° .

Heiduschka and Gareis (J. pr. Chem. 1919, 99, 293) have studied the question of the formulæ for melissyl alcohol and melissic acid obtained from beeswax, and of the formulæ for the similar alcohol and acid obtained from carnaüba wax. They find that the products obtained from carnaüba wax have the formulæ $C_{30}H_{60}OH$ and $C_{30}H_{58}O_2$, whilst those from beeswax contain CH_2 more and are $C_{31}H_{62}OH$ and $C_{31}H_{60}O_2$. They succeeded in preparing from the carnaüba wax alcohol the acid with an added carbon atom, and found that its lead salt was identical with that of beeswax-melissic acid. Analyses of a number of compounds that they prepared also supported these views.

The question of the total amount of hydrocarbons in beeswax can hardly be considered as settled yet. In order to determine it A. and P. Buisine (Bull. Soc. chim. 1890, [3] 3, 872 and 1891, 5, 656), using Dumas and Stas's reaction (Annalen, 1840, 35, 129), heated beeswax with potash and potash lime to 250° . In this way potassium salts of the acids are formed and the alcoholic radicles in the esters are converted into salts of the corresponding acids with evolution of hydrogen; these salts remain undissolved when the product is extracted with ether or petroleum ether, whilst the hydrocarbons go into solution. They found 12.5–14.5 p.c. and that some were unsaturated as the hydrocarbon mixture absorbed 22 p.c. of iodine. Ahrens and Hett (J. Soc. Chem. Ind. 1899, 18, 591, from Zeitsch. öffentl. Chem. 5, 91), using Buisine's method, found from 12.7 to 17.5 p.c.

in different kinds of wax. Ryan and Dillon (Sci. Proc. Roy. Dublin Soc. 1916, 15, 107) found, however, that the product, supposed to be nothing but hydrocarbons, obtained from beeswax by a series of treatments, including Dumas and Stas's reaction, really contained a little oxygen; this amounted on an average to 0.8 p.c. It therefore seems that Buisine's method gives results which are too high. Ryan and Dillon suggest that some primary alcohol may be present in the product and also some secondary or tertiary alcohols; for they found that secondary and tertiary alcohols when heated with potash-lime evolve no hydrogen, and that primary alcohols do not evolve the full theoretical amount. The method thus requires further study.

The hydrocarbon, *melene*, found by Fictet and Bouvier (J. 1915, 604) in coal, in vacuum-tar, in Galician paraffin, and in the distillation products of beeswax, was assumed to be a solid naphthene, $C_{30}H_{50}$. J. Marcusson and F. Büttger (Ber. 1924, 57, 633) have now found that Indian paraffin wax, which melts at 60° – 80° , consists very largely of *melene*. The hydrocarbon can be readily isolated by crystallisation from benzene and then from benzine. It melts, when pure, at 62° – 63° , has $d_{20}^{25} 0.7913$; $d_{20}^{25} 0.9037$; $n_D^{20} = 1.4228$. Its composition corresponds to $C_{30}H_{48}$, and on oxidation with strong hot nitric acid, it gives a mixture of aliphatic acids, whereas naphthenes, under similar conditions, give nitro-compounds. Further, by catalytic oxidation with air in presence of manganese dioxide, *melene* yields solid fatty acids, whilst naphthenes yield polynaphthemic acids; and *melene* is slowly assimilated at 30° by *Bacterium aliphaticum*, which is incapable of attacking naphthenes. *Melene* is therefore a paraffin and not a naphthene (J. Soc. Chem. Ind. 1924, 43, B 457; cf. Funcke, Arch. Pharm. 1921, 259, 93).

In order to discover the cause of the difficulty experienced in saponifying beeswax completely Berg (Chem. Zeit. 1908, 32, 777) investigated the substances, amounting to about 2 p.c., that remain in solution after boiling beeswax in alcohol and allowing the liquid to cool, thus eliminating the crude cerotic acid and myricin. By evaporating the solution and extracting the residue thus obtained with ice-cold petroleum ether, he first separated as insoluble 0.44 p.c. of a brown semi-fluid mass having an intense beeswax odour. In the part that dissolved he found indications of various acids and then cholesterol esters, discovered by the colour test; he believes that 0.6 p.c. of these are present in beeswax, and probably considerably more. Such esters are difficult to saponify and have high saponification values. He saponified them and found cholesterols and several acids which seemed to be acetic, butyric, valeric, and others which were not volatile on the water bath, and included one that possessed the beeswax odour and was unsaturated, as its lead salt was soluble in ether. He did not succeed in making any ultimate analyses; but his work shows what a large number of compounds are contained in beeswax in minute proportions. He also examined in the same way a white wax bleached by permanganate.

Summing up the results of the various re-

searches, it appears that ordinary beeswax is composed chiefly of melissyl palmitate $C_{15}H_{31} \cdot C_{15}H_{31}O_2$, with some ceryl palmitate $C_{15}H_{31} \cdot C_{21}H_{43}O_2$, and some palmitate of the radicle $C_{21}H_{43}$; these are contained in the part known as myricin, which is very nearly insoluble in boiling alcohol. In the part known as cerin, which is soluble in boiling alcohol, there are present free acids amounting when purified to about 15 p.c. of the beeswax, chiefly cerotic acid. According to Mario, crude cerotic acid contains about 60 to 70 p.c. of cerotic acid $C_{26}H_{52}O_2$, and about 30 to 40 p.c. of melissic acid; but owing to the method he used, some of these acids may have come from decomposition of some of the myricin. There are also indications of the presence of another acid. Hydrocarbons are also present, namely, normal heptacosane $C_{27}H_{56}$, and normal hentriacontane $C_{31}H_{64}$, together amounting to 5 to 6 p.c., and in addition a soft vaseline-like mass has been separated.

Gascard and Damoy (Compt. rend. 1923, 177, 1222, 1442) state that after saponification they have obtained from beeswax the following compounds: (1) Neocerotic acid $C_{26}H_{52}O_2$ (m.p. 77.8°), the same acid that Mario described as having m.p. 77.8° and called cerotic acid. It has the same formula as Carius's hyaenic acid, but they consider that that was not a pure compound. (2) Cerotic acid $C_{27}H_{54}O_2$ (m.p. 82.5°), identical with that obtained from Chinese insect wax, and apparently identical with the acid that Tropsch and Kreutzer (Brennstoff-Chemie, 1922, 3, 49, 177) obtained from montan wax and named carbocerinic acid. (3) Montanic acid $C_{28}H_{56}O_2$ (m.p. 86.8°), apparently identical with the acid that Tropsch and Kreutzer (l.c.) obtained from montan wax and called montanic acid. (4) Melissic acid $C_{21}H_{42}O_2$ (m.p. 90°). They suggest that perhaps the acid that Brodie obtained from myricin is really not palmitic acid $C_{16}H_{32}O_2$, but one with an uneven number of carbon atoms. (5) Neoceryl alcohol $C_{26}H_{54}O$ (m.p. 75.5°). (6) Ceryl alcohol $C_{27}H_{56}O$ (m.p. 80°), identical with that from Chinese insect wax. (7) Montanyl alcohol $C_{28}H_{58}O$ (m.p. 84°). (8) Myricyl [melissyl] alcohol $C_{21}H_{44}O$ (m.p. 87°). The ceryl and melissyl alcohols were the most abundant of the alcohols. (9) Pentaacosane $C_{25}H_{50}$ (m.p. $54^\circ-54.5^\circ$). (10) Heptacosane $C_{27}H_{54}$ (m.p. $59.2^\circ-59.5^\circ$). (11) Nonacosane $C_{29}H_{58}$ (m.p. 63.5°). (12) Hentriacontane $C_{31}H_{64}$ (m.p. $68.4^\circ-69^\circ$).

Indications have been found of many minor constituents which have not yet been fully identified: (1) The yellow colouring matter which is very soluble in alcohol. (2) The substances to which the characteristic odour of beeswax is due. (3) Unsaturated acids (their lead salts being soluble in ether), both free and as esters; the odour seems to be associated with these. (4) Various other acids. (5) Cholesterols combined as esters, perhaps with acetic, butyric, valeric, and non-volatile acids. These cholesterol esters amount to at least 0.6 p.c. of the beeswax and very probably more, and perhaps some cholesterols are also present free. (6) It has been suggested that the difficult saponification of beeswax is due to the presence of lactones as well as to the cholesterol esters, since carnauba wax is known to yield a lactone. (7) Buchner (Zeitsch. öffentl. Chem. 1910, 16, 131) says that traces of

glycerides are nearly always present in beeswaxes.

It must be remembered that a substance like beeswax is not of constant composition and that there are many circumstances likely to cause variations such as the breed of the bee and the weather of the year it was produced in. Further, Reid (J. Soc. Chem. Ind. 1915, 34, 462) points out that usually in melting the comb some of the propolis is absorbed by the wax, and that the wax from old pollen-clogged combs is different from that from new combs.

Foreign varieties of beeswax.—In addition to wax resembling European beeswax fairly closely, varieties giving very different analytical values are imported into Europe; they are products of various species of bees other than *Apis mellifica*. About 1896, samples of Indian beeswax were appearing in Germany under the name of *Ghedda wax* and were examined by Buchner; it turned out later that they were products from *Apis dorsata*, *A. indica*, and *A. florea*. He found that they gave values differing considerably from those of ordinary beeswax, although they resembled it in appearance. They were, however, brighter in colour, more plastic, and had a pleasant odour, which was especially noticeable on saponification. This Indian beeswax continued to come on the German market from Bombay. Buchner (Chem. Zeit. 1905, 29, 79) found that it was characterised by a low acid value, a high ester value, and a high ratio value; thus in 36 samples he found the acid value to range from 5.3 to 12.2, but only in four samples was it over 10. The ester value ranged from 75.2 to 111.5, the saponification value from 81.8 to 120.2, and the ratio value from 7.4 to 17.9. Wax of this description appears sometimes to have been called China wax, and may have come from Annam or French Cochinchina as well as from India. Buchner maintains that Ghedda wax is a true beeswax (Chem. Zeit. 1905, 29, 79 and 1906, 30, 529), so that the difference in its analytical values must be remembered when judging the purity of a beeswax.

Hooper (Agricultural Ledger of India, 1904, 11, 73) describes the species of bees found in India, and the wax and honey trade there. The wax is derived from *Apis dorsata*, *A. indica*, and *A. florea*, but chiefly from *A. dorsata*; *A. mellifica* does not occur there except as an importation. The wax from the combs of these three species seems to be substantially of the same composition. It differs from European beeswax in having a much lower acid value; in the case of 33 specimens from these three species the acid value ranged from 4.4 to 10.2, with an average of about 7, the ester value from 69.5 to 123.8, the saponification value from 75.6 to 130.5, and the Hübl iodine value from 4.8 to 11.4. The m.p. ranged from 60° to 68° . Some Indian waxes of unknown origin gave higher acid values and other values outside these limits. In the comb the upper part gives a clean white wax and the lower part a dirty and coloured substance; but as a rule these parts are not separated before melting. Turmeric is universally added to give the wax a golden yellow colour, as white wax is not appreciated in the native markets. In one district it is said that oil of *Sesamum indicum* is added.

Hooper (l.c. p. 79) also describes another kind

of beeswax produced in India and Burma by minute stingless bees of the *Melipona* or *Trigona* species, sometimes called mosquito bees or dammar bees. It is of a blackish colour and sticky consistency. In 8 specimens the acid value ranged from 16.1 to 22.9, the ester value from 55.2 to 128.3, the saponification value from 73.7 to 150, the iodine value from 30.2 to 49.6, and the m.p. from 66° to 76°.

Most probably the natives do not keep the *Melipona* wax separate, but mix it indiscriminately with the wax of the three *Apis* species.

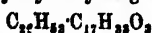
Hooper describes (*ibid.* 1908, 9, [3] 31, Abstract in J. Soc. Chem. Ind. 1909, 28, 664) *Pwé-nyet* (black wax of Burma) obtained from the nests of *Trigona laeviceps* and possibly from those of other dammar bees; it is not always black and seems to be more of a resin than a wax.

In the old records a wax called *Andaquies wax* is described as being collected by the Indians in New Grenada (now Colombia), especially by the Tamas tribe, which lives near the Rio Caquetá. It was probably the product of small *Melipona* bees. A sample was examined by Lewy (Ann. Chim. 1845, [3] 13, 453); after purifying it by treatment with boiling water he found that its m.p. was 77°, its sp.gr. at 0° was 0.917, and that it contained 81.66 p.c. of carbon and 13.55 p.c. of hydrogen. It was used locally for making candles for religious worship.

A black beeswax found in the Dutch Indies is described by Blits (Nederl. Tijdschr. Pharm. 10, 35, abstr. in J. Soc. Chem. Ind. 1898, 17, 468), and the wax of a South Brazilian bee, probably of the *Melipona* or *Trigona* species, is described by Gadamer and Hinderer (Arch. Pharm. 1917, 255, 425), who gives its composition as well as its analytical values.

Returning to the Ghedda wax, there is a long paper by Buchner and Fischer (Zeitsch. öffentl. Chem. 1913, 19, pp. 147, 170, and 188) on East Indian or Ghedda wax, and on so-called China wax, which gives 160 analyses by Buchner and 108 analyses by Schulten, of Calcutta. Further information about the beeswaxes of India and Eastern Asia is given by several papers of Fischer (*ibid.* for 1913 and 1914). Recently 23 samples of comb and beeswax from Bengal and Assam, collected under the supervision of District Officers, were examined at the Imperial Institute by Roberts and Islip (Analyst, 1922, 46, 246); they found that neither Weinwurm's test nor that of Salamon and Seaber could be relied on.

The composition of Ghedda wax or East Indian beeswax has been investigated by Lipp, with Kuhn, Kovács, and Casimir (J. pr. Chem. 1912, 86, 184; 1919, 99, 243, and 256). They found that the principal components are: one of the ceryl hydroxymargarates



ceryl margarate $C_{17}H_{33} \cdot C_{17}H_{33}O_2$, and ceryl palmitate $C_{16}H_{33} \cdot C_{17}H_{33}O_2$; together with roughly 7 p.c. of hydrocarbons, namely: heptacosane $C_{27}H_{54}$ (roughly 5 p.c.), hentriacontane $C_{31}H_{62}$ (roughly 2 p.c.), and indications of another hydrocarbon which they could not isolate. As in European beeswax, they found some free acids, but only in small proportions, namely, cerotic acid $C_{26}H_{52}O_2$ and an acid $C_{24}H_{48}O_2$, which they named *Ghedda acid*. Its m.p. was 94.5°-95°.

An acid with this formula and m.p. 91° was described by Schalteel (Ber. 1876, 9, 278, and 1888). These two acids are present chiefly in the free state and the other acids as ceryl esters. In the products of hydrolysis they found also, but only in small proportion, a different hydroxymargaric acid and traces of formic, acetic, and butyric acids and of a resinous substance.

White or bleached beeswax.—Most beeswax is bleached before use; bleached beeswax is harder, and candles made from it burn better than those made of yellow beeswax. The bleaching is effected by exposure to light and air or by chemical agents, or by both methods. Chemical agents do not bleach it so thoroughly as does light, so that when they are used a final bleaching by light is required to get the best results; they serve, however, to shorten the time taken in bleaching.

The wax is first purified by repeated meltings in hot water until it is no longer grey, and any remaining honey is removed. In doing this the grey underlayer is cut or scraped off from the cooled cake of wax, and is remelted with the next lot treated. If the water used is hard, it is stated (Cheshire, Bees and Bee-Keeping, p. 589) that the cerotic acid of the wax forms an insoluble calcium soap, appearing as a grey spongy material and that thus a waste of wax is occasioned. Rain-water or distilled water should therefore be used, or else the water should be acidified with sulphuric acid. The use of acidified water also checks the formation of emulsions, and is recommended for the various remeltings. Old and dirty combs should be soaked in cold water for some time before melting, as the dirt and cocoon skins when wet do not absorb and waste wax as they would if dry.

In order to expose as much surface as possible to the sun's rays, the wax is reduced to thin bands. The melted wax is poured into a box of metal plate, in the bottom of which are several narrow slits or holes. These are directly over a horizontal wooden roller revolving in a vessel containing cold water, which covers half the roller. The wax escapes from the slits in bands, which pass on to the revolving roller and solidify in the water in the form of thin ribbons. These ribbons are removed from the water, spread on canvas stretched over wooden frames, and exposed to the sun; they are sprinkled from time to time with water to keep them moist, and turned over to expose fresh surfaces to the sun. If the sunshine is very powerful, the heat may cause the ribbons to stick together; this can be avoided by watering, but not more than is necessary should be employed, as Heinz (Seifensieder Zeitung, 1913, 40, 1140) thinks that evaporating water vapour checks the oxidizing action of the air. The inner portion of the ribbon bleaches more slowly than the outer surface, so to accelerate the bleaching the partially bleached wax is remelted and again made into ribbons, so that new surfaces are exposed; this remelting, however, causes some loss. Wax from different sources bleaches with varying facility, and some varieties cannot be bleached, so samples should first be tried on a small scale.

The addition of a little oil of turpentine to the yellow wax before making it into ribbons reduces the time taken in bleaching, but in acid

by Heins to impart an unpleasant odour to the wax. Rectified oil of turpentine free from resin should be used. The bleaching effect of oil of turpentine was noticed by Ostermaier (Repert. f. d. Pharm. 1834, 48, 97). Sometimes a few p.c. of tallow are added to the wax to hasten the bleaching and to diminish brittleness, and this is considered allowable and is not counted as an adulteration.

After a longer or shorter period, depending on the intensity of the sunshine and the temperature, the bleaching is complete; it takes from 10 to 60 days. The wax is then once more melted in hot water, strained, and allowed to solidify in suitable shapes.

When chemical agents are used a mixture of potassium dichromate and sulphuric acid is said to be the best (Heinz, Seifensieder Zeitung, 1913, 40, 1140, 1169, and 1192). The wax is boiled with a solution containing 12 parts of potassium dichromate and 35 parts of sulphuric acid to 100 parts of water and wax. The green chromium compound produced by the reduction of the dichromate is removed by washing the wax with water containing 6-8 p.c. of lactic acid, or containing sulphuric acid. This process has been found effective even with some waxes that were considered unbleachable.

Potassium permanganate solution, followed by sulphurous acid has been tried, but the results were not very satisfactory. Other chemical agents that have been tried or recommended are the use of artificially made ozone, of hydrogen peroxide acidified with sulphuric acid, of barium peroxide of potassium chlorate with sulphuric acid, of a liquid prepared from bleaching powder and soda. The formation of chlorine compounds in the wax is objectionable, however, as hydrochloric acid is liberated when the wax is burnt. Whenever chemicals are used they should be thoroughly washed out of the wax when the bleaching is accomplished.

Another proposed way of decolorizing beeswax is by the use of agents that absorb the colouring matters, such as animal charcoal, fuller's earth, and the like.

The theory of bleaching and the effect of various methods and also the effect of the addition of a little tallow to the yellow wax have been studied by A. and P. Buisine (Compt. rend. 1891, 112, 738, and Bull. Soc. chim. 1890, [3] 4, 465); they found that light is necessary, since, in the dark, yellow wax is not bleached when kept in a current of air or of oxygen or of ozonised oxygen, whilst in sunlight it is bleached even when kept in carbon dioxide or nitrogen or in a vacuum, though much more slowly than in air. In oxygen it bleaches more rapidly than in air, and very rapidly in ozonised oxygen. They noticed that in air-bleaching the colour does not decrease uniformly, but that white spots are seen which increase in size. They think that the colouring matter undergoes total combustion and that the oxidation of the unsaturated hydrocarbons and unsaturated acids induce this combustion, and that is why the addition of tallow, which contains olein, helps the bleaching. Oil of turpentine acts in the same way because it undergoes oxidation. They think it probable that these substances when undergoing oxidation in the light give rise to ozone, and that this under the influence of light burns up the colour-

ing matter; it being known that oil of turpentine exposed to air and light produces ozone, and that tallow, whilst turning rancid, gives an odour like ozone. They found in most cases that the m.p., the acid value, and the saponification value are increased, and that the iodine value and the percentage of hydrocarbons are lowered; decolorizing by animal charcoal, however, caused little change in the values.

Berg (Chem. Zeit. 1902, 26, 605) also records many experiments on the subject; he finds that the acid value is raised and the ratio value consequently lowered, which should be borne in mind when examining a white wax for admixtures. It is not easy, however, to draw general conclusions from his results. In Chem. Zeit. 1903, 27, 754, and 1908, 32, 778, he again treats of white wax.

Medicus and Wellenstein (Zeitsch. Nahr. Genussm. 1902, 5, 1092) examined the bleaching action of potassium chromate and sulphuric acid; they found: (1) that the acid value and the saponification value were considerably increased, but that the ester value was unaltered; (2) that the m.p. was raised 1°; (3) that the characteristic odour of yellow wax was destroyed or volatilised; (4) that no stearic acid could be found by the Fehling-Röttger test either before or after bleaching; (5) that the ester value of some myricin prepared from yellow wax was only slightly increased by bleaching.

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After dilution with 15 c.c. of water, the mixture is slowly acidified with dilute sulphuric acid (1:4) and filtered; 2 c.c. of the filtrate are treated with 20 c.c. of saturated bromine water till colourless, and 2 c.c. of this solution are treated with 0.1 c.c. of alcoholic solution of codeine and 5 c.c. of pure sulphuric acid (d. 1.84). After shaking and heating on a boiling water bath for 2 minutes, a fine greenish-blue coloration develops if glycerol is present; 1 p.c. of a glyceride can easily be detected in beeswax by this test (J. Soc. Chem. Ind. 1924, 43, B. 431). Lipp and Kuhn (J. pr. Chem. 1912, 86, 184), composition of Indian (Ghedda) beeswax. Mastbaum (Chem. Rev. Fett-u. Harz-Ind. 1912, 19, 232 and 260), beeswax of Portugal and its colonies; method of examining. Prettner (Prometheus, 1912, 23, 341), origin, preparation, uses, and adulterants. Leys (J. Pharm. 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Candelilla wax is obtained from plants growing wild in great quantities in the dry and desert-like districts of northern Mexico and the southern parts of the United States; they are called 'candelilla' by the Mexicans. It is a recent addition to the waxes in commercial use, attention having been called to the wax on these plants by Sanders in 1905. *Euphorbia corollata* (Alcoocor), *E. antisyphilitica* (Zucc.), and *Pedicularis Pectoris* (Boiss.) have been given as the plants from which the wax is obtained.

It occurs as an excretion covering all parts of

the plant, except the roots. It can be obtained by boiling the plants with water and skimming off the layer of melted wax; the pieces of plant must be kept from rising by enclosing them in wire cloth or by tying them in bundles and weighting these down. In practice a little sulphuric acid is added to the water when first obtaining the wax, and also when remelting; its action is probably to prevent the formation of an emulsion. Another plan is to subject the plant in suitable containers to live steam, which melts off the wax, and this can be easily separated from the condensed water. It is said that this plan gives a better yield, but that the wax appears softer and contains more water than that obtained by simply boiling out the wax from the plant. The wax can be purified by remelting and straining off plant debris. The yield of wax is from 1 to 5 p.c. In 1918 there were about twenty-five factories producing the wax in the Monterey district.

The wax is hard and brittle, and can be broken down to a powder at low temperatures; when full of air bubbles and water it is opaque and greyish-yellow in colour, but if these are got rid of by melting it is dark brown and translucent. When heated it gives off an aromatic odour. It is only slightly soluble in alcohol, ether, acetone, chloroform, carbon disulphide, gasoline, and oil of turpentine when cold, but is readily soluble in all these when hot; a boiling mixture of three parts absolute alcohol and two parts of 90 p.c. benzene was found to be an excellent solvent. On cooling these solutions become pomade-like masses.

The analytical values that have been recorded vary widely; this may be due to the age of the plant, the time of year at which it was gathered, the mode of preparation, the presence of water in the sample examined, the method of analysis, or even to adulteration. The following are the lowest and highest values found in the literature of the wax: m.p. 65° to 92°; sp.gr. 0.936 to 0.998; acid value 0.03 to 24; saponification value 35 to 104; iodine value 5.2 to 57.6; unsaponifiable matter 65 to 91.2 p.c. There are also variable amounts of dirt, water, and ash. These analytical values vary so much that it may be well to add those of the following authors.

Sanders (Chem. Soc. Proc. 1911, 27, 250) states that a sample of wax prepared in January from plants collected in Coahuila was greenish-white, and contained a considerable proportion of water. When freed from this it was dark brown and gave the following values: m.p. 67.5°; sp.gr. 0.9850; acid value 14.39; saponification value 46.76; iodine value (Hübl) 16.60; unsaponifiable matter 77.00 p.c.; and hydrocarbons 48.60 p.c.; he found hentriacontane and melissyl alcohol (whether free or as ester is not stated).

Lüdecke (Seifensieder Zeit. 1912, 39, 829) gives as normal values: m.p. 68-70°; sp.gr. 0.950-0.990; acid value 13-18; saponification value 50-60; iodine value 15-20; unsaponifiable matter 65-75 p.c.; moisture 2 to 3 p.c.; and dirt 0 to 3 p.c.

Berg (Chem. Zeit. 1914, 38, 1162) gives for a grey crude wax: m.p. 80-88°; acid value 9.8; ester value 44.0; saponification value 53.6; and as the mean of two samples of brown wax: m.p. 68.5°; sp.gr. at 15°/15° 0.986; acid value

11.6; ester value 51.5; saponification value 65.1; iodine value (Wijs) 57.6 after 19 hours standing, 14.5 after 3 hours; unsaponifiable matter 67.5 p.c. Both Berg and Lüdecke used xylene when saponifying.

Composition.—Candelilla wax is remarkable among the waxes for the high proportion of hydrocarbons that it contains, but as in the case of its analytical values the results of investigations as to its composition are discordant. Sanders, in *Anal. Inst. Med. Nacional, Mexico*, for Oct. 1907, recorded the presence of hentriacontane (*J. Ind. Eng. Chem.* 1911, 3, 115). Fraps and Rather (*ibid.* 1910, 2, 454) found hentriacontane with m.p. 68°, and indications of another hydrocarbon with m.p. 85°, and of other substances.

Meyer and Soyka (*Monatsh.* 1913, 34, 1159) found that it contained resin amounting to 18 to 20 p.c., to this they attribute the acid value and the iodine value. They removed most of the resin by repeatedly boiling out the wax with alcohol, allowing to cool and then separating the alcoholic resin-solutions; they then removed from the residue all that ether would dissolve. In the soluble part, after removing the last traces of resin by the charring action of thionyl chloride, they found a hydrocarbon which they believe to be normal dotriacontane $C_{32}H_{66}$, with m.p. 71°, and in the insoluble part they found an oxylactone $C_{30}H_{58}O_2$, with m.p. 88° to 88.5°, identical or isomeric with the lactone of lanoceric acid. They sum up the composition as 18 to 20 p.c. of resin, 74 to 76 p.c. of dotriacontane, and 5 to 6 p.c. of the oxylactone.

Berg (*Chem. Zeit.* 1914, 38, 1162) found: (a and b) about 50 p.c. of two hydrocarbons, one with m.p. 68° and the other with m.p. 84°–85°; (c and d) about 10 p.c. of a semi-fluid mixture of two cholesterols, these were free in the wax, when acetylated they yielded acetates, one a white powder, nearly insoluble in alcohol, the other readily soluble in alcohol on warming; (e) a small quantity of a substance containing oxygen, with m.p. 88°–89°, it was fairly soluble in alcohol, could be acetylated, did not give any cholesterol reaction, and must have been present in the wax as an ester; (f) a very small quantity of a substance containing oxygen, melting with decomposition at 243°, it was readily soluble in alcohol, from which it crystallised in leaflets, it could not be acetylated, it gave a colour reaction with acetic anhydride and sulphuric acid, and may be an ester of a lupool-like cholesterol.

Buchner (*Chem. Zeit.* 1918, 42, 374) gives the composition as determined by Staempfli as: 50–52 p.c. of a hydrocarbon $C_{31}H_{64}$, with m.p. 68°; 25 p.c. of melissic acid $C_{31}H_{62}O_2$, present partly free and partly as a melissyl ester with m.p. 88°–90°; 10–14 p.c. of melissyl alcohol $C_{31}H_{64}O$, with m.p. 85° (whether free or as ester is not stated); 1 p.c. of another hydrocarbon, with m.p. 85°; traces of a phytosterol, with m.p. over 130°; and 10 p.c. of resinous matter; but none of the experimental evidence is given.

Uses.—Owing to its hardness it resembles carnauba wax. It is especially valuable in making shoe-creams and polishes, as it imparts to such preparations the power of producing a brighter lustre than any other wax. On the other hand, when mixed with paraffin wax it

has not nearly as great a hardening effect as carnauba wax, and it has little hardening action when mixed with soft wax compositions. For candle making it is considered inferior to carnauba wax, owing to its lower melting-point (given as 65°), and for phonograph records its suitability is considered small. The insulation of telephone cables is another suggested use.

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Cape berry wax. Samples of this wax have been shown at exhibitions in London, and it is capable of being collected in quantities in Cape Colony, but it has not yet come into any extensive use. It is probably derived from one of the species of *Myrica* growing in South Africa, which include *M. quercifolia* (Linn.), *M. cordifolia* (Linn.), and *M. serrata* (Lam.); it is similar to myrtle berry wax in its general characters and in its physical and chemical properties, which were found to be: sp.gr. 0.874 at 99°; m.p. 40.5°; m.p. of the fatty acids 47.5°; mean molecular weight of the fatty acids 236.1; acid value 4.1; saponification value 211.1; iodine value 1.1. It yields a hard white soap, but does not seem to be suitable for candle making (*Imp. Inst. Bull.* 1906, 4, 300). The results of another examination are: sp.gr. 0.9893; m.p. 49°; refractive index at 80° 1.4364; acid value 2.5; saponification value 212.3; iodine value 2.03; unsaponifiable matter 2.51 p.c.; fatty acids 89.7 p.c.; m.p. of mixed fatty acids 48.5°; solidifying-point of these 46.5°; mean molecular weight of these 241.4; it was described as South African berry wax, and was pale greenish-grey with a granular fracture; when melted it formed a greenish-brown muddy liquid, and it was filtered before examination (*Cooking, Chem. and Drug.* 1908, 73, 74).

Berry wax from *M. cordifolia* came into prominence during the war. The plant is grown as a sand-binder in the neighbourhood of Cape Town, Port Elizabeth, and other places. The wax was previously exported to Germany, and

was used for gramophones and for floor polish (J. Soc. Chem. Ind. 1918, 37, 74 R).

Carnaúba or carnaúba wax is derived from the carnaúba palm, *Copernicia cerifera* (Mart.) (*Corypha cerifera*, Linn.), which grows in Brazil, especially in the provinces of Ceara, Rio Grande do Norte, and Piahy. The trunk is 25-35 ft. high with a crown of leaves at the top. The young leaves of about 3 ft. long have a coating of wax on both the upper and under sides, which appears homogeneous to the naked eye. The wax layer is thicker on the upper side, and comes off in scales; on the lower side it is thinner and more adherent. The harvesting extends over the six dry months of the year, and the leaves are cut twice a month, about eight leaves being cut from a palm at a time, those leaves that have reached a certain stage of development being taken, leaving the very young leaves to develop later. If the leaves are allowed to become too old the wax is easily detached, and is lost before the leaves are brought to the ground. The leaves are spread out to dry, and are then slit up with a knife and beaten over a cloth to detach the wax which comes off in scales or as a greyish-white powder. A little water is added to the powder, and it is melted and poured into moulds, in which it solidifies in cakes of about 2 kilos. About 850 leaves give 16 kilos. of wax; about 1·8 kilos. of wax, valued at 1s. 6d., are obtained from one palm. On poor land 1200 leaves, and on good land only 500 leaves are required to give the 16 kilos. In some estimates, however, the yields are not so good as these.

The following table, based on Hambloch's Reports on Brazil, Dept. Overseas Trade, 1919, 1921, and 1922, shows the exportation of carnaúba wax:

Year	Metric tons	Value in £	Value per metric ton in £
1913	3867	439,500	114
1914	3315	324,200	98
1915	5897	505,100	86
1916	4166	398,900	96
1917	3669	443,300	121
1918	4215	1,135,200	269
1919	6200		
1920	3500		
1921	1540	January to June (inclusive)	
1922	2200	" "	"

In 1913 Germany took 1710 metric tons; the United States 941; the United Kingdom 687; and France 509. In 1920 the United Kingdom took 1000 metric tons and the United States 2200.

Raw carnaúba wax is of a dirty yellowish or greenish colour, amorphous, hard, brittle, and easy to powder. In its outward appearance it is compact, but penetrated with very many air spaces; it is tasteless, and smells, when fresh, somewhat like fresh hay—i.e. of coumarin; later it becomes inodorous. It is purified by remelting, and has then a greenish-yellow or straw-yellow colour.

Analytical values.—The melting-point is variously given as from 80·5° to over 86°, it increases with the age of the sample, and an old specimen melted at 90°-91°; about 84° seems a common experience; light-coloured specimens have a somewhat lower melting-point than darker ones. The sp.gr. at 15° is 0·978-0·999.

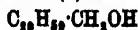
The acid values recorded are from 0·3-10, about 4 being common; the saponification values from 60-85, and even 95; the iodine values from 5-14. In preparing bleached carnaúba wax additions, such as paraffin wax, are made so that the above values do not hold good for it. The wax is not easily saponified. Berg (Chem. Zeit. 1909, 33, 885) recommends the use of xylene as a solvent in order to hasten the saponification and to diminish the risk of oxidation occurring during long boiling with potassium hydroxide.

Composition.—Carnaúba wax is composed mainly of an ester of triacontyl, $C_{30}H_{61}$, with the acid $C_{27}H_{54}O_2$, which is either cerotic acid or an isomer of it. The triacontyl was formerly supposed to be the same as the melissyl of beeswax, but it now appears that melissyl is most probably $C_{31}H_{62}$. Carnaúba wax also contains a considerable proportion of free triacontyl alcohol $C_{30}H_{61}OH$. In addition there are a number of compounds present in small proportions.

Story Maskelyne (J. Chem. Soc. 1869, 22, 87) found: (a) melissin (melissyl alcohol) both free and coming from an ester; (b) a compound with m.p. 105°, corresponding to $C_{30}H_{61}O_2$; (c) an alcohol with m.p. 78°, corresponding to $C_{33}H_{68}O$, and also other compounds.

Von Pieverling (Annalen, 1870, 183, 344) prepared from this wax melissyl alcohol and examined its products, he also obtained a small quantity of ceryl alcohol $C_{27}H_{56}O$.

A long investigation of the composition was made by Sturcke (Annalen, 1884, 223, 283), employing carnaúba wax with m.p. 83°-83·5°. He found that the principal component was the ester $C_{30}H_{61} \cdot C_{27}H_{54}O_2$, and that there was a considerable quantity of free wax alcohol present. When the wax is extracted with boiling alcohol a considerable proportion dissolves but separates again when the alcohol cools. He found when 1200 grms. of wax were boiled out with 5½ litres of alcohol and the hot clear solution was poured off that on cooling 350 grms. (equivalent to 29 p.c.) were deposited. By repeated extraction small quantities of the ester seem to be removed each time; thus when 10 grms. of the wax were boiled with half-litre lots of alcohol, 350 c.c. of the ninth lot contained 0·295 grm. and of the tenth lot 0·286 grm. By saponifying the wax and separating the products with petroleum ether, &c., and by many fractionations he found: (1) A hydrocarbon with m.p. 59°-59·5° present in small proportion. (2) An alcohol $C_{26}H_{53} \cdot CH_2OH$ with m.p. 76° in small proportion. (3) An alcohol



with m.p. 85·5°-85·7° in large proportion. From this he prepared the acid $C_{28}H_{56} \cdot COOH$ with m.p. 80°-80·2°. This alcohol he called myricyl (melissyl) alcohol, but according to Heiduschke and Gareis (J. pr. Chem. 1919, 99, 299) it contains CH_2 , less than the melissyl alcohol $C_{31}H_{64}O$ obtained from beeswax. (4) A dihydroxy alcohol $C_{29}H_{58}(OH)_2$ with m.p. 103·5°-103·8° in small proportion. From this he prepared the acid $C_{28}H_{56}(COOH)_2$ with m.p. 102·5°. (5) An acid $C_{28}H_{56} \cdot COOH$ with m.p. 72·5° in small proportion, isomeric with lignoceric acid. This acid was subsequently

called carnaubic acid by Darmstaedter and Edischts (Ber. 1896, 29, 620) in a paper on wool fat. (8) An acid $C_{15}H_{31}COOH$ with m.p. 78.8° – 79° , either identical or isomeric with the cerotic acid of beeswax, in large proportion. It would not crystallise when it solidified from the melted state, and for this reason he doubted its identity with the cerotic acid of beeswax.

(7) A lactone $C_{15}H_{31}<\begin{smallmatrix}CH\\CO\end{smallmatrix}>O$ with m.p. 103.5° in small proportion. From this he prepared the acid $C_{15}H_{31}(COOH)$, with m.p. 89.5° – 90° .

It should be noted that these products were obtained after saponification. The hydrocarbon, no doubt, was free in the wax, and the $C_{15}H_{31}CH_2OH$ alcohol probably was partly free and partly came from the ester, but the others were not proved to be free before saponification. Besides these Stürcke also noticed, as had von Pieverling, a greenish balsam-like substance with an odour like coumarin, but in too small quantity for examination. Stürcke's results, it should be remarked, do not fully explain the analytical values given above, so further work on the composition is needed.

Liebermann (Ber. 1885, 18, 1979) obtained a substance from the wax by a great many fractional crystallisations with m.p. 92° , which could not be materially raised by further crystallisations; it formed a matted paper-like layer without any lustre; he did not, however, make an analysis of it.

Heiduschka and Gareis's work (J. pr. Chem. 1919, 99, 293) is described above under the composition of beeswax.

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alcohol as solvent. Engler (Chem. Zeit. 1906, 30, 711), the rotatory power. Berg (Chem. Zeit. 1909, 33, 885), xylene as solvent for finding analytical values. Leys (J. Pharm. Chim. 1912, [7] 5, 577), describes a new method of examining this wax and beeswax; he uses a mixture of amyl alcohol and fuming hydrochloric acid to dissolve the wax alcohols and separate them from the hydrocarbons; he found no hydrocarbons in carnauba wax. Lüdecke (Seifensieder Zeit. 1913, 40, 1237, 1274, 1302, 1327), descriptions of the commercial varieties, adulterants (fragments of candellilla wax are sometimes mixed in), detailed methods of finding melting-point, sp.gr., and analytical values. Buchner (Chem. Zeit. 1918, 42, 373) quotes Popp on the formula of melissic acid prepared from carnauba wax (Heiduschka and Gareis do not agree with Popp's formula). Heiduschka and Gareis (J. pr. Chem. 1919, 99, 293) compare melissyl alcohol from beeswax and its derivatives with the alcohol from carnauba wax and its derivatives and find them to differ by CH_2 .

Cochin China wax (Cay Cay fat, Irvingia butter). This is obtained from the fruit of the Cay Cay tree, *Irvingia Oliveri* (Pierre), a forest tree reaching the height of 100 ft., and growing widely in the east of Cochin China. The fruit is the size of a lemon, the endocarp has the size and shape of an almond with its outer covering, and the kernel, too, resembles in size and shape that of the almond. The fruits are ripe in July, and fall to the ground; they are gathered into heaps by the natives, and left for two months to allow the soft outer parts to decompose; they are then carried to the houses and dried in the sun. They are opened with a strong knife, and the kernels are removed, dried in the sun, and pounded in a mortar. The pulp is placed in a vessel having a bottom of plaited material; this is fixed above water in another vessel, and the water is heated, but not to boiling. When the pulp has become a sticky paste it is wrapped in a mat of rice straw, and submitted to pressure in a crude press, the operations being repeated several times, and the melted wax is either allowed to solidify in moulds or else is cast into candles in bamboo tubes. In the laboratory the dry kernels extracted with carbon disulphide gave 52 p.c. of wax. The wax is of a greyish-yellow colour, and is unctuous to the touch. The purified wax softens at 37° , melts at 38° , and solidifies at 34° (Vignoli, Le Cay Cay, Thèse présentée à l'École Supérieure de Pharmacie de Montpellier, 1886).

Bontoux (Les Matières Grasses, 1908, 1276; J. Soc. Chem. Ind. 1909, 28, 429) found that 100 dry seeds weighed 360 grms. and gave 73 p.c. of shells and 22 p.c. of kernels. The latter, on extraction with light petroleum, gave 60.45 p.c. of wax. The wax had the consistency and texture of beeswax, and was more brittle, with the same conchoidal fracture; its sp.gr. at 40° compared with water at 40° was 0.913; it melted at 39.7° in a capillary tube, and solidified at 31° ; its acid value was 0.86; saponification value 235.3; unsaponifiable matter 0.42 p.c.; iodine value 6.7; Reichert-Meissl value 0.62. The insoluble fatty acids, together with the unsaponifiable matter were 04.0 p.c., their m.p. was 38.8° ; solidifying point (titer test) 36.6° ; neutralisation value 250.2;

and mean molecular weight 224. Two samples of the wax of native origin had nearly the same values, but the acid values were 23.5 and 34.9, which, however, are not excessive, and they contained 0.16 p.c. and 0.19 p.c. of unsaponifiable matter. Bontoux prepared methyl esters, and concluded that the wax was mainly composed of myristin 60-65 p.c., laurin 30-35 p.c., and about 5 p.c. of olein. The wax gives a hard white soap. The production in Indo-China has declined, owing to the introduction of petroleum. A Cay Cay wax is also obtained from the fruit of the tree *Irvingia malayana* (Oliver), which grows in Cambodia. Other references are: Heckel, *Annales de l'Institut colonial de Marseille*, 1893; Apoth. Zeit. 1898, 169; Crevost, *Les arbres à suif de l'Indochine*, Hanoi, 1902; Bulletin économique de l'Indochine, Hanoi, 1902; Chem. Zeit. 1903, 27, 43.

Cow tree wax (Milk tree wax). In the north of Venezuela, in the neighbourhood of Caracas and of Lake Maracaibo, and in the valley of Cuncagua, there grows a tree (*Brosimum Galactodendron*) called *Palo de vaca* or *Arbol de leche*, which yields a thick milk when incisions are made in its trunk; this is drunk like milk by the inhabitants. This milk, when heated, forms a skin, and if this is removed and evaporation continued, an oily liquid is obtained, together with a fibrous mass. The oily liquid when it has solidified, is a yellowish-white, hard translucent wax; it begins to melt at 40°, and is completely melted at 60°. It is insoluble in water, but is easily dissolved by essential oils. It dissolves in boiling alcohol and separates on cooling; it is saponifiable by caustic potash. It can be used like beeswax for making candles. Humboldt, *Ann. Chim.* 1817, 7, 182; Boussingault and Mariano de Rivero, *ibid.* 1823, 23, 219; Marchand, *J. pr. Chem.* 1840, [i.] 21, 43.

Esparto grass wax. In preparing the fibre of this grass for paper making the material reaches the mills in tightly compressed bales. It is there loosened by a special machine and at the same time freed from dust by a strong current of air from a powerful fan. This dust contains from 25-50 p.c. of wax, and in most mills is deposited in special dust collectors. The wax when obtained from the dust is hard, rather brittle, and of a light brown colour, and has the following characteristics: m.p. about 74°, loss of weight at 100° overnight about 1.5 p.c., ash 0.02 p.c., acid value 34.42, saponification value 71.41, iodine value 6.48, unsaponifiable matter (soluble in hot CCl_4) 50.34 p.c., fatty acids 45.69 p.c. The wax is in demand by some manufacturers and commands a good price; but unfortunately the quantity of dust obtainable at any one paper mill is not very large, so the output of wax is not equal to the demand (Budds, *J. Soc. Chem. Ind.* 1916, 35, 401).

Fig tree wax (Gondang or Kondang or Getah was, Jass or Sumatra wax). This wax is obtained in Java from the milky juice (*getah* in Malay) which runs from incisions made in the bark of the gondang, a wild fig tree (*Ficus stipitata*, Blume. = *F. cerifua*, Jungh. = *F. suberososa*, Blume.). The juice is boiled with water until the wax separates. It forms a fairly hard cake, cream coloured within, turning brown in the air; it has a conchoidal fracture and can be powdered, but not readily. The

crude wax melts at about 80° to a very viscous mass, which, on cooling, remains viscous for a long time, and from which an aqueous liquid separates. The sp.gr. of the wax after melting is 1.015 at 15°. It softens at 55°, and is only completely melted at 73°. It is soluble in benzene, chloroform, carbon disulphide, oil of turpentine, light petroleum, and boiling ether. Boiling alcohol dissolves it slowly, and the greater part separates on cooling. Cold alcohol keeps in solution a little over 5 p.c. of the wax. By means of boiling alcohol over 70 p.c. of white crystalline purified wax can be obtained, melting at 61°, insoluble in cold alcohol, but soluble in boiling alcohol. Greshoff and Sack (*Rec. trav. chim.* 1901, 20, 68), by analyses and saponification of the wax thus purified, obtained results suggesting that it is an ester $\text{C}_{20}\text{H}_{40}\text{O}_2$ of an alcohol $\text{C}_{17}\text{H}_{34}\text{O}$ (floceryl alcohol), with m.p. 198°, and of an acid $\text{C}_{12}\text{H}_{24}\text{O}_2$ (floceric acid), with a m.p. 57°, this ester is probably associated with some accessory substance; they also think the original wax contains some free floceryl alcohol.

Vogl (Lotos, published at Prag, 1872, 22, 54) describes Sumatra wax or Getah Lahoe coming from the same tree. Kessel (*Ber.* 1878, 11, 2112) assigns formulae to components of the wax which differ from the above. Ultee (*Chem. Zeit.* 1915, ii, 794, from *Pharm. Weekblad* 1915, 52, 1097) examined the milky sap of *Ficus variegata*; it contained 35 p.c. of solids, and when coagulated by heating, or by alcohol, or by dilute acetic acid it yielded gondang wax. From this by suitable treatment, including a saponification, he obtained a wax alcohol, the floceryl alcohol of Greshoff and Sack. This alcohol he identified as being the same as β -amyryn with m.p. 197.5°. (β -amyryn is $\text{C}_{20}\text{H}_{40}\text{O}$ and comes from elemi resin.) In the wax itself he found lupeol acetate with m.p. 190°-197°, but no free β -amyryn.

Insect wax. This is also called *Chinese wax*, *Chinese tree wax*, *Vegetable spermaceti*, and sometimes, but incorrectly, *Japanese wax*; it must not be confused with Japan wax. It is the secretion of an insect *Coccus pela* (Westwood), *Coccus ceriferus* (Fabr.). The industry of its production is peculiar, in that the insects are bred for the purpose of producing eggs in one district, and these eggs are then transported to another district where the insects are reared to produce wax. The Chien-Chang valley in the prefecture of Nung Yuan Fu (Long. $102^{\circ} 26'$, Lat. $27^{\circ} 54'$) in the Sze Chuan province of China is the great breeding-ground of the wax insect; it is about 5000 ft. above sea-level. Here the insects are reared on the *Ligustrum lucidum* (Ait.) or large-leaved privet. In March, when the trees were seen by Mr. Hosie, he found numerous brown pea-shaped excrescences attached to the bark of the boughs and twigs. The larger of these were readily detachable, and when opened presented either a whitish-brown pulpy mass or a crowd of minute animals like flour, whose movements were just perceptible to the naked eye. From 2 to 3 months later these had developed in each case into a swarm of brown creatures, each provided with six legs and a pair of antennae; each of these was a wax insect. Two hundred miles to the north-east of the Chien-Chang valley, and separated from it

by a series of mountain ranges, is the prefecture of Kia-ting-fu (Long. 104° , Lat. $29^{\circ} 34'$), also called Chia-ting-fu, containing the district of Omi and the valley of the Ya river, the headquarters of the wax-producing industry. The scales produced in the Chien-Chang valley are ready for removal by the end of April, and are then full of eggs; they are made up into paper packets, each weighing about 16 oz. Sixty of these packets make a load, and are conveyed by coolies from the Chien-Chang valley to the town of Hung Ya in the Kia-ting-fu prefecture for sale to the farmers. In May thousands of coolies are engaged in the traffic. They travel only at night, in order to avoid the high temperature of the day, which would tend to the rapid development of the insects and their escape from the scales. At the stopping places the packets are opened out in cool places; but in spite of this, each packet is found to have lost on an average an ounce in transit. A pound of scales laid down in Kia-ting-fu, in years of plenty, costs about half a crown; in bad years the price is doubled. In favourable years a pound of scales will produce 4-5 lbs. of wax. In the plain around Kia-ting-fu the plots of ground are thickly edged with stumps of *Fraxinus chinensis* (Roxb.), a species of ash varying from 3 or 4 to 12 ft. high, with numerous sprouts rising from their gnarled heads, and resembling at a distance pollard willows. On the arrival of the scales they are made up into small packets enclosed in a leaf of the wood-oil tree. The edges of the leaf are tied together with a rice straw, by which the packet is suspended close under the branches of this ash. A few rough holes are drilled in the leaf with a blunt needle, so that the insects may find their way through to the branches. On emerging from the scales the insects creep rapidly up to the leaves, among which they remain for a period of 13 days. They then descend to the branches, on the underside of which they take up their position, and commence to deposit the wax. This first appears as an under-coating on the sides of the boughs and twigs, and resembles quinine sulphate or a covering of snow. It gradually spreads over the whole branch, and attains, after 3 months, a thickness of about a quarter of an inch. After the lapse of 100 days the deposit is complete, the branches are lopped off, and as much of the wax as possible is removed by hand. This is placed in an iron pot of boiling water, and the wax on rising to the surface is skimmed off and placed in a round mould, whence it emerges as the insect wax of commerce. Where it is found impossible to remove the wax by hand, the twigs and branches are thrown into the pot, so that this wax is darker and inferior. The insects which have sunk to the bottom of the pot are placed in a bag and squeezed of the last drop of wax, and are then thrown to the pigs. Not only the *Fraxinus chinensis*, but also the *Leguam lucidum* is used in the final wax-producing stage of the industry. The wax is used for coating the exterior of animal and vegetable tallow candles, as it serves to hold in the more fusible tallow when the candle is burning; a little is also mixed with the tallow; it is employed to give a gloss to paper, for coating wood, and for a polish for furniture and iron-ware

(Nature, 1891, 43, 291; Wilson, Chemist and Druggist, 1906, 68, 143; Bull. Imp. Instit. 1924, 22, 64; Pharm. J. 1924, 27, 278).

Insect wax is white and crystalline, resembling spermaceti in appearance, but it is harder and more fibrous; it is brittle, and at 15° can be powdered. Its sp.gr. is 0.970 at 15° (0.926 at 15° , Gehe and Co., Zetsch. anal. Chem. 1895, 34, 765) and 0.809-0.811 at 98° - 99° ; m.p. 80° - 83° ; saponification value 80-83; iodine value 1.4. It is only very slightly soluble in alcohol and ether, but is readily soluble in naphtha, from which it can be crystallised. Brodie (Phil. Trans. 1848, 159) saponified the wax by melting it with potash, and obtained an alcohol and an acid; the alcohol he named *cerotin*, and to it he assigned the formula $C_{17}H_{34}O$, it is now called *ceryl alcohol*; the acid he considered to be the same as the cerotic acid he had obtained from beeswax, to which he had assigned the formula $C_{27}H_{54}O_2$; the wax he regarded as ceryl cerotate, the ester of this alcohol and acid. Brodie's formulæ have been supported by Gascard (see below). Marie (J. Chem. Soc. 1897, 72, 1, 318) proposes $C_{26}H_{52}O_2$ or $C_{25}H_{50}O_2$ for the cerotic acid of beeswax; and Henriques (*ibid.* 460) regards ceryl alcohol and cerotic acid from insect wax as $C_{26}H_{52}O$ and $C_{26}H_{52}O_2$, and it is stated that the identity of the cerotic acids from insect wax and from beeswax is not quite certain. Other substances besides ceryl cerotate are probably present.

Gascard (Compt. rend. 1920, 170, 1326) investigated the formulæ for the ceryl alcohol and for the cerotic acid obtained from insect wax, and confirmed those of Brodie, namely, $C_{17}H_{34}O$ with m.p. 80° for the alcohol and $C_{27}H_{54}O_2$ with m.p. 82° - 82.5° for the acid; but thought that the acid must be different from the cerotic acid of beeswax that Marie prepared with m.p. 77.5° . The following was his method. He started with insect wax with m.p. 80.5° - 81° , and first purified the ester, ceryl cerotate, by extraction with boiling acetone; the undissolved ester after recrystallisations from benzene melted at 84° . He saponified this by boiling with alcoholic potassium hydroxide. He then added calcium chloride and obtained a precipitate of calcium cerotate; from the filtrate he obtained the ceryl alcohol which, after purification, melted at 79° - 80° . From this he prepared the iodide and found that the percentage of iodine in it corresponded to $C_{17}H_{33}I$. From the iodide he obtained the hydrocarbon which melted at 59.5° ; thus agreeing with Kraft's $C_{17}H_{34}$. As regards the acid, he obtained it from the calcium cerotate and found that it melted at 82° - 82.5° . He also prepared some from the ceryl alcohol by oxidation with potassium bichromate in acetic acid solution; after purification it melted at 81.5° - 82° , and by titration he found that its molecular weight corresponded to $C_{27}H_{54}O_2$. By further purification it melted at 82° - 82.5° , like the acid got by saponification.

Japan wax (Japan tallow, *Sesamum* seed, Vegetable wax of Japan). This must not be confused with insect wax which has sometimes been called Japanese wax. Japan wax is one of the most important of the vegetable waxes, large quantities being exported from Japan. Before 1854, whilst Japan was closed to foreigners,

merchants except to the Dutch, it came through China and Singapore, and was imported in small quantities coming in small thin cakes, but after the opening of certain Japanese ports to British merchants, it arrived in large quantities and in square blocks or cases of about a picul each (133½ lbs.).

It is derived from the berries of three species of *Rhus* that grow in Japan, namely, *R. succedanea*, L., *R. vernicifera*, De C., and *R. sylvestris*, S. and Z. *R. succedanea* grows in the southern parts of Japan and yields wax only, but *R. vernicifera*, which has a more northerly range, yields a more important product, namely, the well-known Japanese lacquer, which is prepared from its sap, but its berries are also used as a source of wax. *R. sylvestris* is a less important source. *R. succedanea* and *R. vernicifera* also grow in China. The berries of all three are composed of an outer skin, a mesocarp in which is the wax, and a kernel.

In Japan to obtain the wax the berries are reduced to a meal—some authors say that they are previously slightly roasted; the meal is heated by steam in hempen sacks and then quickly squeezed in a wedge press to force out the wax. The residue is again treated in the same way. In the case of *R. vernicifera* the kernel is easily separated and is removed in the course of crushing, but in the case of *R. succedanea* the wax adheres to the kernel in spots, and it is not clear from the accounts of the process whether the kernel is separated or crushed with the mesocarp. The methods, no doubt, vary in different localities. It has been stated that perilla oil is added to obtain the last portions of the wax, but this is denied by Tsujimoto (Lewkowitch and Warburton, Oils, Fats, and Waxes, 6th ed. vol. ii. 1922, p. 45), who states that a proportion of the kernel oil of *R. succedanea* is added. With respect to this oil, A. Meyer (Arch. Pharm. 1879, [3] 15, 119, 120) found in the cotyledons contained in the kernels of *R. succedanea*, after carefully removing the shells, 36 p.c. (30 p.c. ?) of fat, or 2.65 p.c. on the whole fruit. It was yellowish-green, melted at 30°, was not a drying oil, and dissolved in about 30 parts of alcohol at 30°. Crowe (Consular Rep. for Japan for 1912, p. 43) says that by the use of benzine an additional 10 p.c. of wax can be obtained, and that several works were adopting the system.

The yield is from 15 to 25 p.c. Impurities are removed by melting and skimming off the clear wax. It is bleached by melting it and allowing it to drop through woollen bags into cold water, so as to subdivide it into small pieces. These are exposed to the sun and are sprinkled with water and frequently turned over; the process occupies about 30 days.

The wax is pale yellow and hard with an even or conchoidal fracture; it becomes yellow brown on keeping, and acquires a white powdery surface. The m.p. varies from 48° to 55°, that usually found being 53°; the wax solidifies again at about 41°, and when recently solidified melts at 42°; it slowly regains the higher melting-point. It is said that on warming it becomes transparent 10°–12° below its melting-point (Schaeffler).

Its specific gravity is close to that of water, and as it contracts and expands at a greater

rate than water, it exhibits the peculiar property of sinking, hovering or floating in water at different temperatures, sinking in cold water and floating in water somewhat warmer. After melting and resolidifying its specific gravity is lowered, it rises again in the course of some months. Thus a sample which hovered at 16.2° was melted and resolidified, it then hovered at 8.0°. Remembering that its expansion is greater than that of water, its specific gravity at 16.2° would be materially less than it was before melting, and it would float in water of that temperature. There is some variation in the specific gravity of different samples.

It is readily soluble in benzene and petroleum-ether and sparingly soluble in cold ether; it is insoluble in cold alcohol, but dissolves on warming and separates again on cooling.

In and after 1900 the following analytical values have been recorded: Acid value, 11.2–32.6; it is very variable, but values between 14 and 20 seem most common. Saponification value, 206.6–237.5; values between 215 and 224 being common. Iodine value, 8.3–15.1. Hubl, in 1884, records the iodine value as 4.2, so it is thought that the method of obtaining the wax has been changed. Part of the iodine value has been ascribed to the use of perilla oil mentioned above, as this oil has a very high iodine value. Ahrens and Hott in some wax prepared from berries obtained from Japan found iodine values of 11.9–12.8, and after bleaching in the sun, of 7.6.

Composition.—Japan wax is chiefly composed of glyceryl palmitate together with some free palmitic acid. Besides these a good many other substances have been obtained from it in small proportions; they may have been free in the wax or may have come from esters. These substances are: (1) About 1 p.c. of janic acid $C_{11}H_{21}O_4$ with m.p. 117°–117.0°; it is normal nonadecamethylene dicarboxylic acid $CO_2H \cdot (CH_2)_{11} \cdot CO_2H$. There is some evidence that the janic acid comes from a mixed ester of glycerol with janic acid and palmitic acid existing in the wax. (2) and (3) Smaller proportions of the two next lower acids, namely,



(4) Five to six per cent. of acids soluble in water, perhaps including suberic acid and isobutyric acid. (5) An odour of cœnanthyl aldehyde is given off during saponification. This may be due to the oxidising action of bleaching agents, products being formed from which potassium hydroxide liberates cœnanthyl aldehyde. (6) Pelargonic acid. (7) An acid with m.p. 87° and formula $C_{11}H_{21}O_4$ or $C_{12}H_{23}O_4$. (8) and (9) Very small quantities of liquid acids, one insoluble in water and one soluble. (10) and (11) Very small quantities of oleic and stearic acids, perhaps due to some addition made in the course of the manufacture of the wax.

The unsaponifiable matter resembles cœnantment in appearance, and is recorded as from 0.54 p.c. to 1.63 p.c.; in it have been found:

(12) Melissyl alcohol with m.p. 88°. (13) Ceryl alcohol with m.p. 79°. (14) A saturated alcohol with m.p. 65° and with formula $C_{11}H_{23}O$. (15) A phytosterol with a double binding and m.p. 130°; as air-dried it is $C_{17}H_{33}O.H_2O$, the specific

rotatory power is -22.11° , nearly the same as that of the phytosterol of cotton-seed oil. (16) About 60 p.c. of the unsaponifiable matter is a mixture of liquids, unsaturated and containing oxygen.

Uses.—It is only the bleached wax that is exported. It is said to be used for floor, furniture, and boot polishes and in laundry work; but there appears to be some secrecy about its exact use. Added to beeswax it imparts more solidity to the candles and causes them to leave the mould more easily; it is used instead of beeswax for a similar purpose in some rubber factories. Before 1859 the wax or the free acids obtained from it was used for candles and night-lights (Wilson, J. Soc. Arts. 1858-59, 7, 424). Lewkowitsch and Warburton (Chem. Tech. of Oils, Fats and Waxes, 6th ed. vol. ii. 1922, p. 667), however, says that the difficulties of employing Japan wax fatty acids for candles have not yet been overcome. It emulsifies well with water and has been used for currying leather (J. Soc. Chem. Ind. 1898, 17, 167). In Japan it is used for polishing turned wood and cabinet work; unbleached it is used for the candles of the jinriksha men and (unbleached?) in a composition for keeping the women's hair glossy and straight.

Bibliography.—Japan wax, like other substances which are of pharmaceutical interest, has a long bibliography. Kaempfer (Amoenitates Exoticae, 1712, pp. 791, 794); Thunberg (Flora Japonica, 1784, p. 121); Siebold (Voyage au Japon, 1823-30, published 1838, i. p. 276). These three authors were surgeons in Dutch employ, and thus were enabled to visit Japan when it was closed to other Europeans; they mention the wax and the trees from which it was obtained. Oppermann (Ann. Chim. 1832, 49, 240), percentage composition. Landerer, H. Müller and Buchner (Repert. f. d. Pharm. 1833, 44, 1-34), discussion and experiments as to whether Japan wax is identical with adipoceres from dead animals, and whether it is a North American product. Nees von Esenbeck (*ibid.* 1833, 46, 283), commenting on Landerer's work, says that he has seen wax from *R. succedanea* from Japan, and that it is quite the same as that found in commerce. Trommsdorff (J. pr. Chem. 1834, 1, 151), properties and trial as a candle. Brandes (Arch. Pharm. 1841, [2] 27, 288), composition. He thought that Japan wax was composed of the supposed compound ceric acid that Hess (Pogg. Ann. Phys. Chem. 1838, 43, 382) obtained by the treatment of rye-starch with nitric acid. Sthamer and Meyer (Annalen, 1842, 43, 335), composition, distillation, and oxidation by nitric acid. They found that Japan wax is glyceryl palmitate. Hanbury (Pharm. J. 1852-53, [1] 12, 476, and Hanbury's Science Papers, 1876, 60), description and melting-point. Berthelot (Ann. Chim. 1854, [3] 41, 242) suggested that Japan wax perhaps contains a dipalmitin. Simmonds (J. Soc. Arts, 1858-59, 7, 611) and Wilson (*ibid.* p. 424), source and use for candles and night-lights. The Pharm. J. (1859-60, [2] 1, 176), the J. Pharm. Chim. (1859, [3] 56, 368), and the Neues Repert. f. Pharm. (1860, 9, 74) give summaries from various authors. Jackson and Rogers (Proc. Boston Soc. Nat. Hist. 1859-61, 7, 54, 58), properties. Kopp (Rep. Chim. Appliquée, 1860,

2, 142 and 296), discussion of Jackson and Rogers' work; the melting-points were incorrectly reported on p. 142. Bleekrode (*ibid.* p. 368), particulars some incorrect, also questioning the identity of the wax examined by previous authors. Simon (Bull. Soc. Imp. Zoo. D'Acclimatation, 1862, 9, 596). He was an agent of the Ministre de l'Agriculture and wrote from Nagasaki, giving particulars of the exploitation per 10,000 trees of *R. succedanea* occupying 2 hectares and of the preparation of the wax. Roucher (J. Pharm. Chim. 1872, [4] 16, 20), peculiarities of the melting-point and use in pharmacy for making cerates with olive oil. Ludwig (Arch. Pharm. 1872, [3] 1, 213), particulars. Robertson (Consular Report on Trade of Kanagawa in Japan, 1874, 64; also in J. Soc. Arts, 1873-74, 22, 787; also in Pharm. J. 1874-75, [3] 5, 584), source and preparation. Further particulars about source, preparation and use (J. Soc. Arts, 1873-74, 22, 1000; also in Pharm. J. 1874-75, [3] 5, 425). *Naturalising R. succedanea* in France (Pharm. J. *ibid.* p. 448). Gribble (Arch. Pharm. 1876, [3] 8, 374, from Handels-Bericht of Gehe and Co., Dresden, 1875), preparation written in Nagasaki. Cooke (Oilseeds and Oils in the India Museum, 1876, p. 5), particulars. Simmonds (J. Applied Science, 1877, 8, 55), particulars. Buri (Arch. Pharm. 1879, [3] 14, 403), composition. He saponified and examined the mixed acids and found palmitic acid chiefly, but that others were present, including at least one with melting-point above that of stearic acid, and also an oleic-like acid in small proportion. A. Meyer (Arch. Pharm. 1879, [3] 15, 97), a long paper discussing the work of previous authors and describing the *Rhus* trees with figures of leaves, flowers and fruit of *R. succedanea*, and giving results of a few experiments. Hübl (Dingl. poly. J. 1884, 253, 289), iodine value. Eberhardt (Inaug. Diss. Strassburg, 1888), composition. He found the acid afterwards named japonic acid by Geitel and van der Want. Rein (Japan: Travels and Researches, 2nd ed. 1888). Rein (The Industries of Japan, 1889, 158-164), an account of the three *Rhus* trees and of the preparation of the wax. Kleinstück (Chem. Zeit. 1st. 0, 14, 1303), peculiarities in the specific gravity. Watt (Dict. Econ. Prods. of India, vol. vi pt. 1. 1892, 499, 500, and Commercial Prods. of India, 1908, 914). Schaedler (Technol. Fette und Öle, 2nd ed. 1892, 80, 870), particulars of the wax and also of its m.p. peculiarities. Hehner and Mitchell (J. Amer. Chem. Soc. 1897, 19, 49, and Analyst, 1896, 21, 330), abnormal behaviour of palmitic acid from Japan wax when mixed with stearic acid. La Wall (Amer. J. Pharm. 1897, 69, 18), starch as an adulterant. Lewkowitsch (Analyst, 1899, 24, 319), analytical values and effect of acetylling. Bull. Bot. Dept. Jamaica, 1900 [2] 7, 37, source and preparation of the wax. Geitel and van der Want (J. pr. Chem. 1900, [2] 61, 151), composition. Eichhorn (Zeitsch. anal. Chem. 1900, 39, 640), directions for finding acid value and saponification value, using amyl alcohol.

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Mexican myrica wax (*Mexican myrtle wax*). This wax is obtained by the Indians in Mexico from the fruit of *Myrica jalapensis*, and is sold in Mexico city, where it is used for making candles. The tree is known locally as 'arbol de la cera,' and occurs in Vera Cruz, sometimes in dense thickets covering considerable areas. The wax forms a greenish-white layer on the outer surface of the fruit, and is obtained by boiling the fruit in water and skimming off the floating melted wax; it is refined by melting and straining. On examination it gave the following values, which resemble those of Cape berry wax: sp.gr. 0.8763 at 99°; m.p. 43.2°; acid value 4.07; saponification value 214.5; iodine value 238. It is considered that it would be suitable for making candles and soap (Olsson-Seffer, Bull. Imp. Inst. 1909, 7, 410).

Myrtle berry wax (*Myrtle wax, Laurel wax, Bayberry tallow*) is obtained from the wax myrtle, *Myrica cerifera* (Linn.), a shrub growing on peaty soil in North America, and common along the North Atlantic sea coast. The fruit is brown or blackish and the size of a pea; it secretes the wax and becomes covered with a snow-white crust, penetrated by brown or black points of the skin, so that the wax can only be got off as a powder and not in coherent pieces.

Wax is also got from other Myricaceae, namely, *M. caracasana* (Humb. and Bonpl.) in South America, especially in Colombia and Venezuela, and *M. aethiopica* (Linn.) in Abyssinia. See also *Cape berry wax* and *Mexican myrica wax* above.

To obtain the wax the berries are boiled with water, and the fatty mass that floats on the surface is skimmed off and poured into flat dishes; the yield of wax is from 20 to 25 p.c., and a bush yields from 10 to 15 kilos. of berries. The wax which comes from the United States has a deep green colour, probably due to chlorophyll; this colour is bleached to a grey-yellowish tint by exposure to light and air for several years, but the change extends only a few millimetres below the surface.

The statements as to its composition are not concordant. Smith and Wade (J. Amer. Chem. Soc. 1903, 25, 629), however, examined the wax, preparing it by extracting the berries with light petroleum, and concluded that it was mainly palmitin (glyceryl tripalmitate) with some lower glyceride and a small amount of

free acid; they obtained pure palmitin by crystallising four times from light petroleum. The berries they used were picked in September, and the extraction and examination were made in November. The values they record are: sp.gr. 0.9806 at 22°/15.5°, and 0.879 at 99°/15.5°; refractive index at 80° 1.4363; acid value 30.7; saponification value 317; iodine value (Hübl) 3.9; Reichert-Meissl number 0.5. From these they inferred the absence of oleic and volatile acids. They also concluded that no stearin was present. The m.p. in this sample was 48°, as determined by Allen's method (Coml. Organ. Anal. 3rd. ed. vol. ii. pt. i. 34), and the solidifying point was 45°; but it was found that the melting-point rises considerably on keeping the wax. A redetermination in March of the m.p. gave it as 52.5°, a rise of 4.5° in 4 months. A specimen of wax about 4 years old melted at 57° and solidified at 58.3°. Wax from berries obtained in August and extracted in March melted at 55.4°.

Some other observers have found the acid value to be only about 4. It is inferior to beeswax in ductility and plasticity; mixed with beeswax it can be employed for making candles; these are said to give a pleasant smell when extinguished. It could probably be used for soap making. Chittenden and Smith (Amer. Chem. J. 1884, 6, 217) employed this wax as a source for preparing pure palmitic acid.

Some wax prepared in Colombia from the berries of *M. arguta* was examined at the Imperial Institute (Bull. Imp. Inst. 1918, 16, 287) with the following results: m.p. 45°; solidifying point of the fatty acids 46.4°; acid value 21.2; saponification value 216.7; iodine value 1.03; unsaponifiable matter 0.4 p.c.; the wax was yellowish-buff in colour and had a peculiar odour, similar to that of myrtle wax from South Africa (Cape berry wax). It was stated that the wax is employed in Colombia for the manufacture of soap and candles, that the plant is abundant, that the fruit can be gathered cheaply and easily, and that the extraction of the wax is not difficult.

Ocuba wax is obtained from the fruit of a shrub growing in the Pará province of Brazil. It grows well in marshy places, and is found in abundance along the banks of the Amazon river. The fruit encloses a nut covered with a thick skin. The skin extracted by water gives a fine red colour (Ocuba red); after washing with water the nuts are thrown in heaps, crushed to a paste, and boiled, when the wax separates and floats on the surface. The crude wax resembles beeswax, and by purification can be obtained white and suitable for candle-making. 100 kilos. of the seeds give 20-22 kilos of wax. The product is said to be a mixture of wax, fat, and resin, to melt at 40°, and to have a sp.gr. of 0.920 at 15°; it is only slightly soluble in cold alcohol, but is completely soluble in boiling alcohol and ether (Chem. Revue über die Fett- und Harz-Industrie, 1901, 8, 213). See also *Ucububa wax*.

Palm tree wax is the product of a palm tree *Ceroxylon andicola* (Humb. and Bonpl.), which grows on the Andes in Colombia at altitudes of 7900-9700 ft.; it attains a height of 100 ft., and the trunk is coated with the wax, which gives it a white and marble-like appearance.

The wax is obtained by cutting down the tree and scraping off the coating, which is then boiled with water; the wax is thus softened and floats on the surface, and impurities are removed. One tree is said to yield 25 lbs. The wax is made into balls and dried in the sun. Candles are made from it by the addition of a little tallow, and are sold in Carthago. That which is obtained from the Indians is yellowish-white, porous, and friable. When melted it is dark yellow, slightly translucent and fragile like resin. It is partly wax and partly resin, and melts at a temperature a little above that of boiling water; it becomes strongly electric by friction. It is readily soluble in hot alcohol; on cooling the solution becomes a white congealed mass. By using large quantities of alcohol and allowing the solution to cool the waxy part separates and the more soluble resin remains in solution; by repeating this operation several times the wax can be separated from the resin and from a small amount of a bitter substance. Ether also dissolves it, and by evaporation feathery crystals can be obtained. The purified wax melts below the temperature of boiling water, and then resembles beeswax, whilst the resinous matter melts above this temperature (Boussingault, Ann. Chim. 1825, 29, 330; 1835, 59, 19; Seemann, Pop. Hist. of the Palms, 1856, 222).

Bonastre (J. Pharm. Chim. 1828, 14, 349) obtained purified wax by repeated extractions with cold alcohol, and then dissolving the residue in boiling alcohol and filtering. When cold the solution became thick and opaque, like an aqueous starch solution; on standing for some months crystals appeared. On removing the alcohol white silky crystals were obtained; when dried and ground in a mortar it gave luminous sparks. He named this purified wax *cerosylène*, or, according to Boussingault (l.c. 1835, 59, 21), *cérosiline*. Lewy (Ann. Chim. 1845, [iii] 13, 447) found that the wax purified from the resin melted at 72°, and contained carbon 80.73 p.c., and hydrogen 13.30 p.c. Teschemacher (Mem. and Proc. Chem. Soc. 1845, 25) also describes this wax.

A wax obtained from the leaves of *Ceroxylon andicola* was examined at the Imperial Institute. It was a pale straw-coloured powder. After purification it gave the following analytical values: m.p. 93° by the open tube method, as compared with 84° for carnaúba wax, and 70°-72° for candelilla wax by the same method; sp.gr. at 15°/15° 1.018; acid value 19.8; saponification value 73.7-104.4, varying with the conditions of the experiment; iodine value 32.8. It was thought that when purified it might be used as a substitute for carnaúba wax (Imp. Inst. Bull. 1917, 15, 182, and 1919, 17, 249).

Peat wax. Waxy substances are obtained when peat is extracted with suitable solvents. By means of benzene or toluene from 1 to 8 parts of crude wax have been obtained from 100 parts of the dry material of samples from different sources. This crude wax was found to contain sulphur, usually amounting to less than 1 p.c. of the wax, but in one case reaching 30.3 p.c. The crude wax consisted of some resinous matter, but principally of a mixture of ester and free acid. The acid or acids obtained by the saponification of the crude wax corresponded in composition to a fatty acid containing

about 23 carbon atoms; the alcohols thus obtained appeared to contain about the same number. No trace of glycerides was found (Kraemer and Spilker, Ber. 1902, 35, 1212). A process was patented in 1903 by Bouchaud-Praceiq (Fr. Pat. 338736) for extracting peat, lignite, &c., with alcohol or ethyl esters, &c., and recovering the wax from the solvent. The wax is said to be hard and to resemble beeswax, and to have a higher melting-point and a sp.gr. above 1.000 (J. Soc. Chem. Ind. 1904, 23, 710).

Zaloziecki and Hausmann (Zeitsch. angew. Chem. 1907, 20, 1141), by extracting peat with alcohol, obtained a dark yellow or brown waxy substance, but the yield was only 10 grms. from some kilograms. It had no sharp melting-point, melting between 80° and 96°; it dissolved very easily in amyl alcohol, and less readily in ethyl and methyl alcohols. In ethyl ether or benzene it dissolved only partially, giving a dark green liquid and leaving a brown insoluble residue. By saponifying the substance soluble in ethyl ether an alcohol was obtained, melting between 124° and 130°, and having a composition and molecular weight corresponding to $C_{20}H_{40}O_4$, and also an acid which began to soften at 145° and melted at 184°, having a composition and molecular weight corresponding to $C_{17}H_{34}O_2$. The part insoluble in ether gave on saponification an alcohol having the same melting-point, composition and molecular weight as the other alcohol, but differing a little in its behaviour, and also an acid which had not melted when 260° was reached, and which had a composition and molecular weight corresponding to $C_{21}H_{42}O_2$. Small quantities of other substances appeared also to be present in the wax, and the above substances are very possibly mixtures.

Pisang wax. This wax occurs as an excretion on the leaves of a species of *Musa*, which grows wild in Java, especially in the uncultivated regions of Tjilatjap and Koenigian. *Pisang* is the Malay name for the banana. The natives obtain the wax by scraping the leaves, throwing the scrapings into boiling water, and then collecting the melted wax. It is said that one stem bears on the average seven leaves (a leaf may be as much as 6 ft. in length), and that 100 leaves yield $\frac{1}{4}$ kilo. of wax. The cakes of wax are white, cream, or slightly greenish in colour, and slightly transparent; the wax is hard with a coarsely granular or crystalline fracture and is very friable. It has been examined by Greshoff and Sack (Rec. trav. chim. 1901, 20, 65), who record the following: sp.gr. 0.963-0.970 at 15°; m.p. 79°-81°; acid value 2-3; it is very hard to saponify, and the saponification value found was 109. Boiling alcohol dissolves very little (about 1 p.c.), and on cooling only retains 0.3 p.c. It is easily soluble in boiling oil of turpentine, amyl alcohol, or carbon disulphide. At 15° petroleum, ether, acetone, and oil of turpentine retain 1 p.c. or less; chloroform and carbon disulphide retain less than 2 p.c. On the basis of ultimate analyses of the wax (previously freed from the part soluble in boiling alcohol), and of the acid and alcohol obtained by saponification, the authors propose provisionally the three following formulae: $C_{27}H_{54}O_2$ for the wax, regarding it as an ester formed from $C_{25}H_{50}O$.

stearic acid, and $C_{12}H_{25}O$ pinacetyl alcohol. The acid melts at 71° , and the alcohol at 78° .

Raphia wax. The raphia palm, *Raphia palmiculata* (Beauv.) or *Raffia*, which grows in Madagascar, furnishes the fibrous material used by gardeners and known as 'bass'; this is the epidermis of the upper side of the palm leaf. The dull under surface is coated with a whitish layer or bloom, which can be easily rubbed off. After the bass is removed large quantities of the rapides are available as a source of the wax. They are spread out to dry on cloths in the open air, but must be sheltered from the wind as the light waxy matter is easily blown away. After drying for 2-4 days a white coating is apparent on the under surfaces of the leaves; this is detached as a powder by shaking or rubbing the leaves between the hands. The powder is collected, freed from foreign matter by sifting, and then put into boiling water when the wax melts and floats on the surface, and earthy impurities settle to the bottom. The melted wax is separated and allowed to solidify. It is yellow to dark brown in colour, and rather harder and more brittle than beeswax. In an experimental trial it was found that ten leaves of medium size ($3\frac{1}{2}$ -4 $\frac{1}{2}$ metres in length) weighed 104.5 kilos. and yielded 0.75 p.c. of wax; the yield in practice, however, would be less than this.

Raphia wax in its physical properties resembles carnauba wax but differs chemically; it seems likely to be applicable to the manufacture of candles, polishes, &c., if it can be produced at a sufficiently low cost.

Two specimens were found to have the following properties: m.p. 82° , 83° ; sp.gr. 0.836, 0.832 at $99^{\circ}/15.5^{\circ}$; acid value 4.9, 6.5; saponification value 51.3, 50.3; iodine value 7.7, 10.7 (Bull. Imp. Inst. 1908, 6, 380). It is only slightly soluble in alcohol, ether, acetone, chloroform, light petroleum, and carbon disulphide. It dissolves, but not completely, in boiling alcohol, and separates on cooling. It appears to be mostly composed of an alcohol or mixture of alcohols having a composition corresponding to $C_{26}H_{52}O$, but differing from arachic alcohol (Compt. rend. 1905, 141, 1251; 1907, 144, 594).

In 1918 the raphia wax industry was stated to be still undeveloped, but it was believed that 10 tons would be available annually (J. Soc. Chem. Ind. 1918, 37, 240 R, from U.S. Com. Rep. Apr. 1, 1918).

Rhimba wax. In the Chamber of Commerce Journal, 1901, p. 192, an account taken from the *Moniteur Officiel du Commerce* is given of a product furnished by the Rhimba tree of Madagascar. From the description it appears to be composed of both wax and resin. The wax is said to amount to 14 p.c. The particulars about it are not clearly stated. The wax is said to resist attempts to bleach it.

Snow brush wax. The snow brush (*Ceanothus velutinus*, Douglas) is a shrub from two to six feet in height, which grows in Californian forests; it is considered a nuisance and to involve fire dangers. Scollone and Blakemore made an investigation to see if it could be utilized. Besides obtaining tannin they found that the dried leaves yielded 7.3 p.c. of wax when extracted with gasoline. The wax was greenish in colour,

owing to the presence of a little chlorophyll, and when freed from solvent was brittle with a conchoidal fracture. The crude wax gave the following analytical results: free acid 20.3; saponification number 93.4; iodine value 19.5; Reichert-Meisels number 7.5; sp.gr. at 15° 0.968; melting point 78° - 79° . From experiments made to ascertain the components of the wax, they inferred that it was probably composed in great part of ceryl and melissyl esters of palmitic and stearic acids together with hydrocarbons, free cerotic acid and a small quantity of glycerides (J. Ind. Eng. Chem. 1916, 8, 411, 573).

Spermaceti occurs in special cavities in the head of the sperm whale or cachalot, *Physeter macrocephalus* (Linn.), and also in the blubber; it is held in solution by the sperm oil at the temperature of the whale's body. It also occurs in the bottle-nose whale *Balaena rostrata*, and in some other cetaceans, but not in the oil of the whalebone whales. The spermaceti from *Balaena rostrata* has a slightly higher melting point than that from the sperm whale. The great bulk of the head of the sperm whale consists of dense cellular tissue infiltrated with spermaceti, this is surmounted by the 'case' which holds nearly a ton of very fine oil and spermaceti known as 'head matter.' When removed this head matter is full of spermaceti crystals. The blubber surrounds the whole body in a layer about 18 ins. thick; it is 'tried down,' that is heated to separate the oil from the tissue; on cooling the oil deposits thick scales of spermaceti and becomes semi-solid. The 'trying down' is sometimes done on the ship and sometimes at the factories. At the latter the semi-solid mass undergoes several filtrations and pressings to separate the oil from the spermaceti, which is melted and cast into moulds once or twice during the series of pressings. Finally, the wax is warmed and agitated with a little caustic potash solution to remove the last traces of colour and to neutralize traces of acid, and is cast into blocks forming an almost blue-white glistening semi-crystalline solid (Field, Soc. Arts. Cantor Lectures, 1893). It is said that for some purposes it is best not to free it entirely from the sperm oil.

The sp.gr. at ordinary temperatures is about 0.945, but values as divergent as 0.905 and 0.960 have been given, owing probably to irregularities caused by the crystalline structure. The sp.gr. of melted spermaceti at 98° - 99° is from 0.808 to 0.816 as compared with water at 15° (Kahler, Amer. J. Pharm. 1897, 69, 104). The m.p. is from 41° to 49° , but by repeated purifications it reaches 53.5° . Meldrum (Chem. News, 1915, 111, 37), in order to investigate the phenomena of melting and solidifying points and the rise in temperature on setting, selected spermaceti as the substance, and records numerous experiments on it and also on the effect of impurities such as sperm oil, water, glycerin, and oleic acid. The acid value is from 0 to 1.8; saponification value from 120.4 to 124.6; the iodine value of highly purified spermaceti is 0, but values up to 0.3 (by Wijs' method) have been found, caused, as he holds, by the presence of sperm oil (Dunlop, J. Soc. Chem. Ind. 1906, 27, 63). It is insoluble in water, and alcohol dissolves little except the adhering oil. It is soluble in boiling alcohol, ether, chloroform,

carbon disulphide; it separates in a crystalline form from the solution in hot alcohol or ether. Beilstein and Kricheldorf give a long account of the examination of spermaceti for purity (J. Soc. Chem. Ind. 1921, 40, 59A, from Pharm. Zentralh. 1920, 61, 703, 719, 733).

Spermaceti is mainly composed of cetyl palmitate ($C_{18}H_{34}O_2$). It was examined by Chevreul in 1814, and the purified substance was named by him *cétine*; in 1818 he described the alcohol obtained by its saponification (now known as *cetyl alcohol*) under the name *éthol*, formed from the first syllables of ether and alcohol (Recherches, Chim. sur les Corps Gras 1839, 148). The acid with which the radicle of the cetyl alcohol $C_{18}H_{37}OH$ is combined was found later to be palmitic acid. Although spermaceti has a crystalline appearance, it contains compounds other than cetyl palmitate. Heints (Pogg. Ann. 1854, 92, 609, 93, 536) believes that it yields on saponification stearic, palmitic, myristic, and lauric acids, and the alcohols $C_{15}H_{31}O$, $C_{16}H_{33}O$, $C_{17}H_{35}O$, and $C_{18}H_{37}O$; he named the first, third, and fourth of these *stéthol*, *methol*, and *léthol* in analogy to Chevreul's *éthol*. These very probably exist in the spermaceti as esters of the corresponding acids. He also found another liquid substance in the products of saponification.

Spermaceti is used for making candles which burn brightly and in pharmacy for making ointments. For candle-making the addition of a few per cent. of beeswax or paraffin is advantageous to remove the brittleness of the spermaceti. Spermaceti candles of prescribed composition and properties were formerly used as the standard for measuring the illuminating power of different lights (Young, J. Soc. Chem. Ind. 1891, 10, 185; Met. Gas References, *ibid.* 1894, 13, 65).

Sugar cane wax. A waxy substance is produced by the sugar cane, and is noticeable on the rind of some varieties, especially near the nodes; it is most abundant on the violet cane. It was first described by Avequin (Ann. Chim. 1840, [ii.] 75, 218), who named it *cérose*. Cold alcohol removes some colouring matter, chlorophyll probably, but does not dissolve the wax. The purified wax can be obtained by removing the portion soluble in cold alcohol, then dissolving in boiling alcohol, cooling, pressing, driving off the alcohol, and melting. It is dull yellow, hard, and can be powdered; it is insoluble in water, cold alcohol and cold ether; hot ether dissolves it to some slight extent, and deposits it on cooling in small crystalline grains; boiling alcohol dissolves it completely, and the solution on cooling becomes semi-solid, just as does an alcoholic soap solution. It melts at 82° and solidifies at 80° , and its sp.gr. is 0.961 at 10° . When made into a taper it burns with a fine white flame like wax or spermaceti.

Analyses of the wax were made by Dumas (ibid. 223) and Lowy (ibid. 1845, [iii.] 13, 451) who assigned formulae to it on the supposition that it was a single compound, but from Wijnberg's experiments (Het Rietwas en de Mogelijkheid zijner Verzuimings Winning, 1909; J. Soc. Chem. Ind. 1909, 30, 991, 999) the wax appears to contain cetyl alcohol $C_{18}H_{37}O$, and also a substance with a composition corresponding to $C_{18}H_{35}O$, which is neither an ester nor a primary alcohol,

since it yields no hydrogen when heated with soda lime. Prinsen Goerlign (Arch. v. d. Java-Suikerindustrie, 1893, 1, 67) also examined the wax.

In the manufacture of cane sugar the juice is purified by treatment with lime and heating; the resulting muddy precipitate is filtered off and forms a waste product. Wijnberg proposes to extract the wax from this by the use of benzine or other solvents and utilise it (Fr. Pat. 397843, 1908). He finds that the extract from fresh mud contains a large proportion of fatty matters besides the wax, but that in mud which has been kept for some time the fatty matters undergo a kind of fermentation, and are decomposed and a product is obtained approximating more closely to the wax got by scraping the cane. It is stated that extraction of the wax has been undertaken in Java. The subject is treated of very fully in Wijnberg's book mentioned above. J. Soc. Chem. Ind. 1910, 29, 33, deals with a U.S. Patent and gives analytical values.

W. E. Cross (J. Soc. Chem. Ind. 1915, 34, 845, from Intern Sugar J. 1915, 17, 311) found from experiments that by submitting the raw mill juice to centrifugal action a product containing over 50 p.c. of wax was obtained, and this by one crystallisation from alcohol gave a pure hard product, melting at 82° .

Ucuhuba wax. An investigation of the wax from the fruit of *Myristica surinamensis*, Roland, was made by Reimer and Will (Ber. 1885, 18, 2011), who found that the chief component was trimyristin, glyceryl trimyristate. The wax obtained by an ether extraction melted at 45° . An account of the seeds of this plant, obtained from an exhibit of the Pará Province of Brazil, is given by Tschurch (Arch. Pharm. 1887, [3] 25, 619), who says that the seeds are known in commerce as *ucuhuba*. Other references are: Valenta (Zeitsch. angew. Chem. 1889, p. 3); Bolton and Hewer (Analyst, 1917, 42, 35).

About 4 tons of ucuhuba wax were exported in 1920 (Dept. Overseas Trade, Report for Brazil, 1921, p. 19). See also *Oruba wax*.

Oils, Fats, Waxes, and Resins, by E. B. Bolton and R. G. Pelly. Fats: Natural and Synthetic, by W. W. Myddleton and T. Hedley Barry: E. Benn, Ltd., London. H. H. R.

WEED KILLERS. The best weed killer for the purpose of the agriculturist is generally the hoe in some form or other, aided by the sun and wind. To permit of the ready disinfection, by mechanical means, between the crop and the accompanying weeds is one of the most important advantages of regular drilling or planting. It is only in a few cases that the farmer can derive much advantage from the application of chemical methods of destroying weeds, since, as a rule, any means which will destroy weeds, will render the soil, for a time at least, unfitted for the growth of any plant.

For destroying all vegetation, e.g. for keeping garden paths free from weeds, any general plant poison may be used. Of these there are many; indeed any soluble salt, applied in strong solution, will kill plants by producing plasmolysis. In practice, strong solutions of common salt (10 p.c., i.e. 1 lb. per gallon; dilute solution (1 part in 25 to 50 of water); dilute solution

phenol (about 1 oz. commercial carbolic acid to a gallon of water); of sodium arsenite (about 1.6 p.c. solution); or of calcium sulphide (made by boiling 1 part of sulphur with 50 parts of water and 10 parts of quicklime) are often used, the liquid being simply applied to the surface of the walks from a watering pot, which should be well painted on the inside. Sulphides, thiocyanates, and sulphites act as effective plant poisons, and to their presence the poisonous action of fresh 'gas lime' is largely due. Many metallic salts act as plant poisons, even in excessively dilute solution. According to Coupin (Compt. rend. 1901, 654) the weakest solutions of the various salts which had an injurious effect upon the growth of the roots of the seedlings of wheat, contained 1 part of the anhydrous salt and the following parts of distilled water:—

Copper sulphate . . .	700,000,000
Mercuric chloride . . .	30,000,000
Cadmium chloride . . .	10,000,000
Silver nitrate . . .	1,000,000
Zinc sulphate . . .	40,000
Lithium chloride . . .	12,000
Calcium iodide . . .	10,000
Barium nitrate . . .	4,200
Borax . . .	1,000
Manganese chloride . . .	1,000
Calcium bromide . . .	400
Calcium chloride . . .	260

The extreme dilution of the copper sulphate, which can produce a poisonous effect, *when applied in solution to the roots*, is remarkable. In the presence of soil, however, many of these substances, including copper sulphate, are converted into insoluble and harmless compounds.

But the use of these plant poisons in agricultural practice is limited, owing to the difficulty of restricting their action to the weeds. In some countries, where a particular weed has become a scourge, recourse to these drastic measures is sometimes made, *e.g.* prickly pear in Cape Colony has been destroyed in many districts by the use of sodium arsenite, or of solutions of arsenical sheep dips, 1 or 2 p.c. solution of the former being sprayed over the uprooted plants, which then die, dry, and can afterwards be burnt.

Of more importance to the farmer is the *differential or selective* poisoning of weeds, by the use of solutions which, while destroying certain weeds, produce no injurious effect upon the crop itself. The best known of such methods is in the destruction of charlock or wild mustard (*Sinapis arvensis* [Linn.] or *Brassica Sinapistrum* [Boiss.]). The method, due to an accidental observation by Girard in France, in 1897, is to spray the barley or oat field infested with the charlock in the spring, when the charlock plants are about 2 or 3 ins. high, with from 40 to 70 gallons per acre of a 3 p.c. solution of crystallised copper sulphate, best on a still, dry, dull day. Unless rain soon follows the spraying, in which case the result is spoiled, it will be found that the charlock plants quickly blacken and die, while the barley or oats and clover (if that be also present) are uninjured. In addition to charlock, known in various districts as 'ketlock,' 'wild mustard,' 'yellow flower,' and in Ireland as 'preahagh,' other cruciferous weeds, of which

'runches' (*Raphanus raphanistrum*) is the most important, can be killed by the same treatment. Ferrous sulphate in 10 or 12 p.c. solution may be substituted for the copper sulphate, but according to experience in Ireland (Leaflet No. 6, Dept. of Agric. and Tech. Instruction for Ireland, 1901) is not so efficient. Cereals, clovers (and most other *leguminosae*) are uninjured by the treatment, but docks and thistles, although not usually killed, are seriously checked in growth.

Various explanations of this differential action of copper and iron sulphate solutions have been offered. Girard ascribed it to the solution being retained by the rough and more or less horizontal leaves of the charlock, while the smooth erect leaves of the cereals would permit of the solution running off. Against this is the fact that other plants with horizontal leaves, *e.g.* clovers, suffer little damage. Another possible explanation is that interaction between the metal of the copper or iron sulphate and the sulphur compounds which are characteristic of the *cruciferae*, may take place and lead to the destruction of the plant.

A third and probable theory is that the cell walls of the leaves of charlock are thinner or weaker than those of cereals, and more readily permit of plasmolysis being set up, when they are brought into contact with saline solutions applied to the exterior of the leaves. This view receives some support from the fact, observed by Heinrich (Jahresb. für Agricultur-Chemie, 1901, 351), that 15 or 20 p.c. solutions of sodium nitrate, ammonium sulphate, or potassium chloride—substances which cannot exert any chemical toxic effect—are also effective in destroying charlock. Moreover, the importance of a dull, still, dry day for the spraying, which is always shown in field trials, is in accordance with this explanation, for under such conditions, the droplets of the solution, deposited on the leaves of the plant, would retain their original concentration for a longer period than on windy or sunny days when evaporation would be hastened.

The experience of the Irish Department of Agriculture is that from 50 to 70 gallons per acre of a 3 p.c. solution of copper sulphate, under favourable conditions of weather, is the most effective spray for destroying charlock in cereal crops, and that even when the weed has come into flower, it can be successfully destroyed by this treatment, whilst the cereals and clover are uninjured.

Another example of differential plant-killing is afforded in the use of the so-called 'lawn-sand' for the destruction of plantains and daisies in lawns. The active ingredient in lawn-sand is usually sulphate of ammonia, and to be effective the preparation must be applied in relatively large dressings—usually about 4 oz. per square yard (= 1210 lb. per acre) is recommended. The result is that the flat-leaved plants, *e.g.* daisies and plantains, wither, turn brown and die, while the grasses, though, perhaps, temporarily injured and browned, recover and afterwards grow vigorously. Lawn-sand is generally applied in March and, after its toxic action on weeds, acts as an efficient nitrogenous manure.

A certain amount of indirect 'weed' killing can be achieved by suitable manuring; thus the

growth of grasses is favored at the expense of admitted leguminous plants, by repeated applications of nitrogenous manures, whilst the opposite effect is produced by application of calcareous, phosphatic, and potash manures with avoidance of nitrogenous ones. But this method is of limited application, and is rarely of service to the farmer. It may, however, be used in the adjustment of the relative proportions of grasses and clovers in a lawn. But for the destruction of the more important and troublesome weeds of the farm and garden reliance has chiefly to be placed upon the mechanical methods of cultivating the soil at the most suitable season. H. I.

WEINSCHENKITE. A rare mineral found in the Bavarian Oberpfalz in white matted globular deposits and in radiating needles on brown hematite. Is mainly a hydrated phosphate of yttrium and erbium $\text{PO}_4(\text{Er}, \text{Y})_2\text{H}_2\text{O}$, containing small quantities of other rare earths (Henrich and Hiller, Ber. 1922, 55 [B], 3013).

WEISSENFELS LIGNITE RESINS v. RESINS. WEISSGÜLTIGER v. WEISSGÜLTIGER v. FREIBERGITE.

WEHRLITE v. TETRADYMIT.

WELD is the dried herbaceous plant known as *Reseda luteola* formerly cultivated to a considerable extent in France, Germany, and Austria. Its cultivation in this country has nearly ceased, because not only is the quantity of colouring matter it contains very small, but the carriage of the plant, owing to its bulky nature, is expensive. A special interest, however, attaches to weld, for it is said to be the oldest European dyestuff known, and was used by the Gauls and other nations dwelling north of the Alps in the time of Julius Caesar.

The plant attains a height of about 3 feet, is pale brown in colour, and is sold in sheaves like straw. The colouring matter is disseminated throughout the entire plant, but the greater quantity occurs in the upper extremity and the seeds.

Luteolin, the main colouring matter of weld, was examined by Chevreul (J. Chim. Med. 6, 157; Annalen, 82, 53), who obtained it in a crude condition; its isolation in a state of chemical purity was first achieved by Moldenhauer (Annalen, 100, 180), who assigned it to the formula $\text{C}_{15}\text{H}_{10}\text{O}_6$. It was subsequently investigated by Schützenberger and Paraf (Bull. Soc. Chim. 1861, [i.] 18), who proposed the formula $\text{C}_{15}\text{H}_8\text{O}_6$ and purified it in a somewhat novel manner which is worthy of mention. Weld was exhausted with alcohol, the extract evaporated, and treated with water, which threw down a dirty greenish precipitate. This was collected, introduced with a little water into a sealed tube and heated to 250° . On cooling the sides of the tube were found to be coated with golden-yellow needles of luteolin, and the impurities had collected at the bottom of the tube to form a resinous cake.

Hasiweta suggested that luteolin had the formula $\text{C}_{15}\text{H}_{10}\text{O}_6$ and was isomeric with the paradisoetin, which he obtained during the fusion of quercetin with alkali (Annalen, 112, 169).

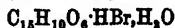
For the preparation of luteolin in quantity, Perkin (Chem. Soc. Trans. 1896, 69, 306, 799) suggested weld extract.

300 grms. of the extract dissolved in 3 litres of water is treated with 100 c.c. of hydrochloric acid (33 p.c.), and the mixture is digested at the boiling temperature for some hours. A quantity of a black resinous substance separates, which is collected while hot, and the filtrate, which contains the colouring matter, is allowed to stand for twelve hours. A brown precipitate of impure luteolin is slowly deposited, and is collected, washed, and dissolved in a little hot alcohol. On pouring this solution into ether, the main bulk of the impurity is precipitated, and the ethereal liquid on evaporation yields a yellow residue, which is crystallised from dilute alcohol. The product in addition to luteolin contains apigenin (Chem. Soc. Trans. 1900, 77, 1316), and the latter can only be removed with certainty by the following method:—

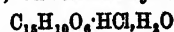
The mixture dissolved in boiling glacial acetic acid is treated with a few drops of strong hydrochloric acid; this causes the almost immediate separation of luteolin as hydrochloride, whereas the apigenin remains in solution. The hydrochloride is collected, decomposed by water, and the luteolin crystallised from dilute alcohol.

Luteolin $\text{C}_{15}\text{H}_{10}\text{O}_6$ crystallises in yellow needles or leaflets, m.p. $327^\circ\text{--}329^\circ$ (Perkin), 327° (v. Kostanecki, Rozycki, and Tambor, Ber. 1900, 33, 3410), soluble in alkaline solutions with a yellow coloration. With alcoholic lead acetate it gives a bright yellow precipitate and with alcoholic ferric chloride a green solution.

Luteolin sulphate $\text{C}_{15}\text{H}_{10}\text{O}_6\cdot\text{H}_2\text{SO}_4$, orange-red needles; *luteolin hydriodide* $\text{C}_{15}\text{H}_{10}\text{O}_6\cdot\text{HI}$, orange prisms; *luteolin hydrobromide*



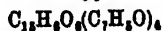
ochre needles; and *luteolin hydrochloride*



(Perkin, l.c.), are readily prepared by the action of the acids on luteolin in the presence of boiling acetic acid. By treatment with water these compounds are quantitatively decomposed into luteolin and acid.

Monopotassium luteolin $\text{C}_{15}\text{H}_9\text{O}_6\text{K}$, fine yellow needles, from luteolin by means of alcoholic potassium acetate, is decomposed by boiling water with separation of luteolin. The sodium compound, $\text{C}_{15}\text{H}_9\text{O}_6\text{Na}$, behaves similarly.

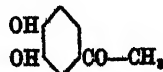
Tetra-acetyl luteolin $\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$, Perkin (also Hertz, Ber. 1896, 29, 1013), colourless needles, melts at $221^\circ\text{--}223^\circ$ (Perkin), $225^\circ\text{--}227^\circ$ (Herzig). *Tetra-benzoyl-luteolin*



colourless needles, melts at $200^\circ\text{--}201^\circ$ (Perkin).

Dibromluteolin $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_6$, yellow needles melts at 305° .

By the action of nitric acid on luteolin Rochleder (Zeitsch. für Chem. 1886, 603) obtained oxalic acid, and with fused alkali *protocatechuic acid* and *phloroglucinol*. Digested with boiling 50 p.c. potassium hydroxide solution, phloroglucinol and *acetyl-catechol* are produced (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1322)—



When methylated with methyl iodide luteolin yields, in addition to luteolin trimethyl ether,

also methyl-luteolin trimethyl ether (Perkin and Watson).

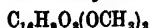
Luteolin trimethyl ether $C_{15}H_{12}O_8(OCH_3)_3$, lemon-yellow needles, m.p. 161°–163°, forms a monoacetyl derivative



colourless prisms, m.p. 156°–158°, and with alcoholic potash gives a bright yellow crystalline salt, which is decomposed by water.

On hydrolysis with alcoholic potash at 170° the trimethyl ether gives *veratric acid*, and *phloroglucinol monomethyl ether*, which was isolated in the form of disazobenzene-phloroglucinol monomethyl ether, orange needles, m.p. 251°–252°.

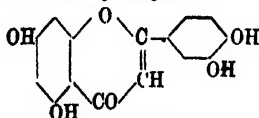
Methyl-luteolin trimethyl ether



melts at 191°–192°, and the monoacetyl derivative $C_{15}H_{10}O_8(OCH_3)_2(C_2H_5O)$ at 175°–176°. By means of alcoholic potash *veratric acid* and *methyl-phloroglucinol methyl ether* (identified as disazobenzene methyl-phloroglucinol monomethyl ether, orange-red needles, m.p. 198°–201°) are produced.

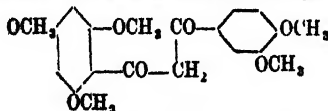
By digestion with boiling hydriodic acid *methyl-luteolin* $C_{15}H_{12}O_8$, yellow leaflets, is formed, m.p. about 307°–309°, which gives an acetyl compound melting at 235°–236°.

Perkin (l.c.) assigned to luteolin the constitution of a tetrahydroxyflavone



and the more recent synthesis of this colouring matter by v. Kostanecki, Rozycki, and Tambor (l.c.) has indicated that this formula is correct.

When *phloracetophenone trimethyl ether* is condensed with *ethyl veratrate* it gives 2:4:6:3':4'-pentamethoxybenzoyl-acetophenone



and this by long digestion with boiling hydriodic acid (sp.gr. 1.96) is converted into luteolin.

Though luteolin when digested with alcoholic potash and ethyl iodide in the ordinary manner gives only a triethyl ether, owing to the presence of an hydroxyl in the ortho position to the carbonyl group, when an excess of the reagents is employed, luteolin tetraethyl ether



colourless needles, m.p. 153°–155°, can readily be obtained (Perkin, Chem. Soc. Proc. 1912, 28, 323). Though quercetin pentamethyl ether on nitration readily gives the 6'-mononitro derivative (Watson, Chem. Soc. Trans. 1914, 105, 335), luteolin tetraethyl ether yields in similar circumstances only the tetranitro compound $C_{15}H_6O_8(NO_2)_4(OEt)_4$, colourless prisms, m.p. 146°. On the other hand, the introduction of only one nitro group can be effected by nitrating mono-bromo-luteolin tetraethyl ether (see below) (Perkin and Watson, *ibid.* 1915, 107, 137). Bromine (4 molecules) in acetic acid yields *bromoluteolin tetraethyl ether perbromide*

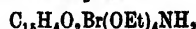
$C_{15}H_6O_8(OEt)_4Br_4HBr$, orange-yellow prisms, m.p. 161° (decomp.), and this on boiling with water gives *bromoluteolin tetraethyl ether* and *tetrabromoluteolin tetraethyl ether*.

With bromine (1 molecule) in acetic acid solution, *bromoluteolin tetraethyl ether hydrobromide* $C_{15}H_8O_8(OEt)_4Br \cdot HBr \cdot C_2H_5O$, pale yellow hair-like needles, is obtained, which when boiled with water gives *bromoluteolin tetraethyl ether* $C_{15}H_8O_8Br(OEt)_4$, colourless hexagonal plates, m.p. 183°, whereas by brominating luteolin tetraethyl ether with 2 molecules of the halogen in acetic acid solution in presence of sodium acetate, *tetrabromoluteolin tetraethyl ether*, colourless crystals, m.p. 111°–114°, is formed.

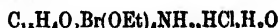
Bromo-6'-nitroluteolin tetraethyl ether



pale yellow rhombs, m.p. 170°–171°, on reduction in alcoholic solution with stannous chloride and hydrochloric acid, gives *bromo-6'-amino-luteolin tetraethyl ether*



yellow prisms, m.p. 165°–169°. This forms the hydrochloride

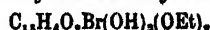


bright yellow needles, which when dried over soda lime become scarlet and melt at 187° (decomp.); with stannic chloride it forms the salt $(C_{15}H_{10}O_8NBr)_4H_4SnCl_6$, crimson prisms. By means of sodium nitrite the amino hydrochloride yields in the usual way, crystalline *bromoluteolin tetraethyl ether diazonium hydrochloride*, and from this by boiling with water *bromo-6-hydroxy-luteolin tetraethyl ether*

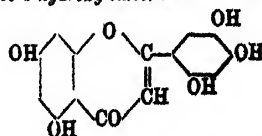


yellow needles, m.p. 255°, the acetyl derivative of which crystallises in white needles, m.p. 270°–272°, is produced.

This latter, probably owing to its insolubility, is not readily attacked by hydriodic acid (D 1.7), the first product of the reaction being apparently *bromo-6-hydroxy-luteolin diethyl ether*



the acetyl compound of which melts at 213°. The more drastic action of the hydriodic acid, employing also acetic anhydride, gave a small quantity of a compound crystallising in yellow needles, soluble in alkaline solutions with a yellowish brown colour, and which was probably an impure 6-hydroxy-luteolin—



The acetyl compound melted at 250°–256°.

When air is aspirated through alkaline solutions of luteolin (and also those of chrysin and apigenin), oxidation does not occur. This property, according to Perkin (l.c.), distinguishes the colouring matters of the flavone from those of the flavonol class, which are readily oxidised by this treatment.

It has already been stated that luteolin contains a second colouring matter, *isolumetin* (v. PARSLAY).

Dyeing properties of weld.—The importance of weld as a dyestuff in silk and wool dyeing has greatly diminished in consequence of its low colouring power compared with quercitron bark, flavin, and old fustic. This in one respect is unfortunate, because, of all the natural yellow colouring matters, it yields the purest and fastest shades. In conjunction with aluminium and tin mordants it gives very bright pure lemon-yellow colours, and these do not change to an olive or reddish tint as in the case of other vegetable yellows. With chromium and iron mordants weld gives yellowish and greenish olives respectively. For yellow, wool and silk are mordanted with alum and tartar in the usual manner and dyed subsequently in a decoction of weld with the addition of chalk to the dye bath. Weld alumina yellow is to some extent still employed in this country for certain army cloths and braid. For silk dyeing, weld extract is manufactured in small quantity, and is used for the production of yellow and olive colours.

A. G. P.

WELDING (*Soude*, Fr.; *Schweißen*, Ger.) is the joining of two pieces of metal under the hammer at a sufficiently high temperature.

WELSIUM. The name given by Eder (*Akad. Wiss. Wien. Ber.* 1920, 129, 421) to an element supposed to exist between terbium and dysprosium, of which he has tabulated more than 300 lines between 26546 and 3038.

WESELSKY'S DYES v. **OXAZINE COLOURING MATTERS.**

WESTFALITES. Explosives consisting of mixtures of ammonium nitrate and resin, with or without potassium nitrate, v. **EXPLOSIVES.**

WETTER DYNAMITE, WETTEREN POWDER, v. **EXPLOSIVES.**

WHALE OIL is obtained from the blubber of various species of the genus *Balaena*, viz *Balaena mysticetus*, Greenland or 'right' whale (northern whale oil); *Balaena australis* (southern whale oil); *Balaenoptera longimana*, *Balaenoptera musculus* (common orqual, the largest of all known animals), *Balaenoptera borealis* (northern or Rudolph's orqual) finback oil, finner-whale oil, humpback oil); *Neobalaena marginata* (Australian whale), *Rhachianectes glauca*, Cope (Japan). Other octaceans, the zoological species of which have not been determined yet, or which are identical with the foregoing species, are known as bowhead whale, Californian grey whale, orca or killer whale, beluga or white whale; these are chiefly caught by American whalers in the Northern Pacific. The northern whale oil is the 'train oil' of commerce proper; but this name has become a generic name, and has been extended to all other 'blubber oils' included in this group and even to fish oils (see **OILS, FIXED, AND FATS**).

The blubber of whales caught in the northern seas of Europe was, in the early days of the whaling industry, 'tried' on board the whalers; but in consequence of the low yield, and also of the low quality of oil thus obtained, the whales are now brought into the 'trying' stations situated in Finnmarken, on the Lofotes, Faro, Shetland, Hebrides, and in Iceland.

To a large extent the American whalers still try the blubber on board ship and deliver the crude oil into the refineries of New Bedford, Mass., on the east coast, and of San Francisco

on the west coast. In British Columbia the most modern methods (see below) are now in vogue.

During recent years a very extensive whale oil industry has sprung up in the whaling grounds adjacent to the South African coast, especially to that of Natal. The whale, killed by a gun-shot, is blown up with air so as to float the carcase, which is brought immediately into the trying stations, when the whale is hoisted on to a working platform where the blubber is stripped clean from flesh, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting pans, and 'boiled' with steam. Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, known in commerce as 'Whale Oil No. 0'; it is of a pale yellow colour, and has but a faint fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are 'water-white,' and are free from volatile fatty acids. On further boiling, the second quality—'Whale Oil No. 1'—runs off, it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified while depositing 'stearine,' which is filtered off, pressed in hydraulic presses, and sold as 'whale tallow,' or 'whale stearine,' for soap making.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is 'tried down' in a digester under a pressure of 40-50 lbs. The oil classed as 'No. 2 oil' is thus obtained. This oil has a brown colour and a strongly developed fishy smell; its proportion of free fatty acids is considerably higher than in 'oil No. 1'. In some stations 'whale oil No. 2' is made from the blubber residues only, and does not contain any oil from the flesh. Hence it represents a superior article to the 'No. 2 oil.'

The bones are worked up in the same manner, and yield a still inferior quality of oil. Such oil ('whale oil No. 3') is darker still, has a more strongly developed odour, and a high percentage of free fatty acids. 'Whale bone oil' of commerce is, however, not exclusively made from the bones, except in those cases where the product is sold under guarantee as 'bone oil.'

All these operations are carried out with the greatest rapidity and precision recalling the routine of the Chicago packing houses which have served as a prototype for the arrangement of a modern whaling station.

In the old whaling stations where the carcases cannot be handled so expeditiously, the oil remains for a longer or shorter time in contact with the flesh, which rapidly undergoes putrefactive changes. The oil suffers in consequence and becomes dark, and is more objectionable as regards smell and free fatty acids than the preceding qualities. This oil is known in the trade as 'carcass oil,' 'whale oil No. 4.'

The residue remaining after the removal of the oil is worked up for manure, 'whale manure.'

This process is carried out in Newfoundland (at Balena) Pacific coast, and South Africa, where the Government has established several new plants. The carcasses of the whales are there completely used up in the manufacture of oil, 'stearine,' bone meal or bones, and other articles of commerce.

If the whale is landed in a perfectly fresh state, cattle meat can be prepared from the fresh meat, as is being done in Iceland and in the Faro Islands, and in South Africa. Some fresh meat is also consumed by the inhabitants locally (Iceland and Faro Islands).

The 'right whale' oil is of better quality than the 'southern whale' oil. The 'finner whale' oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coasts of Norway and Newfoundland, as also to a smaller extent on the Asiatic coast of Russia, and the coast of Japan. For the chemical characteristics of whale oil, see OILS, FIXED, AND FATS.

Doherty (J. Roy. Soc. N.S. Wales, 1922, 46, 266) obtained the following values for oils from Pacific whales: sp gr. at 15.5°, 0.9182-0.9232; $n_D^{15.5}$, 1.471-1.476; acid value, 0.75-5.8, sapon. value, 192-199; iodine value, 95-119.

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited 'stearine' consists to a large extent of palmitin. The iodine value of a sample of pressed cake examined in the author's laboratory was 37.9. Volatile fatty acids are absent. About 10 p.c. of clupanodonic acid can be isolated from whale oil in the form of its octobromide.

According to Milligan, Knuth and Richardson, who separated the fatty acids by fractional distillation of their methyl esters, a specimen of whale oil fatty acids had the following composition: myristic acid, 4.6; palmitic, 11.5; palmitoleic, 17.0; stearic, 2.5; unsaturated acids (mainly oleic), 36.5; unsaturated acids, C_{22} , 16; unsaturated acids, C_{24} , 10; unsaturated acids, C_{26} , 1.5; and unsaponifiable matter, 0.7 p.c. (J. Amer. Chem. Soc. 1924, 46, 157). E. F. Armstrong and T. P. Hilditch (J. Soc. Chem. Ind. 1926, 44, 180) found in a S. Georgia whale oil that the unsaturated acids comprised myristoleic acid, 1 to 1.5 p.c.; palmitoleic acid, 15 p.c.; oleic acid, 35 p.c.; and highly unsaturated acids with 20 and 22 carbon atoms.

Whale oil is not infrequently adulterated with resin oil, the detection of which is simple. For the recognition of seal oil reliance is mainly placed upon the taste.

The 'water-white' and 'pale' brands of whale oil are used as burning oil, and very extensively in soap-making. The lower qualities are employed for leather dressing. For the characteristics of glycerol from whale oil, see COCKS and Selway (J. Soc. Chem. Ind. 1918, 37, 126 T).

Whale oil is also used as a batching oil for jute, for tempering steel, and as a lubricant for screw-cutting machines. In the hydrogenated form (see HARDENED OILS) it is sometimes used as a constituent of margarine on the Continent. Hydrogenated whale oil yields about 0.9 p.c. of unsaponifiable matter and 0.04 p.c. of cholesterol. The unsaponifiable matter, after removal of the

cholesterol, is optically active $[\alpha]_D^{25} = +5.6$. When crystallised from acetone, whale oils yield a larger quantity of insoluble glycerides than do animal fats, and the glycerides remaining soluble in this solvent have a high iodine value (Buttenberg and Angerhauser, Zeitsch. Nahr. Genussm. 1919, 38, 199).

WHEAT. *Estimation of Rye Flour in Wheat Flour.*—J. König and F. Bartshat (Zeitsch. Unters. Nahr. Genussm. 1923, 46, 321) have thoroughly investigated chemical methods for the estimation of wheat and rye flours when present in admixture, and show that the diastase method proposed by several workers (e.g. Amberger, Analyst, 1922, 47, 73), methods dependent on the gluten content, on the solubility of the non-glutenous protein, or on the protein soluble in 20 to 70 p.c. alcohol are not trustworthy for the analysis of the mixed flours. It is shown, however, that the percentage of the total protein soluble in saturated solution of calcium sulphate is constant for each flour, and independent of the actual amount of protein in any particular sample of the flours. Ten grms. of the flour are moistened in a 500 c.c. flask with the saturated calcium sulphate solution at the room temperature (0.22 gm. in 100 c.c.), made up to the mark and shaken in a machine for one hour, after which the nitrogen is estimated in 100 c.c. of the clear filtrate and expressed as percentage of the total nitrogen in the flour. Treated in this way, wheat flour shows 29.1 p.c., and rye flour 51.5 p.c., so that the proportion of the two flours may be interpolated from the following table:

Wheat.	Rye.	P.c.
100	—	29.1
90	10	31.34
80	20	33.58
70	30	35.82
60	40	38.06
50	50	40.30
40	60	42.54
30	70	44.78
20	80	47.02
10	90	49.26
—	100	51.50

The average experimental error with the method is about 5 p.c., but may be exceeded in the case of flour of unusually high acidity (Analyst, 1924, 49, 187. See also CEREALS, vol. ii. p. 130).

A modification of Fleurent's method for the determination of the baking value of flours has been proposed by Braun (Ann. Falsif. 1924, 57, 269; J. Soc. Chem. Ind. 1924, 43, B 762). The ratio of gluten nitrogen to gluten nitrogen is used to indicate the quality of the flour.

WHEEL ORE v. **BOURNONITE**.

WHETSLATES v. **WHETSTONE**.

WHETSTONE (Cortice, Fr.; *Wetzstein*, Ger.), **OILSTONE**, and **HONESTONE**. Hard, fine-grained rocks, usually highly siliceous in character, used for sharpening or whetting edged tools and also for grinding metals. Rocks of several different kinds are suitable for this purpose, such as hornstone, hornfels, lydian stone, quartzite, sandstone, slate, phyllite, schist, &c. (qq.v.). They must possess an evenness of grain and texture combined with a certain degree of friability. If the stone is too hard and tough to wear by friction it becomes

glassed and chipped, and does not present fresh cutting surfaces. At the same time the stone must have a certain degree of firmness and must wear evenly. The cutting power sometimes depends on the presence of minute grains of garnet, rutile, or magnetite distributed through the stone. The chemical composition of materials answering to such a description naturally varies between wide limits, but, as a rule, silica predominates. The following analyses are of I, Novaculite, 'Arkansas stone,' from Arkansas (sp.gr. 2.648). II, Novaculite, 'Ouachita stone,' from Arkansas. III, Novaculite, containing quartz and sericite, from Marquette, Michigan (also P_2O_5 , Li_2O traces). IV, Oilstone (turkey-stone) from Asia Minor. V, Belgian razor-hone from Recht (also P_2O_5 , 0.16, S 0.18, organic matter 0.02; sp.gr. 3.22). VI, Whetstone from Cambrian slates at Lausenstein, Bavaria (also organic matter 1.56).

	I.	II	III	IV.	V.	VI
SiO_2	99.50	99.49	76.99	72.00	46.52	40.81
TiO_2	—	—	—	—	1.17	—
Al_2O_3	0.20	0.13	13.92	3.33	23.54	35.57
Fe_2O_3	0.10	0.06	0.45	—	1.05	1.88
FeO	—	—	0.77	—	0.71	—
MnO	—	—	traces	—	17.54	trace
CaO	0.10	0.04	0.32	13.33	0.80	0.27
MgO	0.05	0.08	1.12	—	1.13	0.25
K_2O	0.10	0.10	3.65	—	2.69	10.63
Na_2O	0.15	0.10	0.50	—	0.30	1.72
H_2O	0.10	0.14	2.35	—	3.28	1.03
CO_2	—	—	—	10.33	0.04	0.28
	100.20	100.20	100.13	98.99	99.13	100.00

The novaculite* of Arkansas is one of the most important whetstones. It is found over a wide area in the vicinity of Hot Springs, occurring as bands a few inches to 15 ft. in thickness, interbedded with sandstones and shales of Lower Silurian age. It has a homogeneous, finely granular structure, and is white with a faint bluish tinge. It is brittle and breaks with a conchoidal fracture; sp.gr. 2.648 (Arkansas stone). Under the microscope it is seen to consist of an aggregate of quartz grains with an average diameter of less than 0.01 mm. The stone is rendered more or less porous by minute rhombohedral cavities, representing crystals of calcite or dolomite which have been dissolved out; and it is on the presence of these cavities that the cutting action partly depends. In the trade two varieties of Arkansas novaculite are distinguished: namely, the more compact 'Arkansas' stone in which the cavities form 0.17-0.25 p.c. of the bulk of the stone; and the more porous 'Ouachita' (or Washita) stone, in which the spaces amount to 5 p.c. The latter has the dull appearance of unglazed porcelain; it is the more abundant and obtainable in larger masses, and is also more in demand. The average of several analyses shows 99.50 p.c. SiO_2 , of which 2.2-7.2 p.c. is soluble in a caustic potash solution, and 0.44-1.14 p.c. in a solution of potassium carbonate (L. S. Griswold, Whetstones and the novaculites of Arkansas, Ann. Rep. Geol. Survey Arkansas, for 1890, 1892, vol. iii.; W. C. Phalen, Oilstones of Arkansas, Min. Res. U.S. Geol. Survey, for 1911, 1912, 2, 842).

The Belgian razor-hones (anal. V) occur as

* This term is now often restricted to the Arkansas novaculite, although it was introduced by B. Kirwan in 1784 from the Latin *seacula*, a sharp knife or razor.

this yellow bands in blue-grey slates or phyllites of Gedinian (Devonian) age, and are quarried at several places in the neighbourhood of Vielsalm and Salm-Château in the Ardennes. They are micaceous slates containing innumerable minute garnets (A. Renard, Mem. Acad. Belgique, 1876, 41). The German razor-hones from the neighbourhood of Ober-Ammergau in Upper Bavaria consist of a very compact, pale-coloured quartzose clayey limestone, and occur as beds in Jurassic limestones. They are very brittle with a splintery fracture, and are composed of $CaCO_3$, 83.57, $FeCO_3$, 2.67, clayey matter 7.63, quartz 5.96=99.85 (C. W. Gumbel, Geogn. Beschreib. Bayern, 1861, 1). The celebrated Turkey oilstone (anal. IV) is also calcareous, containing SiO_2 , 70-75, $CaCO_3$, 20-25 p.c., with often a little alumina. It is obtained in the interior of Asia Minor and exported from Smyrna. Two varieties are distinguished, the white and the black, the latter being slightly the harder.

In England several stones of a more or less similar character are obtained at various places; e.g. the Charley Forest stone or Whittle Hill hornstone, which is a fine-grained, siliceous, slaty rock worked in Leicestershire. The Welsh oilstone is a somewhat similar material from near Llyn Idwal in North Wales. Devonshire oilstones are obtained from the metamorphosed slaty rocks in the neighbourhood of Tavistock. From Scotland come the Water-of-Ayr stone, snake stone, and Tam o' Shanter hones.

The coarser grained scythe stones are made of certain kinds of sandstone. Those from Pike in New Hampshire are the most celebrated, being exported to all parts of the world. This material is a fine grained, thinly laminated, micaceous sandstone (W. C. Phalen, The scythe-stone industry in New Hampshire, Min. Res. U.S. Geol. Survey, for 1909, 1911, 2, 616). Scythe-stones have been long worked near Blackdown in Devonshire, and are known as 'Devonshire batts.' They are made from siliceous concretions embedded in sand, probably of Upper Greensand age. Similar scythe-stones are also made at Penzlewood, near Stourton in Wiltshire.

In preparing whetstone for use, the blocks as quarry dressed are sawn into small rectangular slabs with a lapidary's disc charged with diamond powder, and then smoothed down on an iron plate charged with emery. Tools for special purposes, as used by dentists, engravers, watchmakers, jewellers, &c., are ground to the required shape.

Wheels made of Arkansas stone are used for fine metal grinding; and powdered whetstone is used as an abrasive material by instrument makers. See also ABRASIVES.

References.—On whetstones generally: L. S. Griswold, l.c.; G. P. Merrill, The Non-metallic Minerals, 2nd ed., New York, 1910. L. J. S.

WHEWELLITE. Hydrated calcium oxalate $CaC_2O_4 \cdot H_2O$, crystallised in the monoclinic system. It forms small, water-clear crystals which are often twinned in heart-shaped forms resembling those of calcite. There are perfect cleavages, and the material is very brittle; sp.gr. 2.46; $H=2\frac{1}{2}$. The refractive indices and double refraction, $\alpha=1.4900$, $\beta=1.5552$,

$\gamma=1.6497$, $\gamma-\alpha=0.1597$, for sodium-light, are very nearly the same as those of calcite (viz. $\epsilon=1.4962$, $\omega=1.6585$, $\omega-\epsilon=0.1713$). The crystals could therefore be used for the construction of Nicol prisms for polarising apparatus, if only they were found of sufficient size or if such could be produced artificially. The mineral is found in coal mines, but at only a few localities, namely, Burgk and Zwickau in Saxony, and Brûx and Schlan in Bohemia. It occurs, together with calcite, dolomite, barytes, &c., in small fissures in the shales and sometimes in the coal itself. Crystals have also been found in a metalliferous vein with tetrahedrite and ankerite at Urbeis in Alsace, and under similar conditions at Freiberg in Saxony. L. J. S.

WHISKEY. The term 'whiskey,' applied to the national beverage of Scotland and Ireland, only came into common use in the latter part of the eighteenth century, and is derived from the Celtic 'uisque-beatha' or 'usquebaugh,' meaning 'water of life,' no doubt in reference to its stimulating properties. A similar signification is seen in the terms applied to strong alcoholic liquors in other countries, as 'aqua vitæ,' and 'eau de vie.' Burns employs the three terms 'aqua vitæ,' 'usquebaugh,' and 'whiskey' synonymously.

The introduction of the manufacture of alcohol into Europe is, as the word suggests, due to the Arabs, but in the grape-growing countries of the south, the spirit is naturally produced chiefly from wine, and in the north, from different kinds of grain, the different materials used giving rise to the distinctive flavours characteristic of the spirits of different countries.

In Scotland the manufacture of whiskey was a subject for legislation as early as the sixteenth century, and extracts from the statutes show that 'aqua vitæ' was not the exclusive product of malted barley, but that unmalted grain was also used in the early days of spirit distillation in Scotland, and this has been the practice in Ireland up to the present day.

In 1803, during the Napoleonic wars, and owing no doubt to the possibility of a shortage in the supply of grain for food, the use of grain for the manufacture of spirits was prohibited throughout the United Kingdom.

In both Scotland and Ireland the pot-still was used prior to the invention of the patent continuous still by Aeneas Coffey in 1831, since when the patent still has been increasingly employed for the manufacture of spirit from a mixture of malt and unmalted grain, and known locally as 'whiskey.' About two-thirds of the potable spirit made in Scotland and Ireland at the present time is of this description. The spirit produced from other materials as molasses, rice, starch, potatoes, dates, currants, &c., is almost invariably distilled from a 'patent still,' and is used chiefly for industrial purposes. When malt only is used the whiskey is produced in Scotland chiefly, and in Ireland exclusively, from pot-stills. At the present time (1926) there are 9 distilleries in England; all of which are patent-stills only. In Scotland, out of 124 distilleries, 9 use patent-stills and 115 pot-stills only. In Northern Ireland, only 4 distilleries are at present working, and of these 2 use patent-stills and 2 pot-stills only. In the Irish

Free State, out of 14 distilleries, 3 use patent-stills, one both patent and pot-still, and the remainder pot-stills only. Of the latter, 10 are at present 'silent,' i.e. not working.

In 3 of the distilleries in England, 6 in Scotland, and 2 in Northern Ireland, yeast is manufactured on a large scale as a commercial product. In some instances, yeast is the principal product of manufacture—the spirit produced at these distilleries being really a 'by-product.'

The different characters of the various kinds of whiskey are due to the presence of small amounts of secondary products, sometimes referred to as 'impurities' or 'by-products' (as esters, higher alcohols, &c.), rarely exceeding in the aggregate one-half p.c. of the ethylic alcohol present, but sufficient to impart a distinctive flavour and aroma to the spirit.

These differences in character depend mainly upon (a) the kind and relative proportions of the materials used in the mash; (b) the methods of mashing and fermentation employed; and (c) the type of still used and the manner in which it is worked.

For the processes of mashing, fermentation, and distillation employed in the manufacture of ordinary alcohol, and for a description and diagram of Coffey's patent still, see article ALCOHOL.

This is known as 'silent' or neutral spirit, but grain spirit, distilled from patent stills, when intended for potable purposes, is not so highly rectified as to be deprived of its 'whiskey' character.

In the manufacture of pot-still whiskey in Scotland, barley-malt is practically the only material employed in the mash, whilst in the Irish pot-still distilleries the mash consists of a mixture of barley-malt with unmalted barley or other grain. The proportions vary with a view to securing particular flavours in the whiskey, but a typical mash consists of about four-fifths barley (malted and unmalted), and one-fifth of wheat, oats, and rye, the proportions decreasing in the order of enumeration. Maize is generally excluded from the pot-still whiskeys.

Besides the formation of sugar by the action of diastase during the mashing process, other substances, the exact nature of which is not thoroughly understood, are obtained in solution, from which the secondary constituents of the finished whiskey are both directly and indirectly derived. According to Bell (Select Committee of the House of Commons on British and Foreign Spirits, 1890-1) some of the essential oils naturally existing in the malt and grain, and the empyreumatic and creosotic bodies with which the malt becomes impregnated during the process of drying over peat, anthracite, or coke fires, pass through the operations in a more or less chemically unchanged condition, thus imparting distinctive characters to the whiskey, particularly when the ordinary pot-still is employed for the distillation.

Similarly during the process of fermentation, the conversion of the sugar into ethyl alcohol is accompanied by other chemical changes resulting in the formation of substances which also influence the flavour of the finished whiskey. Of these the principal are the higher alcohols,

which have been shown by Ehrlich and others to be due to the splitting up of certain nitrogenous substances (amino acids) produced by the peptonising action of the malt in the mashing process. The ultimate result is affected by the special nature of the yeast, the temperature at which it works, and the time occupied in fermentation.

The simplest form of pot-stills employed in Scotland are heated by direct fire, and have no special means of rectification. The long neck of the still, however, although originally designed simply to prevent particles of the boiling mash being mechanically carried over by frothing or spraying, incidentally has the further important practical use of effecting considerable rectification.

The pot-stills sometimes have their rectifying power increased by means of perforated plates placed transversely in the neck of the still, or by the use of 'purifiers,' pipes or circular vessels cooled by water and fitted between the neck of the still and the condenser.

Some stills are heated by means of steam-jackets or coils instead of direct fire, and this difference in the method of heating is said to have an important influence on the flavour of the whiskey. Certain empyreumatic bodies are thought to be generated by the open fire method, but according to Bell, Schidrowitz, and Thorpe, these are more probably derived from the peat or coke used for heating the malt kilns.

In the manufacture of Scotch whiskey, two distillations only are usually made, first from the 'wash still' from which the whole of the volatile constituents are collected as 'low wines'; and second, from the 'low-wines still,' the distillate from which is collected in three fractions, viz. (1) 'foreshots,' (2) clean spirit or 'whiskey,' and (3) 'feints.' The first and third fractions are added to the low wines of the next distilling period, and so on throughout the distilling season, the residue left in the wash still ('pot ale'), and that in the low-wines still ('spent lees') being run to waste.

The whiskey is generally run off at a strength of 11-25 overproof, but in the Lowlands, where a third distillation or 'rectification' is generally made, the strength of the whiskey distillate is from 40 to 54 overproof.

In Ireland the pot-stills are generally much larger than in Scotland, having sometimes a capacity of 20,000 gallons. The head of the still is shorter, and the still for low wines and feints is provided with a 'lyne arm,' or long pipe which passes through a tub of water, the liquid thus condensed between the head of the still and the worm being conveyed by a 'return pipe' to the body of the still. By this means a considerable degree of rectification is effected.

Three distillations are the rule for Irish pot-still whiskey, and the fractions are more numerous than in the manufacture of Scotch whiskey, consisting of strong low wines, weak low wines, strong feints, and weak feints. The middle or 'whiskey' fraction is also run off at a higher strength than in the Scotch process, viz. from 24 to 30 overproof.

The point at which the collection of foreshots is stopped and that of whiskey commenced, as well as that at which the running of whiskey ceases and the collection of feints begins, is determined by the judgment and

experience of the distiller, but various simple devices are employed for testing the distillate at different stages, as glass floats or hydrometers, specific gravity beads, and samplers for testing the distillate by dilution with water and observing whether the mixture is opalescent or clear.

Scotch whiskeys may be divided into the following five principal classes: (1) Highland malts; (2) Lowland malts; (3) Campbeltowns; (4) Islays; all made from malt in pot stills; and (5) grains, a name given to patent-still whiskeys. *Irish whiskeys* have no corresponding classification, all the 'self' or non-blended whiskeys being sold under distinctive names.

The secondary products, and therefore the character of the spirit, are considerably affected by the strength at which the whiskey is run off. Some of these products (especially esters) suffer partial decomposition in both the wash and low wines stills, whilst others, of higher boiling-point, remain in the stills and are run to waste with the pot ale and spirit lees. More than two-thirds of the secondary products are lost in this manner, only from 10 to 30 p.c. passing into the finished whiskey. (For the recovery and utilisation of the esters left in still residues, see art. RUM.)

It has not yet been found possible to trace any definite relationship between the commercial characteristics of various pot-still whiskeys and their composition as ascertained by analysis, for the reason that the secondary constituents are not individually identified by chemical analysis, but are assessed in groups consisting of members of the same family though in varying proportions, e.g. acids, aldehydes, esters, and higher alcohols.

There is some reason to believe, from the researches of Guareschi and Mosso (on behalf of the Italian Government), Vaughan of Michigan University, and Husz of Sweden, that other bodies may be present due to decomposition of albuminous matter in the grain and having alkaloid properties. They are alleged to be largely accountable for the deleterious effects of spirit drinking, but, if present, they occur in such minute quantities as to elude identification hitherto.

Husz attributed the unusually deleterious character of the spirits drunk in Sweden in a certain year to the use of unsound grain, and Lombroso has shown that an alkaloid having an action like strychnine is generated in decaying maize. Lauder Brunton, whilst attributing much of the harmful effects of new spirit to furfural, also supports the theory that these effects may be partly due to the presence in minute quantities of alkaloidal bodies, especially in potato spirit.

Schidrowitz has determined the percentage of nitrogen in new pot-still whiskeys with the results shown below, but failed to detect the least trace of substances giving alkaloidal reactions. The nitrogen is calculated as NH_3 , and expressed as grams per 100 litres of absolute alcohol—

Highland malts	0.09-0.12
Lowland malts	0.11-0.20
Campbeltowns (malt)	0.08-0.14
Grains	0.03-0.14
American rye whiskeys (matured)	0.25-0.32

No definite evidence was, however, obtained by the Royal Commission on Whiskey, &c., that the deleterious effects attributed to the consumption of spirits are directly due to the presence of poisonous secondary products, and the bulk of the medical evidence was to the effect that the actual amount of the secondary products is so small compared with that of the ethyl alcohol, that the physiological effects produced by them must also be extremely small in comparison with those due to the ethyl alcohol itself. It would appear to follow, therefore, that whiskey derived either from pot or patent still has much the same toxic effect if taken in the same quantity and at the same alcoholic strength.

At the same time, since many substances are known to produce marked effects on the digestive system merely as a result of the sensation produced by their *flavour*, this plays an important part from a dietetic point of view, and the more agreeable flavour of a mature whiskey may exert a favourable mental effect which promotes the

activity of the digestive processes, whilst the unpalatable flavour of new 'silent' or neutral spirits may tend to interfere with digestion apart from the direct effect due to the alcohol itself.

The methods usually employed for the estimation of the different groups of secondary constituents are given in detail in the Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, 1908-9, vol. ii. App. Q. xii. Thorpe; see also vol. i. App. F. Schidrowitz.

The following tables give the results of analyses of various kinds of whiskey by Schidrowitz, Tatlock, and Thorpe, expressed in all cases as parts by weight in 100,000 parts by volume of absolute alcohol (e.g. grams per 100 litres).

Schidrowitz and Kaye's results of analyses of 100 samples of the principal classes of *Scotch pot-still whiskey* are summarised in the following table, showing the minima, maxima, and averages—

No. of samples	Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Average total 'impurities'
39	Highland malts .	10-83	33-185	112-235	4-66	1-6-6-3	292
16	Lowland malts .	6-60	27-87	82-228	8-54	0-5-2	255
16	Campbeltowns .	12-100	53-140	160-259	11-85	2-4-8-0	335
5	Islays .	15-36	40-86	155-200	17-40	3-8-5-2	294
24	Grains .	3-69	20-55	33-80	trace-17	0-0-9	120
100	Average .	30-9	60-6	143	18-6	3-2	252

ANALYSES OF IRISH POT-STILL WHISKEY (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
A. New .	7	34	145	12	5-5	203
„ 13 years' plain wood .	29	38	185	68	3-3	323
B. New .	6	28	233	8	4-1	279
„ 13 years' plain wood .	32	47	264	21	4-4	368
C. 14 years' sherry .	87	87	226	32	4-5	436
D. Mature .	67	59	147	16	2-6	291
Average .	38	49	200	26	4-2	317

SCOTCH PATENT STILL WHISKEYS (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
New whiskey .	4	25	65	2	—	96
4 months' sherry wood .	24	26	31	4	0-07	85
2 years' plain wood .	14	25	100	5	trace	144
2 years' sherry wood .	58	40	44	7	0-15	149
Average .	25	29	60	4-5	0-05	113-5

WHISKEY.

IRISH PATENT STILL WHISKYS (Schidrowitz).

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehydes	Furfural	Total
Distillery A—new	17	25	38	—	—	80
" " 2 years	21	41	50	—	trace	112
Distillery B—new	10	24	48	3	trace	85
" " 1½ years	3	19	52	—	—	74
Distillery C—new	9	25	46	1	trace	81
" " 1½ years	—	33	50	11	—	94
Average	10	28	47	2.6	trace	87.6

The following analyses by Tatlock show the maxima, minima, and averages obtained from 75 samples of Scotch and Irish malt-pot-still whiskeys, grain patent still, American, and blended whiskeys—

	High-lands, 31 samples	Low-lands, 9 samples	Islays, 4 samples	Campbelltowns, 2 samples	Irish, 2 samples	American, 4 samples	Grains, 7 samples	Blends, 16 samples
Esters—								
Maximum	154.16	85.80	78.05	85.62	44.22	119.52	50.90	92.05
Minimum	45.01	34.52	48.31	61.42	38.42	111.06	22.04	33.56
True average	83.06	66.19	61.51	73.52	41.32	115.99	33.26	58.96
Higher alcohols								
Maximum	190.40	240.66	161.70	206.70	169.10	177.34	68.47	111.25
Minimum	73.51	103.49	130.20	139.58	154.93	102.55	32.47	48.71
True average	144.61	140.40	144.55	173.14	162.01	156.99	45.32	80.76
Volatile acids								
Maximum	89.06	39.86	32.41	56.35	49.23	132.11	32.93	100.13
Minimum	21.76	4.70	17.11	31.16	4.55	65.24	2.86	13.12
True average	41.78	17.35	25.86	43.75	26.89	99.43	16.67	40.61
Aldehydes—								
Maximum	35.06	33.59	31.74	33.54	21.12	32.85	12.95	26.60
Minimum	3.21	4.70	19.82	32.45	4.34	17.01	1.59	1.26
True average	19.48	20.42	28.40	32.90	12.73	26.53	7.66	9.29
Furfural—								
Maximum	7.34	5.85	6.29	3.77	3.02	3.86	0.50	3.17
Minimum	1.58	2.65	3.25	3.23	2.73	1.95	0.10	0.43
True average	4.18	4.39	5.02	3.50	2.87	3.00	0.25	1.63
Total secondary products—								
Maximum	382.35	314.81	294.99	385.98	269.62	452.92	130.38	267.64
Minimum	218.94	218.52	225.94	267.84	222.04	328.76	68.04	106.22
True average	294.41	282.03	265.37	326.91	245.83	396.89	102.08	191.23

The results of analysis of 7 samples of high-class whiskeys as supplied by Government contractors for hospital use are given in the following table (Thorpe):—

Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
7 years	28.2	9.6	90.0	175.5	2.7	306.0
" "	28.2	9.6	87.9	175.5	2.7	303.9
" "	28.2	9.6	90.0	175.5	2.7	306.0
10 years	24.3	12.1	92.1	877.1	3.5	1009.1
" "	31.5	9.8	93.0	300.0	3.3	437.6
" "	32.0	9.8	114.0	456.1	3.3	616.1
" "	41.0	12.1	124.5	578.9	3.1	759.6
Average	30.6	10.4	98.8	391.2	3.0	534.0

Results of analyses of 5 samples of spirits made in Germany and sold as cheap whiskey in Hong Kong are given on p. 466.

Samples A and B consisted of 'silent' spirit, with an admixture of pot-still whiskey for the purpose of imparting the genuine flavour of whiskey. They are very similar to what is usually sold as 'whiskey' in public houses in England. Samples C, D, and E consisted of highly rectified 'silent' spirit coloured and flavoured to imitate whiskey. The fusel and impurities were much less than is usually found in genuine Scotch and Irish pot-still whiskeys of high commercial quality, whose furfural and other aldehydes were practically absent, and there was no evidence that these spirits contained anything of a deleterious nature apart from the alcohol itself.

'Pot-still' and 'patent-still' spirits (Thorpe, Royal Comm. on Whiskey and other Pot-still Spirits, App. Q. vi., vii., viii.). "An examination

WHISKEY.

Secondary products	A	B	C	D	E	Average
Volatile acidity (as acetic acid)	50.7	63.7	10.5	14.0	7.0	29.2
Furfural	1.5	1.2	Nil	Nil	Trace	0.6
Aldehydes (as acetic aldehyde)	1.8	2.1	Trace	Trace	Trace	0.8
Esters (as acetic ester)	87.5	109.5	15.0	7.8	3.6	44.7
Higher alcohols	225.7	205.4	20.4	22.6	33.2	101.4
Total secondary constituents	367.2	381.9	45.9	44.4	43.8	176.6

of the following tables, giving the results of the analyses of a number of representative samples of both kinds of spirits, shows very clearly the broad distinction between the 'pot-still' and 'patent-still' spirit. There is always a much larger amount of the

SPIRITS FROM POT STILL DISTILLERIES (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New	16.9	9.2	77.4	407.2	2.9	513.6	Speyside.
2	6 years	52.2	19.6	93.9	472.1	1.9	639.7	"
3	New	13.2	5.4	63.2	471.4	2.9	555.1	Banffshire.
4	7 years	53.6	32.2	91.0	371.4	1.9	550.1	"
5	New	9.8	9.8	63.1	490.0	2.8	575.5	"
6	"	15.0	21.8	63.8	451.6	4.2	556.4	"
7	7 years	30.1	41.6	92.0	460.5	3.6	627.8	Islay.
8	"	46.0	43.2	99.0	563.2	3.6	755.0	"
9	New	17.0	33.6	72.9	410.9	3.5	537.9	"
10	4 years	37.5	34.8	81.4	453.0	3.3	610.0	Campbeltown
11	10 years	47.3	10.0	98.8	322.8	5.7	484.6	Highland.
12	New	3.3	50.2	102.8	522.6	3.1	682.0	Irish.
13	6 years	32.6	55.9	86.4	771.2	2.9	949.0	"
14	New	1.7	26.3	73.7	861.4	2.2	965.3	"
15	"	1.7	8.7	73.0	729.8	0.1	813.3	"
16	8 years	17.5	10.5	30.0	894.7	3.1	955.8	"
17	New	4.2	7.0	13.6	701.7	1.1	727.6	"
18	6 years	21.0	12.2	35.0	789.0	1.4	858.6	Irish.
19	New	1.4	4.6	75.9	336.9	Nil	418.8	"
20	1 year	5.2	7.0	106.6	571.9	"	690.7	"
21	New	1.4	11.5	46.1	857.9	8.5	925.4	"
Average		20.4	21.7	73.3	567.3	2.8	685.3	

PATENT STILL GRAIN SPIRITS (Thorpe).

No.	Age	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total	District
1	New	1.9	9.6	30.8	39.0	Nil	81.3	Scotch Distillery
2	7 years	19.0	10.8	35.0	21.8	0.1	86.7	"
3	"	36.9	12.0	47.9	21.1	0.3	117.2	"
4	New	1.9	4.7	41.1	97.8	Nil	145.5	"
5	4½ years	15.6	14.1	46.4	81.3	"	157.4	"
6	New	3.8	trace	22.8	14.0	"	40.6	"
7	3 months	5.2	"	45.6	42.0	"	92.8	"
8	New	3.5	"	12.2	28.0	"	43.7	"
9	7 years	40.0	3.3	22.8	57.8	0.3	124.2	Irish Distillery.
Average		14.2	6.1	33.8	44.6	0.1	98.8	

PATENT STILL SPIRITS OF HIGH STRENGTH (Thorpe).

No.	Description	Volatile acid (as acetic acid)	Aldehydes (as acetic aldehyde)	Esters (as acetic ester)	Higher alcohols	Furfural	Total
1	British spirit from molasses	1.2	35.1	62.5	84.0	Nil	182.8
2	British spirit from grain, highly rectified	1.2	trace	11.1	21.2	"	33.5
3	British spirit from molasses, highly rectified	1.2	3.5	7.3	63.0	"	75.0
4	British spirit crude, from molasses	2.5	97.3	187.7	20.9	"	308.4
5	Foreign spirit imported from Hamburg	1.2	Nil	5.5	10.4	"	17.1
6	Foreign spirit imported from Hamburg	1.2	Nil	9.1	20.9	"	31.2
7	Foreign spirit imported from Stettin	1.2	2.2	7.2	83.7	"	94.3
Average		1.4	19.7	41.5	43.4	"	106.0

secondary constituents in the 'pot-still' spirit. Speaking generally, the percentage of every one of the secondary constituents usually determined is greater in the 'pot' than in the 'patent' spirit, but the most marked differences are in the 'higher alcohols' and 'furfural.' 'Patent' spirit contains no furfural when new, although after storage in wooden casks it is sometimes found to contain traces of this substance, but always in much smaller amount than in 'pot-still' spirit, in which it is never absent. The low percentage of the 'higher alcohols,' and the absence of all but mere traces of furfural render it a comparatively easy matter to distinguish 'patent' from 'pot-still' spirit. But the variations in the amounts of the secondary constituents in both classes of spirits renders it less easy to estimate the exact proportion of each kind of spirit present in mixtures. Comparing the 'pot-still' spirits among themselves, it will be observed that there are considerable variations in both the total amount and in each constituent of the secondary bodies. The Scotch whiskeys generally show a somewhat less total amount than the Irish, and the Speyside, Banffshire, and Highland samples have a rather smaller amount than the Islay and Campbeltown samples. The latter, as well as most of the Irish samples, are mainly 'blending' as distinguished from 'self' whiskeys.

The differences between new and old 'pot-still' whiskeys, so far as shown by analysis, are mainly in the increased amounts of the volatile acids and aldehydes, and to a less extent of the esters found in the old spirit when stored in wooden casks. The higher alcohols and furfural appear to remain very much the same. Any changes that occur in 'patent' spirit are of a similar kind.

'Pot-still' whiskey is almost always stored in cherry casks, or in other well-seasoned wooden casks that have formerly contained similar spirit. A large proportion of the increases in the secondary constituents which occur in spirit stored in such casks takes place in the first few months, and is due to a process of extraction of these products absorbed in the wood of the casks from former spirits. This

absorption is to some extent selective. The ethyl alcohol slowly diffuses through the wood of the cask and passes into the air, leaving some of the esters and higher alcohols behind in the wood, which thus becomes more or less charged with the secondary constituents, according to the length of time and other circumstances attending the storage of spirit in the warehouse.

Probably also, especially when the casks are empty, there is some production of acids, aldehydes, and esters by the slow oxidation of alcohols in the wood of the casks.

A comparison of the ordinary 'patent' spirits with British and foreign spirits of high strength which are not usually stored in wooden casks, but in metal drums or vats, shows that the latter spirits contain still less of the secondary constituents, and that the slight changes which occur in ordinary patent spirits do not take place in these high strength spirits. These spirits are used mainly for technical and industrial purposes, and are often of very great purity, although made from molasses, potatoes, and beetroot sugar residues, or other materials not employed for making spirits intended for consumption in this country.

Maturation or ageing.—In addition to the changes above referred to in the secondary constituents due to storing in casks, there are other changes due to the presence of substances not included in the ordinary analysis of spirits, but which have much to do with the difference in flavour of new and old whiskeys. Thorpe, for example, found indications of pyridine bases, allyl alcohol, and allyl aldehyde derived from the peat used as fuel in malting, and acrolein, due either to the fat in the wash extracted from the grain or possibly from the soap which is occasionally added to the contents of the still to prevent frothing. Schidrowitz found in new pot-still whiskey distinct evidence of the presence of pyrrole, phenolic bodies, an alkaline substance (probably an ammonium salt), sulphuretted hydrogen, sulphurous acid, and a trace of nitriles. All of these are readily changed on exposure to air and moisture, as in storage in casks. The pyrrole probably resinifies, the phenols interact with aldehydes, acids, and

alcohols, forming condensation products; the sulphuretted hydrogen and sulphurous acid would readily oxidise, and the nitriles (if present) rapidly condense or be transformed into acids. None of these substances was found in mature spirit.

Numerous processes have been suggested for the artificial ageing or maturing of whiskey. These are, for the most part, oxidation processes, as by treatment with charcoal, or (as in Carroll's process) by passing the spirit vapour mixed with air, and superheated to 300°F. through a pipe enclosed in a steam jacket also heated to 300°F. Hewitt's method, which is a de-aldehyding process, consists of the addition of phenylhydrazine-sulphonate of sodium or calcium to the low wines still, by which means the aldehydes, including furfural, are held back, and the amount of these passing into the distillate considerably reduced. The effect of all these processes is to remove the harsh flavour of new spirits and impart the softer character of mature whiskey, thus accelerating the time when the spirit becomes ready for consumption as a beverage, but without necessarily imparting to it the true characteristic flavour of whiskey which has been matured by long storage.

The changes in the secondary products due to storage of whiskey in wooden casks and bottles are shown by Thorpe in Appendix Q. ix., x., xi. The results show that there is a well-marked increase in each of the secondary constituents during the first six months' storage. After 9-12 months the higher alcohols and furfural remain practically constant, and the increases in the other constituents were very slow. After about 18 months the differences were within the limits of experimental error. Practically no change occurs in spirits stored in glass bottles.

Crampton and Tolman (J. Amer. Chem. Soc. 1908, 30, 98) examined the spirit stored in casks by sampling annually for a period of 8 years,

and found an increase in the higher alcohols due to the fact that the wood was less pervious to these than to ethyl alcohol and water. The other secondary constituents increased rapidly for 3 or 4 years, and then only very slowly. An increase of furfural was probably due to the charred wood of the interior of the casks. It was found also that water passed through the wood of the cask more rapidly than the ethyl alcohol, thus giving rise to an increase in strength. This is unusual and was no doubt due to the exceptionally warm and strongly ventilated place of storage.

American whiskey.—The United States Pharmacopœia prescribes the following requirements for whiskey. It should be at least 2 years old; its sp.gr. should lie between 0.930 and 0.970; its alcoholic content should be not less than 44 p.c., nor more than 55 p.c. by weight; its residue not more than 0.25 p.c.; the residue from 100 c.c., which should be neither sweet nor spicy, should dissolve in 10 c.c. of cold water, and this solution should be coloured only a pale green when treated with a drop of very dilute ferric chloride solution (a deeper colour would indicate more than traces of tannin). In evaporating the liquor on the water-bath for the residue, the last traces volatilised should have an agreeable odour free from harshness, indicative of the absence of fusel oil. Its reaction should be slightly acid, but not more than 1.2 c.c. of deci-normal alkali should be required to neutralise 100 c.c. of the liquor using phenolphthalein as indicator.

Rye whiskey is made in the United States and Canada from rye and malt only. *Bourbon whiskey* (so-called from Bourbon County, Kentucky, where it was originally made) is prepared from a mixture consisting of 50-60 p.c. maize, 10 p.c. malt, and the remainder rye.

The following table gives the results of analysis of Bourbon and rye whiskeys by Schudrowitz:—

Description	Total acid	Esters	Higher alcohols (A-M)	Aldehyde	Furfural	Total
Bourbon whiskey—5 years	126	99	197	11	2.2	435
" " mature	122	78	129	14	3.0	346
Rye whiskey—7 years	140	134	277	20	3.9	575
" " mature	160	141	268	18	3.4	590
" " "	135	125	187	21	3.9	472
" " "	82	71	150	13	3.6	320
" " 10 years	70	79	98	11	2.7	261
Average	119	104	172	15	3.2	428

Results of analyses of 188 samples of new and old Bourbon and rye whiskey examined in the laboratory of the United States Department of Agriculture (Wiley) are shown on next page.

Imitation whiskey is sometimes prepared from strong neutral or 'silent' spirit diluted to the proper strength and flavoured with certain essential oils or artificial fruit essences, as oil of wintergreen, cinnamic and pelargonic esters, and coloured with caramel. Prune juice is sometimes added to give 'body' to this mixture.

Fleischman quotes the following as a recipe for a low grade 'blended whiskey': spirits, 32 gallons; water, 16 gallons; caramel, 4 oz.; beading oil, 1 oz. 'Beading oil' (so-called from its use in producing an artificial bead on cheap liquors) is prepared by mixing 48 oz. of sweet oil of almonds with 8 oz. of commercial sulphuric acid, neutralising with ammonia, adding double the volume of proof spirit, and distilling the mixture (The Art of Blending and Compounding Liquors and Wines, New York, 1885).

Description	Total acid	Esters	Alde- hydes	Furfural	Higher alcohols (A-M)	Total
New rye whiskeys (19 samples)—						
Average	11.4	50.6	17.8	2.4	266.4	348.6
Maximum	28.2	132.8	86.0	5.2	378.4	
Minimum	2.6	8.8	0.0	0.0	187.0	
Old rye whiskeys (76 samples)—						
Average	147.6	137.0	27.6	4.6	352.0	661.8
Maximum	312.4	287.4	47.2	14.0	585.8	
Minimum	72.8	60.0	4.4	0.8	146.6	
New Bourbon whiskeys (18 samples)—						
Average	16.4	45.0	7.8	1.7	229.4	300.3
Maximum	39.2	112.8	36.2	12.8	343.4	
Minimum	3.6	1.8	0.0	trace	70.6	
Old Bourbon whiskeys (75 samples)—						
Average	137.6	103.6	19.4	3.8	287.2	551.6
Maximum	203.8	209.0	46.4	16.2	517.0	
Minimum	69.4	39.0	7.2	1.4	50.4	

Adulteration of whiskey.—Under Sect. 10 of the Licensing Act, 1921, whiskey (like brandy and rum) may not be sold below a strength of 35 p.c. under proof unless the fact of dilution is notified, and the great majority of prosecutions under the Act for the adulteration of whiskey are on account of dilution with water below the legal limit of strength. For the method of calculating the degree of dilution, see art. BRANDY.

Sometimes a neutral or 'silent' spirit made from substances other than grain (as potatoes, beet-sugar residues, &c.) is mixed with sufficient genuine whiskey to give it a more or less whiskey character, and such adulteration is best detected by expert tasting ('degustation') combined with a determination of the secondary constituents and a comparison of the relations which they bear to each other.

Amongst the various substances alleged to have been used for the grosser forms of adulteration may be mentioned creosote, fusel oil,

methylated spirit, sulphuric acid, and salt. Traces of copper, tin, and lead have been found as accidental impurities derived from the stills and other apparatus employed.

In consequence of representations made as to the deleterious character of the whiskey sold in public-houses in the poorer class districts of the larger towns in England, Scotland, and Ireland, and at fairs and markets, particularly in the west of Ireland, an investigation into the matter was made some years ago by the Excise Authorities. Nearly 100 samples were taken from all parts of the United Kingdom and analysed in the Government Laboratory, but, apart from the fact that most of these consisted mainly of plain patent-still spirit, no evidence of the presence of the deleterious adulterants above referred to could be found.

The results of analyses (showing the maxima, minima, and averages) are summarised in the following table (Thorpe):—

	Volatile acid	Alde- hydes	Esters	Higher alcohols	Furfural	Total
England (38 samples)—						
Maximum	25.1	22.5	127.9	310.5	1.9	370.7
Minimum	1.4	2.2	30.1	11.2	Nil	67.0
Average	7.3	9.0	52.2	95.8	0.7	165.0
Scotland (23 samples)—						
Maximum	18.0	23.8	85.7	179.6	1.6	260.6
Minimum	1.2	1.7	30.8	43.7	Nil	77.8
Average	6.1	10.5	47.2	88.2	0.5	152.5
Ireland (30 samples)—						
Maximum	54.0	37.2	71.5	649.2	4.2	767.3
Minimum	1.4	2.4	29.5	32.2	Nil	73.3
Average	8.2	11.1	47.8	232.0	1.2	300.3

There is no legal definition of 'whiskey' in the United Kingdom, but numerous suggestions were made by witnesses before the Select Committee on British and Foreign Spirits in 1890-1, and the Royal Commission on Whiskey and other Potable Spirits in 1908-9, differing

essentially in principle and depending chiefly upon the point of view of the witness.

The strictest definition suggested was that 'whiskey' should be manufactured in a pot still exclusively and from certain prescribed materials grown in the country, as malted barley alone in

the case of 'Scotch' whiskey, and malted barley with unmalted grain (barley, wheat, oats, or rye) in the case of 'Irish' whiskey.

Others would admit patent-still spirit, restricting, however, the materials to cereal grains (including maize), and the saccharifying agent to the diastase of malt, whilst in a few cases the extreme view was held that no restriction should be imposed either on the materials used or the process of distillation.

Since much of the barley used in both Scotland and Ireland is of foreign growth, the definition of Scotch and Irish whiskey cannot well exclude the use of foreign grain, and therefore maize (which came into use in 1846 immediately after the repeal of the Corn Laws) is not excluded in the manufacture of 'whiskey.'

With respect to the blending of patent-still spirit made from grain with pot-still spirit, it was held that since whiskey (consisting as it does of alcohol and water, with certain by-products derived from malt and grain) does not cease to be whiskey when diluted with water, so the addition of patent still spirit, also made from grain, does not remove the mixture out of the category of 'whiskey.'

After full consideration of all the evidence the Royal Commission of 1908-9 arrived at the following conclusions and definitions:—

(1) That the term 'whisky' having been recognised in the past as applicable to a potable spirit manufactured from (a) malt, or (b) malted and unmalted barley or other cereal, the application of the term 'whiskey' should not be denied to the product manufactured from such materials.

(2) That no restrictions should be placed upon the processes of, or apparatus used in, the distillation of any spirit to which the term 'whiskey' may be applied as a trade description.

(3) *Definition*—'Whiskey' is a spirit obtained by distillation from a mash of cereal grains saccharified by the diastase of malt, that 'Scotch whiskey' is whiskey, as above defined,

distilled in Scotland; and 'Irish whiskey' is whiskey, as above defined, distilled in Ireland.

J. C.

WHITE ANTIMONY. *Valentinite v. Arsenic.*

WHITE ARSENIC. *Arsenious oxide v. Arsenic.*

WHITE COPPERAS. *Native ferric sulphate or coquimbite $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.*

WHITE IRON PYRITES. *Ferric sulphide or marcasite FeS_2 , v. IRON.*

WHITE LEAD v. LEAD; also PAINTS and PIGMENTS.

WHITE LEAD ORE v. CERUSSITE

WHITE METAL v. TIN.

WHITE MUNDIC. *Mispickel v. ARSENIC.*

WHITE PRECIPITATE. *Mercuric ammonium chloride v. MERCURY.*

WHITE SAPPHIRE v. CORUNDUM.

WHITE VITRIOL. *Zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ v. ZINC.*

WHITING v. CHALK.

WILKITE A rare mineral consisting of tantalic and titanic acids, zirconia, silica, cerium, and yttrium earths, thorina, uranic oxide, ferrous oxide, &c., and of interest in containing scandium (Sc_2O_3 , 1.17 p.c.) in relatively large amount. It is a black, brown, or yellow, amorphous mineral resembling euveitite or yttriotantalite in appearance, and has been found, together with monazite, in a felspar quarry at Implaks, Lake Lagoda, Finland. It supplied the material for Crookes's work on scandium (Proc. Roy. Soc. 1908, A, 50, 516, Phil. Trans. 1908, A, 209, 15). Orthite from the same locality has also been found to contain 0.8-1.0 p.c. of scandia (R. J. Heyen, Sitz. Ber. Akad. Berlin, 1911, 379). More recently, a mineral containing scandium as an essential constituent has been described (v. THORNTONITE) L. J. S.

WILD RICE. A comparison between wild rice (*Zizania aquatica*) and cultivated rice gave the following analyses for wild rice:—

No.	Moisture. p.c.	Ash. p.c.	Protein. p.c.	Ether Extract. p.c.	Fibre. p.c.	Starch p.c.	Soluble carbohydrates as dextrose. p.c.
1	7.74	1.09	13.36	0.46	1.39	65.26	2.08
2	7.85	1.38	13.97	0.89	1.41	61.69	3.69
3	8.93	1.17	14.62	0.72	1.94	60.47	2.33
4	7.83	1.25	14.40	0.66	1.29	62.03	2.93

Although these results show a high proportion of proteins in wild rice, both these and the mineral salts present are of a variety unsuitable for dietetic purposes. There is just sufficient vitamin A to prevent xerophthalmia, but not enough to promote growth. Wild rice is somewhat superior to the cultivated variety as regards its content of vitamin B, but still is not an adequate food (C. Kennedy, J. Agric. Res. 1924, 27, 219; Analyst, 1924, 49, 342).

WILKITE v. THAUMASITE.

WILLEMITE. A mineral consisting of zinc orthosilicate Zn_2SiO_4 , crystallising in the rhombohedral system (with parallel-faced hemihedrism). It is abundant at Franklin Furnace,

and Sterling Hill in New Jersey, where it is mined, together with zincite and franklinite, as an ore of zinc (Zn 55.5 p.c.). Here it is usually massive, but a few clear prismatic crystals of a pale amber-yellow colour, and up to 6½ cm. in length, have been found. Some of these have been cut as gem stones. Portions of the better coloured or clearer massive material is also suitable for cutting as gems. The mineral has also been found at a few other localities, but only in sparing amounts. It varies considerably in colour, being yellowish, apple-green, flesh-red, &c.; the lustre is vitreous to resinous; sp. gr. 4.0-4.1; H. 5½. Troostite is a variety containing up to 10 p.c. of MnO replacing the zinc

oxide, and found as large rough crystals at Franklin Furnace. When struck with a hammer or when exposed to the emanations of a radium salt, the mineral displays a brilliant green phosphorescence. Crystals of willemite have been obtained artificially, and have also been observed in slags and in the muffles of zinc furnaces.

L. J. S.

WILLESSEN FABRICS AND PAPER v. CELLULOSE.

WILLOW BARKS v. TANNING.

WILLYAMITE v. ULLMANNITE.

WINE. Wine, strictly speaking, is the fermented juice of the fruit of *Vitis vinifera*. The term *British wines* is applied to beverages made after the manner of wine from substances other than the juice of fresh grapes.

The vine is cultivated for the manufacture of wine in the middle and south of Europe, the northern and southern extremities of Africa, some of the western parts of Asia, the islands of the Atlantic, portions of America—from the Potomac in the north to the centre of Mexico in the south—in California, and in Australia. The number of varieties is very large; but experience shows that the vines employed in particular districts should either be indigenous to those districts or be improved varieties of the indigenous strain. Thus, European vines when tried in America were but partially successful; whilst, on the other hand, American vines transplanted to the Gironde degenerated and yielded no potable wine. The vine grows on chalky, silicious, aluminous, and magnesian soil, best along the borders of rivers, and on ground which, though not itself soaked with water, can constantly attract it from the sub-soil.

Vintage and vinification.—The methods of procedure vary with the character of the wine—i.e. whether white or red wine is to be produced. The practice as regards the period of ripeness at which the grape is gathered varies considerably; thus, in the case of champagne, where the greatest attainable paleness is desired, the grapes are gathered before the point of fullest maturity, whereas the wines of Burgundy are vintaged when the grapes produce the deepest colour. Wines from imperfectly-ripened grapes require longer time to mature after manufacture, and, theoretically speaking, the grapes should hang until excessive dryness or danger of frost threatens; but other and conventional considerations, such as colour, have to be taken into account. In exceptional instances, as in the Sauterne district, those berries only are cut out of the bunch which have attained the desired point of ripeness; but the common practice is to gather all the grapes carried by the vines, the vintagers either separating immature and spoiled berries as they proceed, or carrying the whole bulk to a kind of specialist, who performs this part of the labour. Whichever course may be taken, the selected fruit is carried to the press house, and the question then arises whether the stalks are to be removed or pressed with the grapes. In the case of white wines the almost universal practice is to leave the grapes upon the stalks, for the reason that the resulting liquor is almost at once separated from the marc, and before the astringent principle of the stalks can be communicated to it, whereas red wines must be allowed to remain upon

the marc for some time, and the stalks are removed. The commonest mode of separation is to cause the grapes to pass through a series of sieves, by which the stalks are retained. The grapes are now crushed, either by being trodden underfoot in vats or by being passed through machines furnished with grooved rollers, the one thing to be avoided in either case being the bruising of the seeds and stalks if these have not been removed. The next process is pressing. The machines employed for this purpose were formerly boxes, so made that the must was expelled through apertures by superincumbent pressure exerted by a screw; but latterly centrifugal machines have been employed, with a saving of labour and time. In white wines the must is separated as much as possible from the marc before pressing; whilst in the preparation of champagne the grapes are not crushed at all previous to being placed in the press. In pressing grapes for the manufacture of champagne the pressure is so regulated that the juice is separated into four fractions; generally, 4000 kg. of grapes yield a first fraction (cuvée) of 20 hectolitres of juice, second and third fractions of 3 hl. each, and a fourth fraction of 2 hl. The first fraction is the most valuable and yields a wine containing a relatively higher quantity of total acids and free acids (tartaric and malic acids); the presence of these acids increases the resistance of the wine to 'sickness' and to the action of bacteria. The keeping qualities of the wine are also due to the fact that only very small quantities of nitrogenous substances, phosphates, and potassium salts are present. The other fractions of the juice are less valuable, and the wines prepared from them are more readily attacked by micro-organisms (E. Manceau, *Ann. Falsif.* 1923, 16, 517; *J. Soc. Chem. Ind.* 1924, 43, B. 227). According to L. Mathieu (*Chimie et Industrie*, 1923, 10, 847), white wines are liable to the same causes of turbidity as red wines, but the effect is more marked, as a slight haze, imperceptible in a coloured wine, completely destroys the limpidity of the colourless wine. The author classifies turbidity—under which heading he includes all degrees of haze, from the pale bluish fluorescence due to the most minute particles, to actual cloudiness with visible particles—under two headings: (1) normal, i.e. arising in the actual constitution of the wine, such as bacterial infection, cloudiness caused by chilling or heating, or by oxidation of resinous substances or the mutual interaction of the constituents of the wine, and (2) accidental, i.e. caused by some irregularity or oversight in the manufacture or manipulation. As in the case of other wines, one of the most fruitful causes of trouble is the presence of iron in more than insignificant traces. This may arise from the use of unprotected iron vessels. The rigid exclusion of iron vessels, unless the metal be protected in some way from the attack of the acids of the fruit, is essential (*J. Inst. Brewing Abstr.* 1924, 30, 234). In the case of red wines the colour is obtained by allowing the juice from the crushing to ferment, after which it is stirred with the grape husks, whereby the requisite amount of colouring matter is dissolved. So much of the must as can be drawn off by this is run off by that means, and the marc is pressed

the two portions of the must are then added together. The proportion of must depends upon whether the stalks are removed or not; in the former case it is about 95-97 p.c. of the whole, in the latter it may only be 70 p.c.

The following is a summary of analyses by König of a large number of musts of different origin:—

	Specific gravity	Water	Nitrogenous p.c. matter	Sugar	Acid	Other non-nitrogenous matter	Ash
Minimum	1.0690	51.53	0.11	12.80	0.20	1.03	0.20
Maximum	1.2075	82.10	0.57	35.45	1.18	11.62	0.63
Average	1.1024	74.49	0.28	19.71	0.64	4.48	0.40

Fermentation.—The natural fermentation of grape juice is due to the action of various yeasts (*Saccharomyces Ellipsoideus*, *S. Pastorianus*, *S. Marzianus*, &c.) existing on the skin of the grape, and to 'Zymæe' and other enzymes present in the juice. Sergeant and Rougebief (Compt. rend. 1924, 178, 732; J. Soc. Chem. Ind. 1924, 43, B. 207) have drawn attention to the dissemination of grape yeasts by insects. They concluded from their experiments that certain insects, particularly *Drosophyla*, play an important part in spreading the yeast. White wines are generally fermented at a temperature of 10° or 12° in barrels with only the bunghole open for the escape of carbon dioxide. Red wines are generally fermented in vats open at the top, on account of the bulk caused by the retention of the husks and the necessity of stirring, an operation variously performed during or at the completed period of fermentation, according to the district. The higher the temperature the sooner the fermentation is finished; at low temperatures a moderate fermentation takes place, which becomes more violent as the liquid becomes warmer, and reaches a maximum at 27°. By the employment of high temperatures a must rich in sugar can be converted into a wine feebly alcoholic, sweet, and yet having tasting properties. Medium musts are best fermented at from 20° to 24°, and this temperature is reached when the fermentation begins at 15°. When fermentation is completed—i.e. after 10 to 14 days—the liquor has become clear, the yeast cells and other suspended matters are deposited at the bottom of the vessel, and the 'young' wine is racked off and allowed to rest for some weeks.

The young wine slowly loses its sugar by after-fermentation, and albuminous substances, colouring matters, together with the acid potassium tartrate, and calcium tartrate, separate out, forming a crust known as *argol* or *argal* (q.v.; also TARTARIC ACID). It is then racked again into clean casks (which are often 'sulphured' before use), fined, if necessary, with isinglass or white of egg, and occasionally with dried blood or with potassium ferrocyanide. When clear it is racked again and sometimes pasteurised before being bottled or stored in casks to mature.

Influence of the 'marc' on wine.—By allowing the skins and stones of ripe grapes to remain in contact with the must, the resulting wine is said to improve in bouquet, &c., and is less liable to become stale and ropy. In order to redden wine with the skins of black grapes the temperature of the wine should be between 15° and 17°. Bad grapes impart to white and red wines a brown colour. Such wines soon become

turbid. Bad grapes and mildewed skins, as well as bad casks and puncheons, precipitate the red colouring matter, so that the wine becomes pale. The following are some of the cases in which the treatment of wine with 'marc' has been successful: Wine which is muddy and cannot be clarified by the ordinary fining agents; wine in which a fining agent has been used which failed to sink to the bottom; wine which has become weak and flat; wine which is assuming or has assumed a black colour; wine having a barrel taste or a by-taste; wine which is 'corked'; wine remaining after casking off; and wine which is obtained by pressing the lees. In cases where the fermentation of new wine has been checked suddenly, the addition of marc prevents the separation of yeast (J. Nessler, Chem. Zentr. 1882, 265; Chem. Soc. Abstr. 1882, 1014). Wines from pressed marc have a greater content of extract, tannin, ash, total and ammoniacal nitrogen, phosphoric acid, sulphate, and chloride than wines from the vat (Hugues, Ann. Falsif. 1925, 18, 347; J. Soc. Chem. Ind. 1925, 44, B. 936).

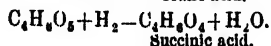
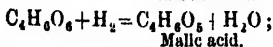
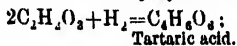
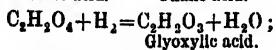
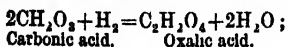
Composition.—Wine contains alcohols, glycerol, acids, salts, extractive matter, and those principles which give to it its particular colour, special flavour, smell, or bloom (*bouquet*, *Blume*). Whilst some of the constituents can be accurately isolated and described, others can only be detected by the smell.

The principal alcohol is ethyl alcohol. In rare instances some butyl alcohol, and in others amyl alcohol, together with ethylene glycol and isobutyl glycol (Henninger) are present. The quantity of alcohol in natural wines from grapes varies from 6 to 12 p.c. by weight, or from 13 to 26 p.c. proof spirit, but these limits are extended in exceptional cases. The quantity of glycerol is usually from 7 to 14 p.c. of the alcohol present.

The principal acids present are tartaric, malic, and tannic acids, due to the original grape juice, and carbonic, formic, acetic, and succinic acids as products of fermentation. These greatly aid in the preservation of the wine by preventing the formation of fungi. Traces of propionic, butyric, and cœnanthic acids also occur in wine, together with acetaldehyde and possibly some of its homologues. Salicylic and boric acids have also been found as natural constituents of wine. As regards the origin of the fixed vegetable acids of wine, H. Brunner points out (Chem. Zentr. 1877, 4) that malic, succinic, glycollic, and oxalic acids—which are found in unripe grapes, together with tartaric acid—may either be formed by direct building up of the molecules in the plant, or their formation may be partly direct and partly indirect.

Tartaric acid occurs mainly as the dextro-variety; lævo-tartaric acid is only of comparatively infrequent occurrence. If tartaric acid is not found—as, for example, in certain samples of sherry—its absence is probably due to its removal by 'plastering,' to which reference is made later on. The amount of free acid in sound wine, reckoned as tartaric acid, varies between 0.3 and 0.7 p.c. (inclusive of volatile acid, which should not exceed 0.15 p.c.); a greater amount than this imparts sourness to the wine.

It can be demonstrated in the laboratory that the first reduction products of carbonic acid are formic and oxalic acids, and that, from the latter, we can (by the action of hydrogen) pass successively through glyoxylic, tartaric, and malic, to succinic acid, and all these acids have been found in the grape in its various stages of growth. The principal reactions may be represented as follows:—



The characteristic smell of wine is said to be due to enanthine and other esters. These esters probably confer the bouquets which distinguish one vintage from another. Among them are acetopropyl, butyl, amyl, capryl, butyro-ethyl, caprylo-ethyl, capro-ethyl, and pelargo-ethyl, and the tartaric esters.

According to Jacquemin (Compt. rend. 110, 1140), the characteristic bouquets of wines are due to the special characters of the yeast used in each district. One and the same must fermented with the yeast obtained from several different districts gave wines having the bouquet characteristic of the district from which the particular yeast had come.

Babo states that the bouquet of the wine from Riesling grapes is produced by the action of frost; wines from other grapes also possess a like bouquet if the grapes are frozen. Rommer (Bull. Soc. chim. [iii.] 2, 297) fermented the juice of an inferior grape and of hot-house grapes respectively with yeast cultures obtained from the Champagne, Côte d'Or, and Baxy districts, and found that in each case the wines had the bouquet of those from which the yeast has been derived. Certain of the odoriferous principles are no doubt in the nature of essential oils, which have not hitherto been isolated owing to their small amount and extremely unstable character under the influence of heat and air. In order to retain the bouquet, wines should be bottled as soon as they have attained their maximum bouquet.

According to Berthelot, the amount of the esters in wine is, after a certain time, a constant quantity independent of the nature of the alcohols and acids, but a function only of their relative amount: If A be the percentage weight of alcohol in the mixture, a the amount of alcohol equivalent to the total free acid contained in one litre of wine, on the assumption that it is acetic acid (46 alcohol = 60 acetic acid), y the proportion p.c. of a present as ester in one litre of wine when the alcoholic strength of the wine is A , and x be the amount of alcohol present in the compound esters of one litre of wine; then

$$y = 1.17A + 2.8$$

$$x = \frac{y \times a}{100}$$

The alcohols other than ethyl alcohol present

are left out of the account, but as they are insignificant in amount the error is trifling. This formula affords a mode of judging of the age and genuineness of wines, except in the case of very young wines, or wines which have been recently fortified, the esters in these cases being less than that required by the formula. The maximum esterification is reached in from 4 to 6 years. The alcohol obtained by the decomposition of all the esters rarely exceeds 0.06 p.c. of the wine. (For Thudichum and Dupré's method, v. their Treatise on Wine, 203.)

Sugar in wine.—The sugars occurring in must and in wine are dextrose and levulose. Cane sugar is never naturally present in must, but it is sometimes added, as in the case of champagne, but even then it is rapidly transformed into invert sugar. Glycerol is formed as a by-product of the growth of yeast during the process of fermentation, and is accompanied (amongst other changes) by the decomposition of sugar. For every 100 parts of sugar which disappear, from 3 to 4 parts of glycerol are produced. After complete fermentation the sugar seldom reaches 0.5 p.c., but when fermentation is arrested by the addition of alcohol, as in the liqueur wines of France and Spain made from dried grapes, and the sweet wines of Hungary, the sugar may be as much as 20 p.c. or more. In some wines—as e.g. Sauternes and sweet Rhine wines—sugar occurs in the form of inositol.

The colouring matters in wine are due to two sources. In white wines—which range from an almost colourless liquid, as champagne, to the deep yellow sherry—the colour is derived from the oxidation of the so-called extractives contained in the juice, which, as was before explained, is separated from the husks as quickly as possible. The grapes of some of the best red wines yield an almost colourless juice if pressed before fermentation, and it is only by the joint action of alcohol and acid upon the husks, stalks, and seeds during fermentation, that the red colour is extracted from the marc. Mulder separated the colouring matter contained in red wines by means of lead acetate, and found it to consist of a substance which was bluish-black in colour and amorphous in structure. It is only sparingly soluble in alcohol, insoluble in water, ether, chloroform, carbon disulphide, oil of turpentine, oil of olives; but soluble in solution of tartaric acid or cream of tartar, and in alcohol containing a trace of acetic acid, the saturated solution showing a blue colour; more acetic acid turns the solution red. It is soluble also in alcohol containing tartaric acid, exhibiting a red colour, but neither of these acids renders it soluble in ether or chloroform. The colour of wine, consequently, depends both upon the amount of colouring matter and the amount of free acid contained in it, as the violet colour becomes redder in proportion to the quantity of free acid acting upon the blue colouring matter.

The colouring matter precipitated by hydrochloric acid—in which it is deposited slowly at the ordinary temperature, but more rapidly on boiling—has been examined by Terrell (Bull. Soc. chim. [ii.] 44, 2). The precipitate always contains a substance resembling ulmic acid, from which the colouring principle may be dissolved

out by alcohol. Thus obtained it forms brittle varnish-like scales, insoluble in water and ether, but readily soluble in alcohol, forming a brownish-red solution with a slightly yellow tinge. Acids change this colour to an intense red, while alkalis give a green coloration, which changes rapidly to a brownish-yellow on exposure to the air (cf. O. Griessmayer, *Dingl. poly. J.* 123, 531; *Chem. Soc. Trans.* 1887, 368).

The generally held view that the browning of wines is due to unsound grapes is not correct. The presence of stalks in the fermenting mash contributes appreciably to browning. Very acid wines are particularly prone to browning. The browning is most probably due to the oxidation of tannin-like substances of phenolic character by the action of oxidases or by auto-oxidation, or probably by both processes. It can be prevented, at least to a considerable extent, by immediately pressing the grape mash, but this course is not always possible in practice (H. Müller-Thurgau, A. Osterwalder, and H. Haller, *Landw. Jahrb. Schweiz*, 1923, 37, 215; *Chem. Zentr.* 1923, 74, [iv.] 1010; *J. Soc. Chem. Ind.* 1924, 43, 109).

The browning of wines, which is not only accompanied by a discoloration, but also with a strong turbidity and an unpleasant flavour, can be arrested by the use of sulphur dioxide in the form of potassium metabisulphate, which is added to the juice in the cask before fermentation. The yeasts can withstand without risk quantities of sulphur dioxide towards which *Bacterium gracile*, which effects the decomposition of malic acid at the close of the fermentation, is sensitive. The inhibition of the decomposition of the acid, whether it be temporary or complete, is mainly dependent on the quantity of free sulphur dioxide. Further, the duration of time during which the sulphur dioxide remains in the free condition must be borne in mind, as combination proceeds at different rates with different juices, and therefore the action of the same quantity of sulphur dioxide is not always identical. The commencement of the decomposition of the acid is, moreover, influenced not only by the number of acid-decomposing bacteria present, but also by the nature of the juice and its chemical composition, e.g. the content of tartaric acid. From very extensive experiments it was found that the addition of 2-4 grms. of $K_2S_2O_5$ to a hectolitre did not in any case hinder the decomposition of the acid. With 5-6 grms. inhibition was produced with juices rich in tartaric acid, and by the addition of 7.5-8 grms. of $K_2S_2O_5$ to different juices a slight retardation was observed. Quantities of 10-14 grms. of $K_2S_2O_5$ per hectolitre, corresponding with an initial content of free sulphur dioxide of 28 mg. and more per litre, produced complete inhibition of the decomposition of the acid (H. Müller-Thurgau, A. Osterwalder, and H. Haller, *Landw. Jahrb. Schweiz*, 1923, 37, 241; *J. Soc. Chem. Ind.* 1924, 43, B. 109).

The colouring matter of red wines may be estimated with sufficient accuracy for technical purposes by the method of Cari Mantrand (*Bull. Soc. chim.* 1906, [iii.] 35, 1017), by precipitating with lead acetate, decomposing the precipitate with sulphuric acid, filtering, and weighing the residue from an evaporated portion of the

filtrate. The extracted colouring matter may be concentrated and preserved in glycerol for use in confectionery, &c. The maximum amount found was 17.2 grms. per litre in Algerian wine.

According to Willstätter and Zollinger (*Annalen*, 1915, 408, 83; 1916, 412, 195) the colouring matters of wine, viz. *oenidin* and *œnin*, are derivatives of delphinidin. *œninidin*, which has been isolated from the black Italian grape, is the dimethyl ether of delphinidin, and *œnin* is the monoglucoside of *œninidin*.

The pigments present in two varieties of American grapes, namely, Norton (*Vitis æstivalis*, *V. labrusca*) and Concord (*V. labrusca*), have been examined by the methods of Willstätter and Zollinger (*Annalen*, 1915, i, 295; 1917, i, 47). The same anthocyanin chloride, $C_{28}H_{30}O_{11}Cl_3H_2O$, has been isolated from both varieties. On hydrolysis, it yields dextrose and an anthocyanidin chloride, $C_{17}H_{18}O_7Cl_3H_2O$. The substances are identical in composition with the *œnin* and *œninidin* chlorides obtained by Willstätter and Zollinger from European grapes (*V. vinifera*), but they differ from these substances in that the anthocyanidin contains only one methoxyl group, whereas *œninidin* contains two. The colour reactions are, moreover, different. The anthocyanin gives with ferric chloride in aqueous solution a purple colour which quickly fades to light brown, and in alcoholic solution an intense blue which changes to purple and finally to wine-red; the anthocyanidin gives with the same reagent both in aqueous and alcoholic solution a momentary purple colour fading to an almost colourless or faintly yellow solution. Evidence of the presence of a diglucoside has also been obtained (R. J. Anderson, *Bio-Chem. J.* 1923, 57, 795; *J. Chem. Soc.* 1924, 126, i, 251).

Some additional colour is imparted to white wine by the tannin extracted from the oak casks during maturing. On the other hand, the natural colouring matter of red wine is reduced by the operation of fining as well as on ageing.

Caramel is frequently used to colour white wines (e.g. brown sherry), and occasionally boiled must is added either to the juice before fermentation or to the finished wine. (For foreign colouring matters, see below.)

Tannin is derived from the grape skins and stalks, the juice itself being practically free. It is sometimes added, however, to champagne and other white wines to prevent 'scuddiness' or turbidity. The natural tannin of grapes is decomposed by acids or by fermentation into glucose and an acid which is not gallic acid.

The *albuminous substances* in the grape, which set up the ferment, ought by that action to be removed in the yeast when the fermentation is properly carried out, and should not exceed 4 parts per 1000 of wine, unless the latter has been 'fined.' The albuminous matter is also reduced by 'plastering,' and in old wines it is thrown out together with tannin and colouring matter. In imperfectly fermented wines a certain amount remains, and, in the case of white wines, may again render them liable to fresh fermentation. In red wines this danger is obviated by the presence of the tannin of the

husks, which preserves the albuminous matter from change.

The small quantity of ammonia which is present in grape juice, or is formed during fermentation out of albuminous substances, is, for the most part, precipitated during fermentation as magnesium-ammonium phosphate; a small amount, however, remains, and in some wines is accompanied by minute traces of trimethylamine.

Under the term 'extractives,' some chemists include all matters other than water, alcohol, and volatile acids; others only those substances which are not volatile up to 100° or 110°. The latter would, however, exclude glycerol, which is properly included amongst the extractives. The composition of certain constituents of the extract which contribute to the smell and taste of the wine is still very obscure. The extractives are, of course, abnormally increased by plastering and addition of sugar (*v. infra*).

The mineral constituents of wine, as found in the ash, are potash, soda, and lime as phosphates, chlorides, carbonates, and sulphates, traces of iron, magnesia, and silica, and occasionally alumina, lithia, and manganese. In pure natural wines the ash rarely exceeds 0.3 p.c., but may be much higher in wines which have been plastered, or to which alkalis have been added to reduce their acidity.

As regards the amount of alcohol, a very comprehensive set of tables, embracing the results of the examination of 133 wines, is given by Thudichum and Dupré (Treatise on the Origin, Nature, and Varieties of Wine, 128-304), from which the following résumé is compiled:—

	Strength of wines in degree of proof spirit
German wines, 35 samples	16.2-26.3
French wines, 22 samples	18.0-36.2
Spanish wines, 22 samples	26.7-47.7
Sicilian wines, 6 samples	35.5-31.3
Portuguese wines, 14 samples	21.9-46.5
Hungarian wines, 10 samples	19.2-22.4
Greek wines, 8 samples	17.8-36.1
Cape wines, 7 samples	36.1-52.7
Atlantic Islands, 3 samples	38.2-31.1
Elbe wines, 1 sample	34.99
Australian wines, 5 samples	23.5-40.1

Sugar solution wines.—Musts which are too thin, and deficient in sugar, are sometimes concentrated by evaporation (as in Portugal) or, more frequently, a solution of sugar is added. The latter process was first sanctioned by the French minister, Chaptal, and is known as 'Chaptalising.' A similar process (applied chiefly to acid musts), and known as 'Gallising,' from its inventor Gall, is also practised in Germany. The must of bad years, which contains a deficiency of sugar and an excess of acid, is mixed with sugar, preferably cane sugar, so as to bring the amount of sugar in the liquid to about 20 p.c., and to reduce the amount of acid to about 2 p.c. Frequently, however, commercial glucose is used, and its addition can frequently be detected in the finished product by its dextrorotatory polarisation (*cf.* Fresenius and Grünhut, *Zeitsch. anal. Chem.* 1921, 60, 188).

The acidity of natural wine can also be

reduced, as suggested by Liebig, by the addition of neutral potassium tartrate, which throws down the free acid, if present as tartaric acid, as acid potassium tartrate. Wine deficient in alcohol and containing much acid may often be improved by adding to it the pressed residue of a succeeding vintage (*cf.* J. Nessler, *Bied. Zentr.* 1884).

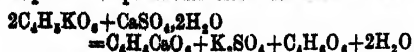
A considerable quantity of wine is now made by covering the marc with an aqueous solution of sugar, and allowing the mixture to ferment. The sugar solution contains 18 grms. per litre for every degree of alcohol which it is desired to obtain, and 250 grms. of marc are used for each litre of solution. Analyses of wines prepared in this way by Girard, and of other samples found in commerce, prove that these wines have an approximately definite composition. When they contain from 9 to 10 degrees of alcohol, the proportion of soluble matter, cream of tartar, tannin, and colouring matter is much less than in the ordinary vintage wines. The amount of solid matter varies from 14 to 18 grms. per litre; the amount of cream of tartar is about 2 grms., but not less than 1.6 gm. per litre; whilst the proportion of tannin and colouring matter varies considerably with the nature of the marc. Girard concludes that those wines constitute a highly useful beverage, and can be produced at a very low cost (*A. Girard, Compt. rend.* 95, 227; *Chem. Soc. Abstr.* 1882, 1335).

Plastering of wine.—The practice of adding gypsum or plaster of Paris to must, either before or after fermentation, which prevails in Spain, Portugal, and the South of France, is said to have for its object the reduction of the amount of the water in the juice, and the production, consequently, of a must relatively richer in sugar. The fermentation is much more rapid and complete, and it is alleged that the wine keeps longer when it has been plastered, and that the colour is richer and more lasting. This explanation leaves something to be desired, because the sacrifice of other constituents of juice than water due to absorption by plaster is entirely out of proportion to any gain by the absorption of the water, and the result desired could be attained either by the addition of sugar or the evaporation or freezing out of water. It is probable that the reason for the practice, although unknown to those who employ it, is that gypsum precipitates some albuminous matters which injuriously effect the wine. An obvious advantage to the wine-maker is that it clarifies the wine rapidly and so enables it to be brought sooner to market.

The plaster of Paris, in the form of powder, is either thrown upon the grapes before they are crushed, or added to the must after fermentation has commenced, or even to the finished wine, and the chemical changes that take place vary accordingly. The quantity used is generally from 1 to 2 kilos. to every 100 kilos. of fruit, although sometimes it reaches as much as 10 kilos.

According to Griessmayer, when gypsum is added to the must, it forms, with the tartar present, neutral calcium sulphate and free tartaric acid, which latter reacts on the sulphate, forming bitartrate and acid calcium sulphate. According to Borntraeger (*Annali. Chim. Applic.*

1919, 12, 1), the reaction between calcium sulphate and potassium bitartrate is as follows:



It was shown by Bussy and Baignet that the system ($\text{K}_2\text{SO}_4 + \text{C}_4\text{H}_5\text{O}_6$) is converted into $\text{KHSO}_4 + \text{C}_4\text{H}_5\text{KO}_6$. The ash of such wine is neutral, and does not give off carbon dioxide when treated with hydrochloric acid. When gypsum is added to the finished wine, the alcohol prevents its solution, but it carries down many impurities. Kayser (Bied. Zentr. 1881, 632) made experiments which confirmed these conclusions, and states that from the proportions of the ash to the extractive matter, it is possible to declare with certainty whether the wine has been plastered as must or as finished wine; in the first case the ash is disproportionately high, in the other it remains normal. Kayser also states that by the interaction of KHSO_4 and KH_2PO_4 , free phosphoric acid is formed together with neutral potassium sulphate, the former producing the bright colour of plastered red wines. The main change, however, appears to be a decrease in the tartrates and an increase in the proportion of potash and sulphates.

The injurious effects attributed to plastered wines have been the subject of investigation by several commissions appointed by various foreign governments. The most exhaustive inquiry yet made on the hygienic aspect of the subject was by a commission appointed by the French War Department owing to complaints made by the French army in Algeria, where many cases of illness were said to be due to the use of plastered wines. The symptoms are said to be colic, and slight vomiting. The acid potassium tartrate acts towards many reagents in the same manner as free sulphuric acid, and when introduced into the system may have the effect of reducing the alkalinity of the blood.

In view of the inconclusive nature of the evidence, the Commission recommended the maintenance of the regulation forbidding the sale of wines containing more sulphate than that corresponding with 2 grms. of potassium sulphate in the litre, and this limit has been also adopted in Germany, Switzerland, and other countries.

The attempts to 'de-plaster' wine are, from a hygienic point of view, more injurious than the plastering, owing to the use of poisonous barium and strontium salts.

Wine is liable to be affected by a number of injurious ferments, and is especially subject to acetous fermentation, due to *Mycoderma aceti*, which principally attacks the alcohol with production of acetic acid, whilst *Mycoderma vini* attacks principally the cream of tartar and extractive matters. The action of foreign ferments may frequently be prevented by the process devised by Pasteur, which consists in heating the wine for some time to about 70° in absence of air. The bouquet, and in some cases the colour, is thus found to be improved. The heating must be quickly performed, and, as far as possible, out of contact with air.

Numerous substances are employed for the preservation of wine by chemical means as *abrotol* or *asaprol* (the calcium salt of β -naphthol sulphonic acid), benzoic, boric, and cinnamic

acids, fluorides, formaldehyde, saccharin, salicylic acid, sulphurous acid, and sulphites. It should be noted that of these, boric acid, fluorine, and salicylic acid may be present in minute quantities as natural constituents of the wine (*v. infra*).

Sulphuring is carried out either by burning sulphur, sometimes placed on strips of paper, linen, jute, asbestos, &c., in the casks, or by addition to the wine of sulphurous acid or one of its salts. For small works the use of aqueous sulphurous acid or potassium metabisulphite, $\text{K}_2\text{S}_2\text{O}_5$, is most convenient, and in large works that of liquid sulphur dioxide. The colouring matter of red wine is at first bleached by sulphur dioxide, but with proper sulphuring the wine later assumes a more vivid red colour than the non-sulphured wine. In the wine the sulphur dioxide is converted partly into sulphuric acid and into compounds with acetaldehyde and dextrose, the rest remaining in the free state—sulphites are blood- and stomach-poisons, but they are readily and rapidly changed in the human body. Most German wines contain less than 200 mg. of total or 50 mg. of free sulphur dioxide per litre, but with choice wines, which require repeated sulphuring to bring their slow fermentation to a close, as much as 546 mg. per litre has been found; similar results are obtained with sweet sauternes (Journ. Soc. Chem. Ind. 1923, 285 A.). According to Dubaqué, the clouding of white wines after keeping in glass bottles may be due to the action of sulphur dioxide in the wine upon iron silicates of the glass (Ann. Falsif. 1925, 18, 418; J. Soc. Chem. Ind. 1925, 44, B. 821).

The essential oil of black mustard seed (b.p. 150-7°C.) is soluble in alcohol and ether, but in water only to the extent of 1.16 grms. per litre at 15°C. Its antiseptic power, when used in wines, is such that 1 c.c. of a 1 p.c. solution added to 1 litre of wine is efficient, but the amount required varies with certain factors, such as the amounts of sugar and sulphurous acid in the wine, the quantity and vitality of any yeasts present, and the temperature. The souring of red wines, which generally contain no sugar, can be stopped by the addition of 0.8 c.c. of the 1 p.c. solution above mentioned. Essential oil of mustard is about 200 times as active as sulphurous acid and does not affect the odour or flavour of the treated wines. It does not volatilise from the wine, and therefore does not require to be renewed. It has no action on the colouring matters of red wines, fruit juices, caramel, etc. It is estimated by heating 5 c.c. of the preservative on a water bath for 1 hour, with 10 c.c. of ammonia solution and 55 c.c. 0.1N silver nitrate solution in a graduated 100 c.c. flask connected with a reflux condenser. The solution is cooled, diluted to the mark, filtered from the precipitate, and the silver estimated volumetrically in 50 c.c. of the filtrate (P. Malvezin and G. Bidart, Ann. Falsif. 1923, 181, 534; Analyst, 1924, 49, 140; cf. Moreau and Vinet, Ann. Falsif. 1924, 17, 477; J. Soc. Chem. Ind. 1925, 44, B. 49).

Manufacture of 'sparkling' wines.—The effervescence of a sparkling wine is due to the presence of carbonic acid, produced by the fermentation of added sugar. The chief wines of this class (champagne) are produced in the departments of Marne and Haute-Marne, and in

the vicinity of the Moselle and the Rhine. Both white and red grapes are used, and the wine is amber in colour, the depth of tint depending on the vintage and the proportion of dark grapes employed. The vintage is in the early part of October, and in the pressing the must is separated into two portions, that first produced being of the higher quality. The young wine is allowed to ferment until the winter, when it is racked, and after the expiration of a month the operation is repeated, when the wine is fined. It is then mixed with a certain proportion of old wine, and the amount of sugar present determined. If necessary, a quantity of cane sugar is added, and the wine is bottled, the bottles being placed horizontally in piles and left at rest throughout the summer. Carbonic acid is formed, together with a quantity of sediment. The pressure of the gas in the bottles can readily be ascertained, when desired, by means of a manometer (such as Salleron's modification of Maumené's 'Aphrometre'), and ranges from 5 atmospheres in *grand mousseux* to less than $4\frac{1}{2}$ in *crémant* wine; in ordinary *mousseux* wine the pressure varies between 4 and $4\frac{1}{2}$ atmospheres. When required for the market, the bottles are first carefully brought into an inclined position, so as to cause the sedimentary matter to fall gradually on to the cork; on removing the clip which holds the cork within the neck the pressure of the dissolved gas forces out the cork, together with the sediment. A certain amount (from 1 to 4 p.c., depending upon the sweetness desired) of liqueur, made of fine wine, sugar, and cognac or a still spirit, is quickly added, and the bottles are again filled up, corked, and wired.

Dry champagnes—i.e. containing relatively little sugar—are mainly exported to this country, the sweeter varieties being usually consumed in America and on the Continent.

Wines of France. The pre-eminence of France as a wine-producing country is due mainly to its favourable conditions in regard to both climate and soil, and, no doubt, also to the system of small holdings worked by the thrifty and industrious French peasantry. The chief wine-growing district in France is the Gironde, which is practically divided into five portions, viz., the Médoc, the Graves, the Côtes, the Palus, and the Entre-deux-Mers. To these must now be added the wines from the Alsace-Lorraine territory restored to France by the Treaty of Versailles. Although formerly retained almost exclusively for home consumption, they are now (1926) obtainable on the British market. In the Médoc some six or seven different varieties of vine are cultivated.

Most of the *red wine* is obtained from the Carbenet Sauvignon, Franc Carbenet, Malbec, and Merlot grapes. The vintage usually begins towards the end of September, and lasts about a fortnight. The wines (usually known as 'clarats') are divided into *payaan*, *artisan*, *bourgeois*, and *fine growths*, the last group being further sub-divided into what are known as 'crus' or 'classed growths,' named after the place (Château or Commune) where they are produced; e.g. *Château Latour*, *Pauillac*; *Château Lagrange*, *St. Julien*; *Château Margaux*; *Château Cantenac*, &c. The official classification into 'crus' or 'growths' was made so long ago as 1855 by the *Chambre Syndicale des Courtiers*,

since when it has not been found necessary to make any alteration. (*Vide* 'Bordeaux et ses Vins,' by Feret, Bordeaux, and *Encyclopædia Britannica*; art. 'WINE.')

The chief *white wine* producing district is to the south of Bordeaux. The principal vines are the Semillon, Sauvignon, and Muscatelle. The vintage is much later than in the Médoc—viz. in the last weeks of October or early part of November, when the grapes have entirely ripened. Three qualities of must are produced: the first and ripest juice yields a sweet luscious wine (*vin de tôle*), mainly consumed in Russia; the second forms *vin de milieu*, the wine usually known as *Sauterne*; the third quality, or *queue*, yields a dry white wine. The principal varieties are *Barsac*, *Sauterne*, *Graves*, and *Bommes*, *Château Latour-blanche*, and *Château Yquem*, which is generally considered to be the premier white wine of France, if not of the world, and in the classification of Sauternes it takes precedence of the 'First Growth,' being placed in a class by itself.

The department of the Pyrénées Orientales produces a considerable quantity of wine, mostly from the Grenache noir and Carignane grapes. The generic name of the wine of the district is *Roussillon*, of which the most esteemed varieties are muscat of *Rivesaltes*, *Maccabeo*, *Mulvoisie*, and *Grenache*, which are liqueur wines (the last-mentioned being simply unfermented must preserved by means of added spirit and sulphurous acid, with frequent racking from deposits); and *Rancios*, dry *Mulvoisie*, and *Picfoule*. Languedoc also produces a large quantity of wine (*vins du Midi*), much of which is mixed with the wines of the Gironde and of Burgundy: whilst a considerable amount of the rest is distilled to make 'trois-six' and *eau de vie*. Cognac is produced from the wines of the Charente district (*v. BRANDY*).

The Rhône and Saône valleys produce the chief wines of the east of France, which, with the exception of *Hermitage* and the wines of the *Beaujolais*, seldom occur in trade under their own names.

The best qualities of *champagne* (*v. supra*, *Sparkling wines*) are produced in the departments of Marne and Haute-Marne, the chief centres of the trade being at Rheims, Épernay, Ay, Avize, Châlons, and Dizy. The most famous brands are *Ayala*, *Bollinger*, *Cliquot*, *Heidsieck*, *Irroy*, *Mott*, *Mumm*, *Perrier Jouët*, *Pommery-Greno*, and *Roederer*. Large quantities of sparkling wine are produced in the Saumur, in the department of Maine-et-Loire. Sparkling *Saumur* is made from both black and white grapes—the black being the product of the Breton vine, the white that of the Pineau blanc. The wine is made much in the same way as champagne, except that, as a rule, the finished product is a mixture of two successive vintages.

The wines of *Burgundy* (both red and white) are produced in the departments of Côte-d'Or, Yonne, and Saône-et-Loire. The principal red wines are *Mâcon*, *Beaune*, *Le Corton*, *Romanée Conti*, *Chambertin* and *Clos Vougeot*. *Hermitage*, when it can be obtained genuine, is a rich wine with purple colour, produced in the department of Drôme. The white wine of Yonne is known as *Chablis*, and is frequently, though incorrectly, described as 'White Burgundy.'

Spain. *Sherry*, the best known of Spanish white wines, is mainly produced in Andalusia, and derives its name from Jerez or Xeres de la Frontera, the chief centre of the trade, and where most of the wine is produced from must or fruit purchased from the growers. Sherries are essentially 'blended' wines, and are divided as regards type or quality into three classes: *Finos*, *Rayas*, and *Cortados*. The *Finos* are 'clean' and 'dry' in character, the *Rayas* being fuller in 'body,' whilst the *Cortados* partake of the characteristics of the other two types. These wines are exported, however, under various other names, as *Amontillado*, *Manilla*, *Montilla Solero*, &c. Sherries are almost invariably fortified and plastered, and the commoner kinds sulphured in addition, for the British market.

The sweet red wine known as '*tent*,' which is used for ecclesiastical purposes, is mainly obtained from the Rota district. This and the somewhat similar wines from the Tarragona, Valencia, and Alicante districts were formerly sold under the name of 'Tarragona Port,' or 'Spanish Port.' As the result of recent legislation, such descriptions are now illegal, the use of the term 'port' being applicable only to wines the produce of Portugal (*vide infra*).

Portugal. Port is mainly the produce of the rugged and mountainous district of the Alto Douro in the north-east of Portugal. The vintage usually begins at the end of September. The grapes, from which the stalks are removed, are emptied into stone tanks holding from seven to thirty pipes, and are pressed, first by treading and then by means of a beam or screw press. After from 48 to 60 hours' treading the must is left to ferment, drawn off into vats, and mixed with a sufficient quantity of alcohol to prevent acetous fermentation. After the lees are deposited the wine is again racked and mixed with more alcohol, which is usually obtained by distilling wine. If necessary, the wine is sweetened with 'jericopa,' or sweet must preserved with brandy. In the spring it is sent down to Oporto, where it is stored previous to shipment. 'Vintage wines' are those of the same origin, year, and quality, and are kept separately. The other principal types of port are 'Ruby' and 'Tawny.' These are usually blends, the former being intermediate in character between 'Vintage' and 'Tawny' ports. The latter is matured in wood, thus losing much of its deep red colour. Nearly half the wine exported from Oporto is sent to the United Kingdom.

Port first appeared in England at about the end of the seventeenth century, and its consumption in this country gradually increased up to the middle of the eighteenth century, since when it has gradually declined. The disfavour into which port has fallen may be partly due to the manufacture of numerous brands of inferior wines of port character, which may or may not be distinguished by qualifying names, as 'Hamburg Port,' &c.

As the result of representations by the Portuguese Government, definitions of 'Port' and 'Madeira' have been embodied in recent Acts of Parliament. Thus, in Sect. 1 of the Anglo-Portuguese Commercial Treaty Act, 1914, it is laid down: 'The description "Port" or "Madeira" applied to any wine or other liquor, other than

wine the produce of Portugal and the Island of Madeira respectively, shall be deemed to be a false trade description within the meaning of the M. M. Act, 1887.' Still later, in the Anglo-Portuguese Commercial Treaty Act, 1916 (Sect. 1) it is provided that, 'The description "Port" applied to wine the produce of Portugal imported into the United Kingdom after the passing of this Act shall be deemed a false trade description within the meaning of the M. M. Act, 1887, if the wine on importation into the United Kingdom was not accompanied by a certificate issued by the competent Portuguese authorities to the effect that it was a wine to which by the law of Portugal the term "Port" may be applied.' These enactments apply also to British 'made' wines.

The South of Portugal (Torres Vedras and Colares) produces a considerable quantity of a rough kind of claret, and also a white wine known in England as *Bucellas Hock*, which is obtained from the Riesling grape.

Italy. It is only within recent years that Italian wines have found much favour in this country, as they were formerly too sweet for the British market and deficient in keeping qualities. These defects have been largely removed by the adoption of more scientific methods of manufacture resulting in an increased popularity. Northern Italy produces *Barolo*, a red, and *Asti*, a white wine, together with a certain amount of sparkling wine. *Montepulciano* and *Chianti* are made in Central Italy; whilst the Neapolitan district yields *Lacryma Christi* and a variety of Malvoisie and good class Muscat wines. The island of Capri produces a good wine of *chablis* character.

Sicily. The chief Sicilian wine is *Marsala* (a white wine of light amber or brown colour, somewhat resembling sherry), obtained from a mixture of selected and thoroughly ripe grapes of the Madeira variety. It is carefully manufactured and is very uniform in quality, although, as a rule, somewhat heavily fortified, but not plastered.

Austro-Hungary. Both white and red wines are made, but those of German Austria are consumed for the most part locally. The best known are from *Vöslau* and *Gumpolds-Kirchen*, and the Tyrol. The most famous of Hungarian wines is the *Sweet Tokay* or *Essencia*, which is made from the first runnings of the ripe grapes obtained without pressure. Only a small portion is so obtained, and it rarely, if ever, appears in the market. Other varieties of Tokay are known as *Ausbruch* and *Mastas*. *Carlowitz* resembles port in character, and is produced on the banks of the Danube, about 40 miles to the north-west of Belgrade.

The greater portion of the wine produced in Bohemia (now incorporated in Czechoslovakia) is obtained from the province of *Melnik*, chiefly from the blue Burgundy grape, originally procured from France.

Excellent red wines, resembling Burgundy, are now made in Dalmatia. The most esteemed varieties are *Moscato Rosso*, *Maraschino*, and *Malvasia*.

Germany. The chief wine-producing districts of Germany are *Baden*, *Bavaria*, *Hesse*, the *Rheingau*, and *Württemberg*. The celebrated *Steinberg*, *Johannisberg*, *Riesling*, &c.

Grüfenberg, and *Rauenthal* wines are produced in the neighbourhood of the Rhine, not far from Mainz, which is the centre of the hock trade. The vineyards of Hesse yield *Liebfraumilch*, *Nierstein*, and *Scharlachberg*; *Hochheimer* is obtained from the Maingau. The chief Rhine wine is the Riesling, which is said to be indigenous, and which has been transplanted and successfully cultivated in many other parts of the world as South Africa, Australia, and the United States

of America. The *Moselle* district also produces excellent wines of characteristic but rather weak flavour, which is often artificially enhanced by the addition of tincture of elder flowers.

The chief product is a white wine. A certain amount of red wine is obtained, notably *Assmannshausen*, from Riesling and mixed grapes. The results of analyses by König of wines from the principal European countries are shown in the following table.

ANALYSES OF EUROPEAN WINES (König).

	Number of analyses	Specific gravity	Grammes per 100 c.c.									
			Alcohol by weight	Extract	Total acid as tartaric	Free tartaric acid	Cream of tartar	Volatile acid as acetic	Sugar	Glycerol	Nitrogen	Ash
<i>Germany :</i>												
<i>Moselle</i>	14	0.9984	7.99	2.24	0.79	—	—	—	0.03	0.72	—	0.175
<i>Rhine</i>	23	1.0005	8.00	2.60	0.81	—	0.200	—	—	0.85	—	0.230
<i>Baden</i>	46	—	6.65	2.16	0.91	0.018	0.358	—	0.09	0.49	—	0.207
<i>Württemberg, white wine</i>	5	0.9995	6.10	2.27	0.95	0.065	0.262	—	—	0.57	—	0.250
<i>red wine</i>	16	—	4.73	2.64	1.14	0.091	0.028	—	—	0.46	—	0.250
<i>France :</i>												
<i>Alsace</i>	15	—	6.59	2.07	0.70	0.018	0.168	0.052	—	0.55	0.028	0.229
<i>Lorraine, red wine</i>	10	0.9967	8.08	2.27	0.56	0.032	—	0.155	0.09	0.60	0.019	0.185
<i>Red wine</i>	29	0.9982	7.80	2.56	0.57	—	—	—	0.30	0.73	0.043	0.248
<i>White wine</i>	5	0.9963	8.30	3.03	0.66	—	—	—	—	0.97	—	0.250
<i>Austria :</i>												
<i>Tyrol, red wine</i>	60	0.9940	9.08	2.34	0.62	—	—	—	—	0.65	0.021	0.222
<i>white wine</i>	17	0.9927	8.84	1.87	0.59	—	—	—	—	0.65	0.020	0.175
<i>Russia :</i>												
<i>Red wine</i>	10	0.9939	10.76	2.76	0.56	—	—	0.142	—	0.64	0.036	0.267
<i>White wine</i>	12	0.9931	11.96	2.57	0.49	—	—	0.100	0.46	0.59	0.028	0.204
<i>Italy</i>	20	—	10.61	3.44	0.52	—	—	—	1.44	0.45	—	0.290
<i>Spain :</i>												
<i>Ordinary red wine</i>	7	—	12.30	3.53	0.49	—	—	—	0.38	1.09	—	0.610
<i>Sweet wine</i>	4	1.0233	12.78	9.69	0.59	—	—	—	6.55	0.63	—	0.740

The Atlantic Isles. Grand Canary and Tenerife produce a small quantity of wine, but since the production of cochineal has fallen off on account of the preference for coal-tar colouring matters, vine culture is increasing, and wines of the Madeira type are being made in larger quantity.

Madeira. The best-known varieties of Madeira wine are *Malmsey*, and *Sercial*, the former being a sweet, and the latter a dry wine. It is a white wine, and its characteristic flavour is probably due to the practice of exposing the young grapes to a prolonged process of partial drying by artificial heat, and of heating the wine shortly after its manufacture to a temperature varying from 25° to 45°. Formerly the same condition was obtained by sending the wine a voyage to the East or West Indies and back. Very little red wine is made in Madeira (*vide supra*, under 'Port').

A small quantity of wine is made in the Azores, particularly on Pico, but it is of very indifferent quality, and is mainly exported as low-class sherry.

Cape of Good Hope. Comparatively little wine is now sent to this country from South Africa, although a century ago the importation of Cape wine into the United Kingdom exceeded that from France. The decline was due to vine diseases and insect pests, to faulty manufacture, and to fiscal changes. The best-known wines are *Veldt Burgundy* and *Claret*, *Wyndberg Okavies*, *Schoonvriest Hermitage*, *Tafelberg Hock*, and the sweet pale-red *Constantia* produced

near Cape Town. A great increase in the importation of South African wines has occurred since the war, the quantity imported during the last five years immediately preceding the war being only 15,000 gallons, as compared with over 200,000 gallons imported during the corresponding period since the war (1919-23).

Australia. Of late years the amount of wine from Victoria, New South Wales, and South Australia imported into this country has increased enormously. The industry may be said to be still in its infancy, but the most scientific methods and appliances are adopted, and the produce of such vineyards as Albury, Great Western, Highercombe, and Tintara bids fair to rival the best European wines of similar type.

In Australia (as in the case also of South Africa and California) the practice obtains of naming the wines after the well-known European types they more or less resemble in character, as 'Burgundy,' 'Chablis,' 'Hock,' &c., or after the variety of vine originally imported from Europe, as *Riesling*, *Hermitage*, and *Cabernet*.

United States. The manufacture of wine has been firmly established in California. The produce was originally derived from the 'Mission' grape, supposed to have been imported from Mexico by Franciscan monks, but German, French, and Spanish varieties were introduced, and wines in some degree resembling those of these countries (and named after their original types) were made on a considerable scale. The vine has been also cultivated on a large scale in Ohio, and clarets and champagnes have been

WINE.

made in the vicinity of Cleveland and Sandusky. Other wine-producing States were New York, Missouri, Illinois, and Pennsylvania. Whilst the finer wines consumed in the United States were obtained from France and Germany, the importation of foreign wines steadily decreased in favour of the home product.

It is understood that at the present time (1926) the national prohibition law prevents the manufacture and sale of wines in the United States.

The following are analyses, by Bigelow (U.S. Dept. of Agric. Bur. of Chem. Bull. 59), of 525 samples of wines manufactured in California:—

Description	Specific gravity	Alcohol by volume p.c.	Grams per 100 c.c.						
			Alcohol	Glycerol	Total acids	Extract	Reducing sugar	Proteids	K ₂ SO ₄
Red wines (204 samples):									
Bordeaux, Rhine, Burgundy (Min.)	0.9900	8.00	6.35	0.330	0.201	1.91	0.030	0.1864	0.0455
and South French types (Max.)	1.0050	19.28	15.30	0.852	0.888	6.88	0.628	0.5544	0.2515
White wines (321 samples):									
Rhine, Sauterne, South (Min.)	0.9866	5.00	3.98	0.163	0.181	1.00	0.060	0.0859	0.0453
French, Sherry, and Madeira types (Max.)	1.0560	22.19	17.61	0.971	0.798	19.06	17.219	0.9379	0.1861
									Ash
									0.188
									0.480
									0.056
									0.447

ANALYSIS OF WINE.

The chemical examination of wine is usually restricted to the determination of those constituents which enable an opinion to be formed concerning its purity or freedom from adulteration, but expert tasting is of great importance, and microscopical examination of the deposits obtained from wine may afford useful information. For methods based on the latest chemico-physical principles, the work of Baragiola may be consulted (Zeitsch. anal. Chem. 1914, 53, 100; Analyst, 1914, 127).

For the estimation of the *specific gravity* a determination should be made by the bottle or other form of pycnometer and given accurately to four decimal places. Carbonic acid should first be removed by vigorous agitation.

The *results* are usually given in grms. per 100 c.c. or per litre. Koenig (Zeitsch. anal. Chem. 28, 202), however, deprecates this practice, on the ground that for sweet wines, which are liable to differ widely in sp.gr., the results are no longer directly comparable.

The *alcohol* is best determined by the distillation method, the sp.gr. of the weighed distillate being taken and the proportion of alcohol found from tables. For more exact determinations, the volatile acids should be neutralised before distillation.

Detection of cider in wine.—F. Schaffer (Mitt. Lebensm. Unters. Hyg. 1923, 15; Ann Chim. anal. 1924, 6, 88) has devised a method for detecting cider in wine, based on the diminished reducing power of the wine. The following modified procedure is recommended: Forty c.c. of the wine are decolorised by boiling with 3 grms. of pure animal charcoal and filtered, and the filtrate is heated to boiling with excess of precipitated calcium carbonate. After further filtration the cooled liquid is treated, slowly and with shaking, with 8 c.c. of 10 p.c. barium acetate solution, and again filtered. Five c.c. of the neutral filtrate are mixed with 2 drops of 0.2N silver nitrate solution, and, after being made alkaline by addition of 1 c.c. of 0.1N sodium hydroxide solution, are placed in the dark, and the time elapsing before distinct reduction is apparent is noted; the test should be made in duplicate or even triplicate.

With cider the reduction becomes evident in a few minutes, and with wines containing a marked proportion of cider in 10 to 20 minutes; in some cases comparison of the suspected wine with the natural wine of known purity is advisable (Analyst, 1924, 49, 235). If 1 c.c. of concentrated sulphuric acid be mixed (keeping cool) with 5 c.c. of wine and set aside till next day, genuine wine should remain clear (von Fellenberg, Mitt. Lebensm. Hyg. 1925, 16, 55; J. Soc. Chem. Ind. 1925, 44, B. 936).

Determination of extract.—The various methods in use for determining extractive matter in wine differ considerably both in principle and in the details of manipulation. The direct method (by evaporation) does not give comparable results unless the sugar of sweet wines and the potassium sulphate in plastered wines are deducted, and not then unless the estimation is conducted under exactly similar conditions.

The French official method of prolonged heating on a water-bath gives low results, owing chiefly to loss of glycerol. The sugar and potassium sulphate are deducted, an allowance of 1 gm. of each per litre being made to cover the amount of these substances assumed to be naturally present in fully fermented wine. The result is known as the 'reduced extract.'

The most exact determination of extract is made by evaporation (at the ordinary temperature) over sulphuric acid *in vacuo*, but as this requires from 3 to 6 days (according to the temperature) it is unsuitable for ordinary commercial use.

By Njegovius' modification of this method, however, the time may be reduced to within the limits of a working day. The wine (5 c.c.) is absorbed by anhydrous sodium sulphate (5 grms.) in a tared bottle and dried in a desiccator under diminished pressure, not exceeding 15 mm.

The German official method is as follows:—

(a) For wines with an extract amounting to not more than 3 grms. per 100 c.c. (ascertained by the indirect method (c) given below): 50 c.c., measured at 15°, are evaporated to a syrupy consistency on the water-bath in a platinum basin of 85 mm. diameter, 20 mm. height, and 75 c.c. capacity, and the residue is dried for 2½ hours in the water oven.

(b) For wines containing from 3 to 4 grms. of extract per 100 c.c. an amount yielding from 1 to 1.5 gm. of residue is taken. For the necessity of using dishes of similar area and surface in order to obtain comparable results, v. Bouchon (Compt. rend. 103, 498).

(c) For sweet wines, or those containing over 4 grms. of extract per 100 c.c., the indirect method of determining the extract from the sp.gr. of the wine after removal of the alcohol is to be preferred (v. Tables in Windisch, Die chemische Untersuchung und Beurtheilung des Weines, 338; abstracted, J. Soc. Chem. Ind. 1896, 280).

The amount both of extract and of alcohol may be determined by Riegler's refractometer method (Zeitsch. anal. Chem. 1896, 27). One gm. of alcohol and of extract in 100 c.c. of wine are found to raise the refraction by 0.00068 and 0.00145 respectively above that of water. Then if a = the refraction of pure distilled water; $(a+b)$ = the refraction of the wine from which the alcohol has been removed made up to the original volume taken; and N = the refraction of the original wine; then the formula
$$\frac{N - (a + b)}{0.00068}$$

gives the weight of alcohol, and $\frac{b}{0.00145}$ that of the extract as grams per 100 c.c. of the wine.

In completely fermented wines the amount of extract is seldom less than 14 grms. per litre. Wines containing less than this amount after removal of the sugar may be suspected of dilution.

After separation of the non-volatile acids, the remaining extract in natural wine is seldom less than 11 grms. per litre, and after separation of the free acids, as a rule, not less than 10 grms. per litre. The mineral constituents are usually about 10 p.c. of the extract.

The free acid is determined by titration with standard potash or soda-solution, using litmus-paper as indicator, and calculating the result as tartaric acid ($C_4H_4O_6$). Carbonic acid should first be expelled, either by heating just below boiling-point (but rapidly so as to avoid loss of acetic acid), or by agitation and subsequent titration in the cold. Volatile acids are determined by distillation in steam, or, since this partially volatilises lactic acid (Windisch, Zeitsch. Nahr. Genussm. 1905, 9, 70), by the difference in the acidity of the wine before and after evaporation to a small bulk, and are expressed as acetic acid ($C_2H_4O_2$). The fixed acids are estimated by difference between the total and volatile acids, or by direct titration of the extract obtained by evaporation *in vacuo*, and are expressed as tartaric acid. In France the acidity is usually given in terms of sulphuric acid (H_2SO_4).

Old wines have an acid reaction, in consequence of the presence of a certain amount of free acid and potassium hydrogen tartrate. A wine not exhibiting this acid reaction tastes flat. For a long time it was believed that the free acid of wine is tartaric acid alone. Nessler's researches have, however, shown that this is seldom the case. Tartaric and malic acids often occur together, and more frequently the free acid consists of malic acid entirely. Wines containing tartaric acid alone taste more tart than

those with only malic acid, or a mixture of malic and tartaric acids.

The presence of free tartaric acid in wine does not necessarily show an improper admixture of tartaric acid with the wine. According to Mach and Rolandi, the amount of free tartaric acid in the grape increases in proportion to the degree of unripeness, so that its absence from wine can only occur under certain conditions of ripeness of the grapes employed. Although unripe grapes are frequently used in considerable quantity in wine-making, yet if the ripe grapes are in excess, the potash salts in them are more than sufficient to separate the free tartaric acid in the form of tartar, and this explains the fact that wine so made generally contains no free tartaric acid. A wine may be suspected of having been sophisticated if, with a small amount of free acid, an undue proportion of it is tartaric (J. Nessler and H. Wachter, Bied. Zentr. 1886; Chem. Soc. Abstr. 1880, 775).

The estimation of total tartaric acid, free tartaric acid, potassium bi-tartrate, and tartrates of the alkaline earths (lime and magnesia) is best made by the methods of Halenke and Möslinger, and of Barth (Zeitsch. anal. Chem. 1895, 279-290). These methods were officially adopted by a German Imperial Decree of 1896, an abstract of which is given in the J. Soc. Chem. Ind. 1898, 277. Certain modifications were introduced by Kulisch in 1901. Full details of these, as well as the French official methods, will be found in Post and Neumann's *Traité complet d'analyse chimique appliquée aux essais industriels*, 1910, tome ii. 661. The last three estimations are necessarily empirical, being founded on the assumption that all the bases present in the organic salts of the wine, or as carbonates in the ash, were originally combined with tartaric acid to form bi-tartrates.

A rapid and fairly accurate method of estimating tartaric acid and potassium in wine is that of Kling and Lassieur (Ann. Falsif. 1914, 7, 410; Analyst, 1915, 155). Mathieu (Ann. Falsif. 1919, 11, 80) recommends a method originally described by Pasteur in 1873. For details, see Analyst, 1919, 238. In a later communication he describes the process as follows: about 20 c.c. of the wine are shaken with 20 c.c. of amyl alcohol; the alcoholic layer is separated and shaken with an equal volume of water; the aqueous layer is drawn off, evaporated to dryness, the residue dissolved in 5 c.c. of water and the solution treated with 1 drop of calcium chloride solution (150 grams of crystallised $CaCl_2$ and 40 grams of NH_4Cl per litre) and 2 c.c. of 1-ammonium tartrate solution (20 grms. of the salt per 1 litre of dilute alcohol). A precipitate of calcium racemate forms immediately if the wine contains not less than 0.5 gm. of free tartaric acid per litre (Mathieu, Bull. Assoc. Chim. Sucr. 1921, 38, 352).

Numerous methods have been suggested for the estimation of malic and succinic acids, but they are too uncertain and inexact to be of much value for analytical purposes. The methods for estimating lactic and citric acids are more trustworthy, and the estimation of these is more important, since the former is a constant constituent of wines, and is often the cause of excessive acidity, whilst the latter is never present in genuine wines, except in small

but is sometimes added to sophisticated wines.

The best methods for estimating *lactic acid* are those of Kunz (Zeitsch. Nahr. Genussm. 1901, 4, 673) and Möslinger (*ibid.* 1901, 4, 1123). *Utric acid* may be estimated by Möslinger's method, weighing as lead citrate, as officially adopted by the U.S. Dept. of Agriculture (Bur. of Chem. Bull. 107, 81).

The determination of *glycerol* in wine has given rise to numerous processes, the best known of which are based upon either extraction by means of alcohol and ether or ethyl acetate or acetone and weighing, or oxidation to and estimation as oxalic acid.

Various methods have been proposed, as steam-distillation under reduced pressure (Bordas and Raczkowski, Compt. rend. 1897, 124, 240); or by conversion into triacetin (Böttiger, Chem. Zeit. 1897, 659); or into isopropyl iodide and weighing as silver iodide (Zeisel and Fanto, Zeitsch. anal. Chem. 1903, 549).

The Zeisel-Fanto method always gives low results. Correct values, however, can be obtained when organic acids, such as acetic, propionic, succinic, or tartaric acid, which have a decomposing action on the polyglycerol formed, are added to the reaction mixture. Lowering the concentration of hydriodic acid has no influence on the result: 200 c.c. of wine after treatment with tannin and barium acetate in the usual way are concentrated to about 30 c.c., and diluted with water to 40 c.c. 10 c.c. of the filtrate are then diluted to 50 c.c. with acetic acid, and 5 c.c. of this solution employed for the determination (C. Marchi, Staz. sperim. agrar. ital. 1923, 56, 231; Chem. Zentr. 1923, 94, [iv.] 1011; J. Soc. Chem. Ind. 1924, 43, B. 110).

A method by Rothenfusser, claimed to be more rapid and less laborious and expensive than the official method described below, is given in Zeitsch. Nahr. Genussm. 1913, 26, 535.

The older methods, especially extraction with alcohol and ether, are generally preferred, since, although somewhat empirical, they yield results which are comparable with the enormous amount of similar data acquired by previous observers. It is essential, however, that the exact details of the given methods should be rigidly followed.

The method officially adopted in Germany is as follows, (a) being adopted in the case of dry wines or those containing less than 2 grms. of sugar per 100 c.c.; and (b) for sweet wines containing more than this proportion of sugar.

(a) 100 c.c. of wine are evaporated down to 10 c.c. in a porcelain capsule on a water-bath. 1 gm. of quartz sand is added and milk of lime (40 p.c.) equivalent to 1½–2 grms. CaH_2O_2 for each gram of extract present, and evaporation continued almost to dryness. The residue is then repeatedly boiled with small quantities of 96 p.c. alcohol, the various extracts being decanted into a 100 c.c. flask, made up to bulk at 15°, filtered, and 90 c.c. of the filtrate evaporated in a porcelain capsule on the water-bath (without boiling). The residue is washed into a stoppered graduated cylinder with small quantities of absolute alcohol until 15 c.c. are collected, then shaken up with three successive

portions of ether (7.5 c.c. each time), and, when clear, the whole (including the rinsings of the cylinder with alcohol-ether, 2:3) evaporated on the water-bath to a syrup, but without boiling. The residue is dried for 1 hour at 100°, cooled, and weighed. The weight in grams, multiplied by 1.111, gives the number of grams of glycerol in 100 c.c. of the wine.

(b) 50 c.c. of wine are heated on the water-bath in a large flask, 1 gm. of quartz sand added, also milk of lime until the dark colour at first produced disappears, and an alkaline odour becomes evident. After cooling, 100 c.c. of 96 p.c. alcohol are added, the precipitate filtered off and washed with alcohol. The filtrate is evaporated and treated as in (a). The factor 2.222 is necessary in this case to obtain the number of grams of glycerol in 100 c.c. of the wine.

A method of estimating glycerol in wine is based upon its conversion into acetaldehyde by means of boric acid, the distilled aldehyde being determined by standard silver nitrate solution (Heiduschka and Englert, Zeitsch. anal. Chem. 1921, 60, 161).

For a process involving the use of acetone as solvent, see Beis, Bull. Soc. Chem. 1912, 11, [iv.] 618; Analyst, 1912, 37, 351; Bertinchand, *ibid.* 1913, 38, 368.

The sugar in wine is a variable mixture of dextrose and levulose, and occasionally sucrose. The usual method of examination consists in estimating the total quantity of sugar by titration with copper solution, then ascertaining by the optical method the proportions of the two glucoses and estimating the sucrose after inversion with hydrochloric acid.

Valuable information as to the nature and proportions of the sugars (both natural and added), as well as of other optically active substances introduced for the purpose of sophistication, may be obtained by the use of the polarimeter. Pure wine which still contains unfermented sugars turns the plane of polarisation to the left, whilst perfectly fermented wine either does not polarise at all, or only very slightly to the right. Wines sweetened with commercial glucose may contain considerable proportions of dextrorotatory non-fermentable substances.

It is essential to remove alcohol and colouring matters, and Neesler and Barth show that it is a matter of considerable importance also to remove the tartaric acid present in the wine, and they add, before precipitating with alcohol, a few drops of a strong solution of potassium acetate, thus separating the tartaric acid as potassium hydrogen tartrate.

The wine is carefully neutralised, and the alcohol eliminated by evaporation, the residue filtered, if necessary, and made up to original bulk, decolorised with lead acetate, the excess of lead removed with sodium carbonate or sulphate, and the polarimeter reading corrected for the increased volume due to these additions. The use of bone black should be avoided if possible, and complete decolorisation is not necessary if the liquid is clear. Turbidity can be removed by the addition of alumina cream.

A complete scheme, based upon the German official methods (Veröffentl. d. Kaiserl. Gesundheitsamts, 1896, 20, 557) is given in Allen's

Commercial Organic Analysis, 1924, vol. i. 230. The results are obtained from observations in a 300 mm. tube, and expressed in terms of the sugar scale of the Schmidt and Haensch half-shadow saccharimeter.

For the estimation of sugar by Barreswil's (Fehling's) solution, the tannin must first be removed by lead acetate, the excess of lead being precipitated by sodium carbonate or sulphate. Ordinary fully fermented wine usually contains under 0.1 p.c. sugar, and may be decolorised by a small quantity of animal charcoal. Either the gravimetric method (weighing the precipitated copper as CuO) or the volumetric (using as indicator either potassium ferrocyanide or ferrous thiocyanate as recommended by Ling (Analyst, 1905, 182; 1908, 160)) may be used.

Sucrose may be determined by difference between the directly reducing sugars formed as just described, and the total reducing sugar after inversion with hydrochloric acid on the water-bath, deducting one-twentieth of the difference (invert sugar) thus found to obtain its equivalent as sucrose; or the Clerget polariscopic method may be employed, using Herzfeld's modification of the Clerget formula (*v. art. SUGAR*).

The shoots and leaves of the vine, as well as unripe grapes, contain both sucrose and dextrose. The quantity of sucrose in the grapes gradually diminishes to zero as the grapes ripen, whilst the quantity of dextrose reaches a maximum at the period of ripeness. Sucrose, when added to wine, is gradually converted into dextrose, an addition of 5 p.c. being no longer traceable after five months, and 8.5 p.c. being completely transformed in six months. Boiled grape juice contains a substance which, after hydrolysis with acids, reduces Fehling's solution, and might thus be taken for sucrose. No rotation of polarised light can, however, be detected, and the substance is probably glucosan. In the case of wines, therefore, which have been sweetened with boiled grape juice or coloured with caramel, it is unsafe to conclude, from the reduction of Fehling's solution, that sucrose is present unless its presence is also indicated by examination in the polarimeter (O. Klein, Zeitsch. angew. Chem. 1924, 37, 111; J. Soc. Chem. Ind. 1924, 43, B. 486).

Gum arabic and *dextrin*, which are sometimes used for sophisticating wines, may be detected by adding to a little of the wine about twice its bulk of the strongest alcohol. If a decided flocculent and viscous precipitate be formed, the gum is obtained by evaporating 100 c.c. of the wine to about 5 c.c., and precipitating by the gradual addition of 90 p.c. alcohol. The precipitate is filtered off, dissolved in about 30 c.c. of water, 1 c.c. of strong hydrochloric acid added, and the liquid heated in a flask provided with a long glass tube as a reflux condenser for 3 hours on a bath of boiling water. The sugar thus produced is then estimated in the usual manner by Fehling's solution.

Tannin.—There is no very exact method for the estimation of tannin in wine. That of Neubauer-Löwenthal is recommended, and is described, with modifications, by Fresenius and Borgmann in 'Analyse des Weines,' 1922, p. 74.

Mineral matter is found by cautious incineration of the residue from the evaporation of 50 c.c. of the wine, taking the usual precautions for

separation of carbon from the alkaline salts. Rapid weighing is essential owing to the hygroscopic nature of potassium carbonate.

The determination of the ash (and of several other constituents) of wine containing much sugar is often facilitated and made more exact by eliminating the alcohol and removing the sugar by fermentation.

Wine containing less than 1.3 mineral matter per litre may be suspected unless it can be shown that natural wine from the same district and of the same vintage actually contains so small an amount of inorganic matter. The ratio of mineral matter to extract is, as a rule, about 1 to 10.

Estimation of chlorine in wine.—It is well known to wine falsifiers that chemists lay much stress on the proportion of mineral matters contained in wine, and therefore they frequently add sodium chloride to artificial or adulterated wines in order to increase the extract and to bring the total amount of ash up to the normal quantity. It is also said to hasten clarification and to have a preservative effect. Owing to the volatility of sodium and calcium chlorides on incineration, chlorine is best determined in the wine itself and not in the ash, but the ordinary method of titration is inapplicable owing to the solubility of silver chromate in the free acid of the wine. The chlorine is either precipitated and weighed as silver chloride, or the method of Nessler and Barth may be employed as follows:—50 c.c. of the decolorised wine are acidified with nitric acid, an excess of standard silver solution is added, and then standard thiocyanate solution is run in until a drop of the liquid when mixed on a plate with ferric sulphate solution just shows a pink coloration.

Wines containing more than 0.05 p.c. sodium chloride may as a rule be suspected. Exceptions may occur in the case of wines which have been produced in the neighbourhood of the sea-shore.

Alkaline earths in wine.—The ash of wine always contains calcium and magnesium salts. The amount of calcium (3.11.4 mg. in 100 c.c. of wine) is greatest in young wines and gradually diminishes with age, probably in consequence of the separation of neutral calcium tartrate. The amount of magnesium, on the other hand, remains almost constant and is always in excess of the calcium. The largest amount of magnesium found by Kayser was 24 mg. in 100 c.c. of Malaga wine. The phosphoric acid and magnesia show a constant proportion of 10:6, corresponding with the formula MgHPO_4 , (Kayser, Chem. Zentr. 1881, 394; Chem. Soc. Abstr. 1882, 121).

Barium and strontium salts are sometimes added, to remove sulphuric acid, in the process of 'deplastering' wines, and are best detected in the ash, which should be taken up with dilute hydrochloric acid, filtered, and the filtrate evaporated to dryness. The dry residue is then examined by the spectroscope. If barium or strontium is present they are determined quantitatively in the usual manner.

Sulphuric acid is precipitated directly with barium chloride in wine acidified with hydrochloric acid, and determined in the ordinary manner.

A normal wine contains not more than 1.3 gm. K_2SO_4 per litre, and when the amount

exceeds 2 grms., the wine may be regarded as plastered or sulphured.

The determination of phosphoric acid is to be effected in the ash by the molybdc method. (For details, see J. Soc. Chem. Ind. 1898, 280.)

The total phosphoric acid may be determined directly (without incinerating the residue) by Grete's volumetric method (Ber. 1909, 42, 3108).

The addition of dicalcium phosphate is sometimes made instead of 'plaster,' and is said to have certain advantages over the use of gypsum.

Nitric acid is sought for by carefully adding a few c.c. of the wine to a solution of diphenylamine in (pure) concentrated sulphuric acid, without mixing, and avoiding rise in temperature. An intense blue colour at the junction of the liquids indicates the presence of nitric acid.

Fresenius (Zeitsch. anal. Chem. 28, 67) finds that in wines containing much sugar a loss of phosphoric acid takes place during the incineration of the residue. A higher result is obtained when the residue is deslagged with alkaline carbonate and nitrate. Destruction of the sugar by fermentation by addition of a very small quantity of yeast leads to the same result.

The assumption that the better kinds of wine always contain more phosphoric acid than the poorer ones is unfounded. At the same time the amount of the phosphoric acid can, in many cases, serve as a valuable means of ascertaining the character of a wine, especially of wines used for medical purposes, or of those of a particular district in which the amount of phosphoric acid varies between definite limits.

Examination for colouring matters.—The principal substances used in red wines are vegetable colouring matters, coal-tar colours (especially fuchsines), and cochineal. White wines are frequently coloured with caramel or coal-tar colours used as substitutes.

According to Jean and Frabot (Ann. Chim. anal. 1907, 12, 52), wines artificially coloured may be distinguished from natural wines by the following test. The wine (50 c.c.) is heated on a water-bath with a little formalin (1 c.c.) and hydrochloric acid (4 c.c.), and when a precipitate is formed the liquid is made alkaline with ammonia and the excess expelled by further heating. The liquid, on cooling and filtration, yields a colourless filtrate in the case of genuine wines, whilst artificially coloured wines yield a coloured filtrate.

(a) *Vegetable colours.*—These are derived chiefly from bilberries, black cherries, elderberries, hollyhock or rose-mallow, poke-berries (*Physalacca*), indigo and 'lichens (archil, &c.), alkanet root, Campeachy, Pernambuco, and other dye-woods.

The wine is mixed with an excess of lead acetate and filtered. The colour of the precipitate in a genuine red wine may be greyish-blue, bluish-grey, ash colour, or greenish. If a precipitate is obtained not greatly differing from these colours, the search for other vegetable pigments can give no certain result. The colouring matter of bilberries gives a blue precipitate; mallow and elderberries a green. The colour of *Physalacca berries* differs from that of red wine by giving a red-violet lead precipitate (see also Lens, Zeitsch. anal. Chem. 1895, 635).

Alkanet-red, which, with Dupré's test (a.

ing), behaves very like the natural colouring matter of wine, is very easily taken up from its solutions by amyl alcohol. On adding to the amyl alcohol a solution of a few drops of olive oil or oil of almonds and evaporating off the alcohol, the oily residue (after washing with water) has a fine red colour, which, on saponification becomes a rich blue, or if the alkanna used was old, a green (Herz, Zeitsch. anal. Chem. 23, 637; Chem. Soc. Abstr. 1890, 311).

Beetroot juice is used in colouring wines for the purpose of concealing the presence of magenta. The absorption-bands of magenta are hidden by those of beetroot, but if a few drops of copper sulphate solution are added to the wine, the beetroot bands gradually vanish and the magenta spectrum becomes visible.

The fresh colouring matters of bilberries and wines are similar but not identical, and, according to H. W. Vogel (Ber. 21, 1746), they are readily distinguished by their absorption spectra after careful neutralisation with ammonia, or, better still, when they are treated with a trace of alum before addition of ammonia. Care must be taken that the wine is not too concentrated or the ammonia in too great excess.

Detection of logwood in wine.—When a solution of logwood is treated with manganese dioxide it becomes brown, and this brown liquid, by the action of zinc and hydrochloric acid, gives a colourless solution of hæmatoxylin. This may be detected by the ordinary reagents for that substance, alkalis and their carbonates giving a blue-violet coloration, calcium hydroxide a red-violet, stannous chloride or ammonium molybdate, in a solution slightly acid with nitric acid, a violet coloration. Advantage has been taken of this reaction for the detection of logwood in wines. 20 c.c. of the wine is agitated with 2 grms. finely powdered manganese dioxide, filtered, and the brown liquid treated with zinc and hydrochloric acid, which reduces the oxidised logwood colouring matter to hæmatoxylin. The solution is then divided into several portions, and tested with the reagents given above. Pizzi has examined wines to which other red colouring matters have been added, and although these yield brown solutions with manganese dioxide, the reduced solution does not give the hæmatoxylin reactions. Brazilwood is the only one which has any analogy to logwood, but here also there are differences (Chem. Soc. Abstr. 1881, 761).

Spaeth (Zeitsch. Nahr. Genussm. 1899, ii. 635; Analyst, 1900, 11) gives a table of reactions which may be found useful for the detection of the most commonly used vegetable colours.

(b) *Coal-tar colours.*—In most cases the presence of a coal-tar colour in wine may be recognised by the following methods:—

a. By shaking the filtrate, after precipitating with basic lead acetate, with amyl alcohol, or (i.) the wine itself, also (ii.) a portion of the wine acidified with sulphuric acid, and (iii.) a portion made alkaline with ammonia. In the latter case, excess of ammonia should be avoided, as, if more than 3 p.c. the amyl alcohol may remain colourless, although the wine contains a coal-tar colour. The amyl alcohol extract in (i.) and (ii.) may contain natural colouring matter of the wine, but if the colour remain unchanged by ammonia, the presence of a coal-tar colour may

be inferred. The amyl alcohol extract from (d.) should be shaken up with water and the aqueous solution tested with ammonia or by the wool test.

b. By the wool test, using alum and sodium acetate as a mordant, and adding about 1 p.c. of potassium sulphate in solution.

c. By Cazenueve's oxide test (Vierteljahrsschrift für Chemie der Nahrungsmittel, 1896, 80; Compt. rend. 102, 52).

The oxides employed are yellow mercuric oxide in the proportion of 0.2 grm. per 10 c.c. of wine; lead hydroxide, containing 50 p.c. of water, in the proportion of 2 grms. per 10 c.c.; and gelatinous ferric hydroxide, containing 90 p.c. of water, in the proportion of 10 grms. per 10 c.c.

Mercuric oxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, erythrosin, eosin J, methylene blue, Coupler's blue, and diphenylamine blue. It partially absorbs orange I., safranine, chrysoidine, chrysoine, methyleosin, yellow II., red NN, red I., and Ponceau RR. It does not absorb the sulpho-conjugated derivative of rosaniline, Bordeaux red B, Ponceau R, Ponceau B, orange R, orange RRR, orange II., orange RR, tropaeoline M, tropaeoline II., yellow L, solid yellow, dinitronaphthol yellow, U. S. yellow.

Lead hydroxide completely absorbs the natural colouring matter, cochineal and foreign vegetable colours, methylene blue, Coupler's blue, diphenylamine blue, and erythrosin. It differs from mercuric oxide in not absorbing the rosanilines, and also in absorbing the sulpho-conjugated derivative of rosaniline, Bordeaux red B, the purple red, and soluble red of rocelline.

Ferric hydroxide does not absorb erythrosin, the sulpho-conjugated derivative of rosaniline, Bordeaux red B, purple red, soluble red, and solid yellow. It absorbs the natural colouring matter and foreign vegetable colours, cochineal, and all the derivatives of rosaniline, except the sulpho-conjugated derivative.

Zinc hydroxides and stannous hydroxide behave similarly. The latter retains the natural colouring matter, but does not absorb cochineal or orshil. After the wine has been treated with the hydroxides, the colouring matters must be distinguished by special tests. If the wine is treated with magnesia and hot amyl alcohol, a number of blues which are precipitated by the above-mentioned hydroxides can be isolated and distinguished.

d. Shaking the wine with ether before and after supersaturation with ammonia.

Five to 6 c.c. of the wine to be tested are poured into a glass test-tube of about 20 c.c. capacity, and then three-quarters of its bulk of ether is added. After a few minutes the ether rises to the surface of the wine. If the ether be coloured yellow, and assumes, on addition of some drops of ammonia, a deep-red tint, Campeachy-wood has been used to colour the wine. If the ether becomes red and violet, and remains so even on addition of a large quantity of ammonia, the wine contains colouring matter derived from some of the lichens.

If the red-coloured ether loses its tint on mixing with ammonia, without passing into violet, then only the natural colouring matter of the wine is present. If the red-coloured

ether loses its red tint with ammonia, without imparting any colour to the latter, then fuchsin has been added to the wine. When the ether rises uncoloured, a fresh sample of the wine to be tested is taken, twice its volume of water is poured into it, and half its volume of ammonia added. If the wine now assumes a brownish-red colour, it contains cochineal; if, however, it turns green, then it can be assumed that none of the substances mentioned is present.

e. The formation of isonitriles when aniline derivatives are warmed with potash and chloroform serves for the direct determination in wine of even minute traces of many of the aniline colours. The evolution of the isonitrile is accelerated by adding excess of strong sulphuric acid.

According to A. Dupré, fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about $\frac{1}{2}$ -inch side. These cubes are made by dissolving 10 grms. of gelatin in 100 c.c. of warm water, and pouring the solution into a flat dish or mould; from the plate thus obtained the cubes are cut. After 24-48 hours the cube, on examination by transmitted light, will be found to be coloured more or less deeply by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of $\frac{1}{8}$ -inch at the most. The colouring matter of alkanet root also penetrates but slowly, whereas rosaniline, cochineal, logwood, brazilwood, indigo, litmus, red cabbage, beet-root, *Malva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly (Chem. Soc. Trans. 1880, 572).

The nature of the colouring matter may be determined either by the colour of the jelly or spectroscopically, or by the action of dilute ammonia, which turns cochineal purple, logwood brown, red cabbage dark green, and decolorises rosaniline (r. SPECTRUM ANALYSIS).

Bordeaux verdissant or 'colorant introuvable' is a mixture of acid fuchsin with methylene blue and diphenylamine orange, the two latter colours being used to produce a green which becomes visible on decolorising the Bordeaux red with ammonia, thus simulating the effect of ammonia on natural red wine. The diphenylamine orange can be extracted with amyl alcohol, the acid fuchsin detected by Girard's mercuric acetate test, and the methylene blue by dyeing cotton fibre.

A substance known as *Tintura por los vinos* is said to have been largely used for colouring certain Spanish wines. It is alleged to contain Biebrich red, sodium sulphate, and arsenious oxide. The presence of arsenic, if a fact, is of special importance.

The methods employed in the Paris Municipal Laboratory for the investigation of the colouring matters in wine will be found in Girard and Dupré's *Analyse des matières alimentaires*.

Removal of added colouring matter from wine.—So much artificially-coloured wine is confiscated in certain districts in Italy that the authorities are considering the advisability, in the interests of economy, of merely removing the added colouring matter from the wine instead of denaturing the latter before returning it to its owners. For effecting this removal the following methods may be employed: (1) Addition

to the wine of must, thus causing a fresh alcoholic fermentation; (2) addition of young wine, the proteins of which may form insoluble compounds with the colouring matter; (3) clarification by means of egg albumin, fish glue gelatin, &c.; (4) keeping the wine for some time, with repeated transference. The colouring matter most commonly used is 'vinolin,' a mixture of Bordeaux B, Bordeaux R, and Ponceau RRR, which may be eliminated by re-fermentation of the wine in presence of vinasse (F. Scurti, *Annali Chim. Appl.* 1923, 13, 194-200; *J. Soc. Chem. Ind.* 1923, 42, 993 A).

Detection and estimation of *preservatives* most commonly used in wine. *Abrastol* or *asaprol* (calcium α -monosulphonate of β -naphthol) is a white or slightly reddish scaly powder readily soluble in water and alcohol, and decomposing at 50°. It is extracted from alkaline solution by amyl alcohol, the extract evaporated to dryness, and the residue tested by Sinibaldi's method (*Mon. Sci.* 1893, [iv.] 7, 842; U.S. Dept. of Agric. Bur. of Chem. Bul. 59, 91).

Boric acid (according to Baumert, Ber. 21, 3290) is naturally present in many wines as well as in the leaves and tendrils of the grape-vine. It is detected in the ash by extracting with a large excess of strong hydrochloric acid, and testing with turmeric paper. For its quantitative estimation, see Windisch, *Die Chemische Untersuchung und Beurtheilung des Weines*, 235.

Fluorides are strongly antiseptic and are usually employed in very small quantity in the form of the ammonium or sodium salts which are soluble in water. The fluoride is precipitated as calcium fluoride from alkaline solution by means of calcium chloride, and the precipitate, after filtering, washing, drying, and heating in a platinum crucible, is tested by means of the 'etching' test. A blank experiment should be made with the reagents employed. For *fluoborates* and *fluosilicates* the ash containing the calcium salts is extracted with dilute acetic acid and filtered. The filtrate contains the boric acid which, if present, is detected as above. The calcium fluoride and silicate remain in the insoluble portion, and can be detected by the usual methods (v. Bull. 59, 63, U.S. Dept. of Agric. Bur. of Chem.).

For detecting *saccharin* (which is used as a preservative as well as a sweetening agent), the wine (about 100 c.c.) is shaken up with a mixture in equal parts of ether and light petroleum, and the extract, after evaporating off the solvent, is fused with sodium hydroxide and tested by means of ferric chloride for salicylic acid. It is assumed, of course, that the absence of salicylic acid in the original wine has been proved and the presence of saccharin indicated by the sweet taste of the residue from the ether extraction.

The estimation of the saccharin may be made by acidifying (if necessary) with phosphoric acid, extracting with ether as above, and fusing the evaporated residue with a mixture of sodium carbonate and nitre, precipitating the resulting sulphate with barium chloride and calculating the saccharin from the weight of barium sulphate obtained ($\text{BaSO}_4 \times 0.785 = \text{saccharin}$).

Saccharin may also be estimated by hydrolysing the residue from the ether extract with hydrochloric acid, and estimating the ammonia

thus formed by distillation into standard acid (Proctor, *Chem. Soc. Trans.* 1905, 242).

Salicylic acid is best sought for by agitating the wine with carbon disulphide or a mixture of equal volumes of ether and light petroleum (taking care to avoid an emulsion), evaporating down and testing the residue with ferric chloride. If much more than 100 c.c. are used, a faint colour may be occasioned by other substances giving a similar reaction and present as normal constituents of the wine.

An approximate estimation of the quantity of salicylic acid may be made colorimetrically, by comparing the colour given by an alcoholic solution of the residue after ether extraction with that yielded by standard alcoholic solutions of salicylic acid of known strength, using, if possible, a liquid similar to that under investigation.

Sulphurous acid and sulphites.—Wine will absorb as much as 0.36 gm. of sulphurous acid per litre when it is shaken in a barrel in which sulphur has been burnt, and if the treatment is repeated the sulphurous acid may reach 0.5 gm. per litre. Sulphur is burnt in the barrels to prevent the formation of mildew, and sulphites are sometimes used as a preservative. Much of the sulphurous acid is combined with aldehyde when it is considered to be much less objectionable than in the free state.

Sulphurous acid is determined by distilling a portion of the wine, to which phosphoric acid has been added, in a stream of carbon dioxide, receiving the distillate in solution of iodine, and determining the sulphuric acid thus formed. The details of the method are as follows (B. Haas, Ber. 15, 154): the wine, to which 5 grms. of syrupy phosphoric acid have been added, is distilled in a current of carbon dioxide, and the distillate is collected in a suitable apparatus (a bulb U-tube) containing 50 c.c. of iodine solution (containing 5 grms. pure iodine and 7.5 grms. potassium iodide per litre), thus oxidising the sulphurous acid. As soon as the distillate amounts to about half the original volume of the wine used, the contents of the U-tube are washed out, acidified with hydrochloric acid, precipitated with barium chloride, and the barium sulphate washed, dried, heated to redness, and weighed. This method gives very good results. The sulphurous acid may also be oxidised by means of hydrogen peroxide, using barium peroxide, and weighing as barium sulphate (Levi, *Ann. Fabrif.* 1913, 6, 5; *Analyst*, 1914, 87).

Opinions vary as to how much sulphurous acid a wine may contain. According to the medical faculty of the University of Vienna, not more than 8 mg. per litre should be allowed, whereas other authorities regard 80 mg. as not an excessive amount. In France and Switzerland the maximum limit is fixed at 200 mg. of SO₂ per litre, of which, in France, not more than 30 mg., and in Switzerland, not more than 20 mg. should be 'free' or uncombined.

Poisonous metallic substances in wine.—Traces of arsenic may be present owing to the use of impure coal-tar colours (acid fuchsine, &c.), and commercial glucose. Copper and mercury may be due to the compounds used as insecticides and fungicides, but are, no doubt, largely removed in an insoluble form during the process of fermentation.

mentation. Lead has been traced to the use of litharge to mask acidity and to lead shot used for cleaning bottles. Zinc is often present in appreciable quantities when the wine has been stored in vessels of unalloyed zinc. These metals may be detected and estimated by the usual methods.

Hydrocyanic acid may be present in wine to which potassium ferrocyanide has been added to remove the iron. For its detection and estimation, see Mach and Fischler (Zeitsch. Unters. Nahr. Genussm. 1924, 47, 329; Reichard, *ibid.* 1924, 47, 339; Zeitsch. angew. Chem. 1924, 37, 957).

Alum is occasionally present in the coal-tar colours employed, and is sometimes added to wine as a clarifying agent, and to impart astringency, particularly to wines which have been diluted. The alumina may be estimated as follows (Louvet, Chem. Zentr. 1881, 252): 200 c.c. of wine are evaporated to dryness, the residue incinerated, and the ash fused in a platinum crucible with 3 grms. sodium carbonate, whereby the lime, magnesia, and ferric oxide are converted into insoluble carbonates. The mass is dissolved in water, and the solution filtered. As the solution may contain sodium aluminate, it is acidified with hydrochloric acid, treated with a large excess of sodium carbonate, and the alumina collected on a tared filter. The insoluble portion of the fused mass, containing the chief portion of the alumina, is fused with a few grams of pure soda, and the fused product digested with water and the solution treated for alumina as above described. The precipitates are collected, thoroughly washed, dried, ignited, and weighed. If any considerable proportion of phosphate is present, the phosphoric acid should be estimated and deducted from the total weight, the difference being Al_2O_3 .

Adulteration of wine.—Of the various processes already described which, strictly speaking, might be considered as 'adulteration,' some, as fortifying with spirit, sweetening with sugar, glucose, or glycerol and 'plastering,' are defended as legitimate trade practices of long standing or are officially tolerated within certain limits. Others, as dilution with water, the addition of antiseptics, astringents, colouring matters, and mineral acids, and of potassium hydrogen tartrate and ceanothic ether to give the fictitious character of age, have, as a rule, no other object than that of fraud.

In addition, wine is mixed with the juice of fruit other than the grape, and spurious wines containing no grape-juice whatever are made to simulate well-known types, as port, sherry, claret, and burgundy. The fruit basis of these is usually apple juice (v. p. 480), the other principal ingredients employed being crushed raisins, alcohol, sugar, tartar, flavouring essences, and colouring matters derived generally from the juice of such fruits as bilberry, elderberry, black currant, etc.

For the detection of dilution with water, fortifying with spirit, the addition of acids, tartar, glycerol, sugar, and other forms of sophistication of wines, reliance is placed in France and Germany upon the ratios which the proportions of the principal constituents of the genuine wines of those countries bear to each other (e.g. in France, alcohol : extract (reduced) : and in Germany, alcohol : glycerol); and certain

maxima and minima are adopted for the constants of genuine wines; but it does not necessarily follow that these can be accepted as standards applicable to the wines made in other countries and by different methods of manufacture. Whenever possible the suspected wine should be compared with a similar wine from the same district and vintage and known to be genuine. A concise and clear *résumé* of these constants and ratios will be found in Allen's Commercial Organic Analysis, 1924, vol. i. 242-7; see also Thudichum and Dupré's Treatise on the Origin, Nature, and Varieties of Wine; Windisch's Die chemische Untersuchung und Beurtheilung des Weines; Villiers et Collin, Traité des alterations et falsifications des substances alimentaires; Leach's Food Inspection and Analysis; and Post and Neumann's Traité complet d'analyse chimique appliquée aux essais industriels. J. C.

WINE GUM v. GUMS.

WINTER GREEN, OIL OF, v. OILS, ESSENTIAL, and SALICYLIC ACID

WITGATBOOM. The dried root of *Boscea Transvaalensis*, Pest., *B. rehmanni*; *Marua pedunculata*, Sim.; and *Capparis albitrunca*, Burch. Used as a substitute for chicory in certain parts of South Africa. For the microscopic and analytical characters of the roots and their aqueous extracts, see McCrae and Klooh, Analyst, 1918, 373.

WITHANIA SOMNIFERA, a plant found in South Africa, on the west coast of India, and along the shores of the Mediterranean. The root contains an essential oil, a quantity of sugar yielding *d* phenyl-glucosazone (m.p. 210°); a black resin from which the following substances have been isolated: hentriacontane $C_{31}H_{64}$; a phytosterol $C_{27}H_{46}O$ (m.p. 135°-136°); palmitic, stearic, cerotic, oleic, and linolic acids; ipuranol $C_{22}H_{40}O_2(OH)_2$; a monohydric alcohol, *withanol*, $C_{22}H_{42}O_2(OH)$, decomposing at 305°, and having $[\alpha]_D +91.2^\circ$, and an amorphous alkaloidal principle, which, on treatment with alkalis, yielded a crystalline base, $C_{17}H_{21}N_2$ (m.p. 116°).

The leaves and stems contain, in addition, a monohydric alcohol, *somnirol*, $C_{22}H_{44}O_2(OH)$, decomposing at 205°, and having $[\alpha]_D +34.8^\circ$; a dihydric alcohol, *somnitol*, $C_{22}H_{46}O_2(OH)_2$, decomposing at about 250°, and having $[\alpha]_D +21.2^\circ$; and an acidic hydrolytic product, *withanic acid*, $C_{20}H_{38}O_4 \cdot CO_2H$ (m.p. 226°), the methyl ester of which decomposed at 255° (Power and Salway, Chem. Soc. Trans. 1911, 98, 490). These authors were unable to confirm the sedative and hypnotic properties attributed to this plant.

WITHERITE. Native barium carbonate ($BaCO_3$) crystallising in the orthorhombic system and isomorphous with aragonite and cerussite. The crystals are, however, invariably twinned, giving rise to pseudo-hexagonal forms; these may be either lenticular or pyramidal in habit, and in the latter case the six-sided pyramids present a certain degree of resemblance to crystals of quartz. Globular aggregates and compact fibrous masses also occur. The colour is white or grey; sp. gr. 4.3; H. 3½. The mineral occurs in some abundance in the lead-bearing veins traversing limestones, &c., at several places in the north of England and

on the borders of Shropshire and Montgomeryshire. It has been formed, in some instances at least, by the action of carbonated waters on barytes (L. J. Spencer, Min. Mag. 1910, 15, 310); and it is itself sometimes altered to barytes, as shown by the pseudomorphs of barytes after witherite. The best known locality, which has yielded many finely crystallised specimens, is the Fallowfield mine near Hexham; whilst the largest quantity (about 8000 tons per annum) is produced by the Settling-stones mine also in Northumberland. The mineral is also known from a few foreign localities, but only in small amounts.

Witherite is used in the manufacture of plate glass and porcelain, and for the preparation of barium dioxide (used in the manufacture of hydrogen peroxide), barium hydroxide (for refining beet-sugar), and barium salts (used, e.g. for giving the green light of fireworks). The mineral is also used for the preparation of the finer quality of barium sulphate ('blanc-fixé') used for facing glazed papers. The addition of a small proportion of witherite to clay (1 oz. per cwt.) in brick making prevents any efflorescence and discoloration due to soluble sulphates. Although insoluble in water, it is poisonous, since it is readily acted upon by the gastric juice; and the powdered mineral, mixed with meal, is used as rat poison.

References.—Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 2nd ed. 1916, vol. ii.; Barium Minerals (1913-1919), Imperial Mineral Resources Bureau, London, 1921. L. J. S.

WITT'S RULE v. COLOUR AND CHEMICAL CONSTITUTION.

WOAD (*Youssef*, Pastel, Fr.; *Waid*, Ger.). This commercial product is a dark clay-like preparation made from the leaves of the woad-plant, *Isatis tinctoria* (Linn.), an erect, herbaceous, biennial plant, belonging to the *Cruciferae*, bearing yellow flowers, small flat elliptical pods, and large smooth lanceolate or spatulate leaves.

The term 'woad' is derived from the Saxon 'wad,' which it has been suggested is derived from Woden, the Saxon God of War. It is synonymous with the Gallic *glastum*, with which, according to Pliny, the ancient Britons dyed their skin blue, in time of war and in connection with certain religious observances.

The plant is a native of Southern Europe, and from very early times has been employed in dyeing blue, for which purpose, previous to the introduction of indigo from India, it was largely cultivated in various parts of Europe—e.g. Thuringia, Languedoc, Piedmont, &c. Its cultivation has now declined almost to the vanishing-point.

In this country woad is now only grown, to a very small extent, in the fen lands of Lincolnshire and Huntingdon. The seed is sown in the early spring, March or April, and the young plants having been duly thinned and weeded, the leaves are ready for the first plucking in June, which, at intervals of five or six weeks, is repeated once or twice, or as often as fresh leaves shoot up.

The newly-gathered leaves are at once crushed or ground in edge-runner mills to a pulp, which is then placed in small heaps, to

drain, till sufficiently dry to cohere and be submitted to the 'bailing' process. This consists in working the pasty mass by hand into balls, 4-6 ins. in diameter. These are at once spread out on wicker-work trays or 'fleaks,' and thoroughly dried in well-ventilated sheds. The balls are stored in a dry airy place till the whole crop has been gathered, and are then submitted to the so-called 'couching'—i.e. a fermentation—process. For this purpose the balls are ground to a coarse powder, which is spread on the floor of the couching-house to a depth of 2 or 3 feet, and there reduced again to the consistency of a paste by frequent sprinkling with water and turning over with shovels. During this process, which lasts from twenty to forty days, the mass becomes heated and abundant offensive odours are given off. The operation needs to be conducted with some care and skill, so that the fermentation is neither so slow that a 'heavy' product is obtained, nor so rapid as to give one which is 'foxy.' When the fermentation has subsided, and the stiff, pasty mass is sufficiently cooled, it is packed in casks ready for the market.

It has been calculated that 9 parts by weight of woad leaves yield one part of the prepared product.

Although woad was formerly used for the indigo contained in it, it is at present only employed for the purpose of exciting fermentation in the indigo-vat ordinarily used by the woollen dyer, which is therefore termed the 'woad-vat.'

According to Wendelstadt and Binz (Ber. 1906, 39, 1627) woad contains two distinct micro-organisms, one of which under suitable conditions appears to be able to reduce indigo.

Spurious woad was sometimes prepared from the leaves of the rhubarb, cabbage, &c., but these products were very inferior to the true woad.

The colouring principle of woad leaves, considered by Schunck to be identical with that present in the *Indigofera*, is now known to be a distinct substance. This has not been isolated in a pure condition, but in its general reactions resembles indoxyllic acid (see INDIGO, NATURAL).

Other Literature.—Chevreul, J. Pharm. Chim. 1808, 66, 369; 1817, 350; Ann. Chim. 68, 284; Gilbert, Annalen, 41, 245; 42, 315; Trommsdorff, J. Pharm. Chim. 19, 93; Paris, Mus. Hist. Nat. Ann. 18, 251. A. G. P.

WÖHLERITE. Silicate, zirconate, columbate, and fluoride of calcium and sodium with the approximate formula $\text{Ca}_{11}\text{Na}_2\text{Si}_{12}\text{Zr}_2\text{Cb}_2\text{F}_2\text{O}_{122}$, and containing ZrO_2 15-23 p.c. The monoclinic crystals have the form of rectangular plates of a honey-yellow colour; sp.gr. 3.4; H. 6; decomposed by hot strong hydrochloric acid with separation of silica and columbic oxide. The mineral is usually regarded as a member of the pyroxene group. It occurs in nepheline-syenites in the Langesund-fjord in the south of Norway, in the Los Islands off the coast of French Guinea, and at Red Hill in New Hampshire; and in nepheline-phonolite in Haute-Loire, Auvergne. L. J. S.

WOLFRAM v. Tungsten.

WOLFRAMINE v. Tungstine.

WOLFRAMITE or WOLFRAM. A mineral

consisting of iron and manganese tungstate (Fe,MnWO_4), crystallising in the monoclinic system. The name *ferberite* is applied to the members at the iron end of the series (FeWO_4), and *hübnerite* to those richest in manganese (MnWO_4). With this wide difference in composition the percentage of tungsten varies only slightly (WO_3 , 76.3-76.6 p.c.; analyses of the pure mineral show 74-77 p.c.). The mineral fuses readily before the blowpipe to a black, magnetic bead; and it is decomposed by *aqua regia*, with the separation of yellow tungstic oxide. Distinctly formed crystals are rare, but cleavage masses are of common occurrence. There is a perfect cleavage in one direction, parallel to the plane of symmetry. The mineral is opaque with a bright, sub-metallic lustre and a dark brown to black colour; the streak is dark reddish-brown to black; H. 5½. The high sp.gr. (7.2-7.5) and the lath-shaped cleavages are characters which assist in the identification of the mineral; while the latter character helps to distinguish it from other heavy black minerals. The name wolfram originated with the old German miners, and means, apparently, 'wolf froth,' since Agricola (1546) refers to the mineral as *lupi spuma*.

Wolframite usually occurs in veins traversing granitic rocks, and is often associated with tin ore. It is, in fact, obtained commercially mainly from tin mining districts; and formerly, before the mineral was of value, it was a source of trouble to the tin miner, since having about the same density as cassiterite it could not be separated from the ore by the ordinary mechanical methods. At one time it was eliminated in a soluble form by fusing the ore with soda (Oxland's process); but now it is extracted by the electromagnet (wolframite being weakly magnetic), and it forms a product as valuable as the tin ore itself. The principal wolfram-producing countries, arranged approximately in the order of their outputs, are: Lower Burma (at Tavoy), United States (Black Hills in South Dakota, Boulder and Gilpin counties in Colorado, Arizona, Nevada, &c.), Portugal, North Queensland (at Wolfram Camp, &c.), Bolivia, Peru, Argentina, Spain, England (Bedruth, Bodmin Moor, and Gunnislake in Cornwall; Carrock Fell in Cumberland), France, Rhodesia, Siam, and New Zealand.

The mineral is used mainly for the manufacture of ferro-tungsten and the hard and tough tungsten-steel for tools and magnets of magnetos, and of some other alloys (e.g. 'partium,' an alloy of tungsten and aluminium). Metallic tungsten is used as the filament of the so-called 'osram' electric lamps; as contacts for magnetos in place of platinum; and as a catalyst in the synthesis of ammonia. Wolframite is also used for the preparation of sodium tungstate and other salts.

References.—R. D. George, 1st Rep. Colorado Geol. Survey (1908), 1909 (with bibliography); G. P. Merrill, *The Non-Metallic Minerals*, 2nd ed. New York, 1910; H. Mennicke, *Die Metallurgie des Wolframs*, Berlin, 1911; Special Reports on Mineral Resources of Great Britain, Mem. Geol. Survey, 2nd ed. 1916, vol. 1; F. L. Hess, *Tungsten Minerals and Deposits*, Bull. U.S. Geol. Survey, 1917, No. 632; T. L. Walker, Report on the Tungsten Ores of Canada, Dept. Mines,

Ottawa, 1909, No. 25; L. Hills and L. L. Waterhouse, *Tasmania Geol. Survey, Min. Res.* 1916, No. 1; L. O. Ball, *Geol. Survey, Queensland*, 1915, Nos. 248, 251; R. H. Rastall, *The Genesis of Tungsten Ores*, Geol. Mag. 1918, 194, 367; Occurrence and Utilisation of Tungsten Ores, Bull. Imp. Inst. London, 1909, 7, 170, 285; J. J. Runner and M. L. Hartmann, *The Occurrence, Chemistry, Metallurgy, and Uses of Tungsten*, with special reference to the Black Hills of South Dakota, Bull. South Dakota School of Mines, 1918, No. 12, 264 pp.; R. H. Rastall and W. H. Wilcockson, *Tungsten Ores*, Imp. Inst. Monographs, London, 1920; Tungsten (1913-1919), Imp. Mineral Resources Bureau, London, 1921. L. J. S.

WOLLASTONITE. Calcium metasilicate CaSiO_3 , crystallised in the monoclinic system, and belonging to the pyroxene group (q.v.) of rock-forming minerals. It differs, however, from the other members of this group in the directions of its cleavages, which are here along two planes perpendicular to the plane of symmetry and inclined to one another at $84^\circ 37'$. The mineral is white and opaque, sometimes with a pearly or silky lustre; sp.gr. 2.88-2.92; H. 5; decomposed by hydrochloric acid with separation of silica. It is a mineral of metamorphic origin, occurring in siliceous limestones that have been baked by intruded masses of igneous rocks. Bladed crystals are found in the limestone blocks ejected by Vesuvius, and large crystals, up to 10 inches in length and partly or wholly altered to quartz and opal, at the Santa Fé mine, in Chiapas, Mexico. Here, as is often the case elsewhere, the mineral is associated with bodies of metalliferous ores (H. F. Collins, *Min. Mag.*, 1903, 13, 356). The name wollastonite is after William Hyde Wollaston (1766-1828).

When heated, wollastonite changes at 1190° into the β -modification called pseudo-wollastonite (m.p. 1540°), which has been long known in slags and devitrified glasses under the name hexagonal calcium metasilicate. The latter has not been observed in nature, and the presumption is that wollastonite has been formed in contact-metamorphic limestones at a temperature below 1190° (E. T. Allen and W. P. White, *Amer. J. Sci.* 1906, 21, 89; 1909, 27, 1; A. L. Day and R. B. Sosman, *ibid.* 1911, 31, 341). L. J. S.

WONGSKY, WONGSHY, WONGSCHY, HOANG TCHY. A Chinese yellow dyestuff. It consists of the fruit of the *Gardenia grandiflora*. According to Rochleder (J. 1858, 475), it contains *rubichloric acid* (see Madder) and *crocin*, the glucoside of *Crocinin*, which is also present in saffron (*Crocus sativus* [Linn.]). Wongsky dyes aluminium and tin mordanted fabrics a yellow, whereas with iron mordant an olive colour is produced.

WOOD APPLE GUM v. GUMS.

WOODBURYTYPE v. PHOTOGRAPHY.

WOOD, DESTRUCTIVE DISTILLATION OF.¹

Wood completely freed from water has the following composition:—

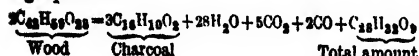
Carbon, 50 p.c.
Hydrogen, 6 p.c.
Oxygen, 42.75 p.c.
Ash, 1.25 p.c.

¹ M. Klar, *Technologie der Holzverkohlung*, 1919 Second Edition. Julius Springer, Berlin.

The chemical nature of wood may be said to consist principally of cellulose, lignin, water, and of ash-forming materials.

The lignin in wood may be oxidised and removed by treatment with chlorine dioxide (Schmidt and Graumann, *J. Chem. Soc. Abstr.* 1921, [I.] 912; A. C. von Euler, *Cellulosechem.* 1923, 4, 109; *Chem. Soc. Abstr.* 1924, 126, [ii.] 129).

If wood is heated in a closed vessel with the air partly or entirely excluded and the vapours and gases are allowed to escape, the cellulose and lignin molecules are broken up by processes, the nature of which is little understood, but which are characterised by the formation of charcoal, which is left as a residue, and by the formation of gases and vapours, the latter of which, when condensed, is known as pyro-ligneous acid. P. Kason, Heidenstam and Norlin¹ concluded that the destructive distillation of wood may be represented by the follow ing equation:—



of products, contained in the pyro-ligneous acid, in the tar, and in the wood gases.

They proved further that the destructive distillation of cellulose forms the most important products, viz. charcoal, acetic acid and tar; whilst lignin forms principally charcoal, acetic acid, wood alcohol and tar.

The destructive distillation of wood is occasionally carried out for the purpose of producing charcoal only, but at present it is more frequently the case that the by-products, acetic acid and the wood alcohol, are the most important substances yielded.

As regards the value of various kinds of wood for the process of destructive distillation, it has been shown that hard woods give the best yields of charcoal, acetic acid, and wood alcohol, whilst soft woods give smaller amounts of these products. Soft woods, however, show a larger yield than pine wood, which yields, besides the above-named products, a certain amount of turpentine, pine oils and pine tar oils. Local market conditions must decide in each case what is the most desirable wood for the purpose.

All wood for destructive distillation is split into cord-wood averaging 6 ins. in diameter and 4 ft. long. This initial preparation is usually carried out in the forest, but at manufactories recently erected in the United States large logs are brought to the saw mill where all the timber is utilised, and only those logs unfit for other purposes are used for cord wood. The cord wood is stacked in an exposed situation if possible, where it is allowed to dry and season for about 18 months, after which the moisture content will be found to be quite constant. The length of time required for this seasoning varies with the climate, and although it is thought that the moisture content of 20 p.c. is the most desirable, it is frequently found necessary to use wood containing 30 p.c. or more. A high percentage of moisture in the wood is undesirable owing to the fact that it delays the distilling process, decreases the

yields of acetic acid, wood alcohol and charcoal, whilst at the same time it increases the amount of noncondensable gases and also the amount of fuel used for the purpose of supplying heat for the distillation.

The process of destructive distillation is carried out in closed vessels built of brick or iron, and heated either by allowing the products of combustion to come directly in contact with the wood, excluding any excess of air; or by transmitting the heat through the walls of the vessel. In either case the distilling apparatus is connected with a condenser, the purpose of which is to condense the vapours formed during the reaction.

The apparatus for the destructive distillation of wood may be said to consist of three principal parts:—

1st. The container for the wood.

2nd. The arrangement for generating and supplying the heat to the container.

3rd. A condenser connected with the container by an intermediate vapour pipe.

After the wood has been placed in the distilling apparatus and the heating started, the water contained in the wood is first driven off; when this is accomplished the destructive distillation of the cellulose and lignin begins and will be indicated by the formation of non-condensable gases and by the appearance of the so-called pyro-ligneous acid, a brown liquor of characteristic odour, in which considerable tar is found. When the temperature reaches 270° an exothermic reaction sets in which supplies most of the heat necessary for the distillation process. The end of the process will be indicated by the cooling of the pipe which connects the distilling apparatus with the condenser.

In carrying out this distilling process on a commercial scale, the three phases of the distillation, namely: the expulsion of the water, the heating of the wood to the point at which the exothermic reaction sets in, and the completion of the process by means of the above-named reaction, will not necessarily take place consecutively, owing to the fact that the large-sized apparatus used will not allow the heat to be transmitted uniformly to all the wood in the vessel. Hence part of the wood situated near the heating surface may be in the third phase of the process, whilst that not so near the source of heat may be still in the first phase.

In general, yields of various products from air-dried hard wood in percentage by weight will be as follows:—

Charcoal, 25 to 27 p.c.

Crude pyro-ligneous acid, 45 to 50 p.c.

Gases, 25 to 28 p.c.

The composition of the charcoal will be variable, depending upon the process used and particularly upon the temperature at which the distillation has been finished. The following table gives the composition of charcoal produced by several processes:—

Process	P.c. C	P.c. H	P.c. O+N	P.c. ash	Temp- erature
Old 'Meller' process	80.36	8.74	8.72	1.7	above 500°
Kiln process	84.18	8.28	11.72	5.72	450°
Retort process	81.15	6.24	12.44	9.79	350°

¹ *Ark. Acad. Min. u. Geol.*, 1908, Bd. 3, 2.

The *crude pyroligneous acid* will be found to be composed chiefly as follows:—

Water, 81 p.c.

Wood alcohol, 3 to 4 p.c.

Acetic acid, 6 to 8 p.c.

Dissolved and suspended tar, 7 p.c.

Other compounds contained, such as aldehydes, ketones, allyl alcohol, amines, phenols, and hydrocarbons are not of commercial importance and are of interest only in the refining of wood alcohol. The wood tar obtained from hard wood has little commercial value and is generally used as fuel. Small amounts, however, are used for the manufacture of creosote and wood tar pitch.

The *non-condensable gas* obtained by the destructive distillation of wood, amounting to 25–28 p.c. of the weight of the wood, varies in composition during the different phases of the process, and is composed on an average of carbon dioxide, 60 p.c.; carbon monoxide, 30 p.c.; hydrogen and hydrocarbons, 10 p.c. This gas is generally used for heating the retorts or boilers, and its heating value is equivalent to about 4–5 p.c. of the heating value of the wood decomposed in the process of distillation.

DESTRUCTIVE DISTILLATION OF PINE WOOD

The destructive distillation of pine wood containing rosin and turpentine, besides the cellulose and lignin, will produce products

different from those obtained from hard wood. The turpentine being volatile with water vapour is almost completely distilled over during the first phase of the distillation. In this phase, also, the rosin melting and flowing from the wood cells, covers the surface of the wood and the bottom of the distillation retort. During the second phase, this rosin will be decomposed, yielding such products as pinoline, rosin oils, and a residue of rosin coke. The pinoline will be mixed, more or less, with the turpentine originally contained in the wood, the rosin oils will combine with the tar formed in the usual course of wood distillation, and the rosin coke will be mixed with the charcoal. The mixture of turpentine and pinoline is known as *crude wood turpentine*. The presence of the rosin oils in the pine wood tar gives it a peculiar orange colour when painted on wood, which property makes it of considerable value. The amounts of acetic acid, wood alcohol and charcoal obtained from pine wood are considerably less than in the case of hard wood distillation.

An active demand for wood turpentine, for pine wood tar and pine wood tar oils, with good prices for these products and cheap prices for the wood, may cause, under certain circumstances, pine wood to be preferred to hard wood. But these conditions will not be frequent, and since the yields of acetic acid and wood alcohol and also of charcoal are considerably less, as the container can be filled with a larger weight

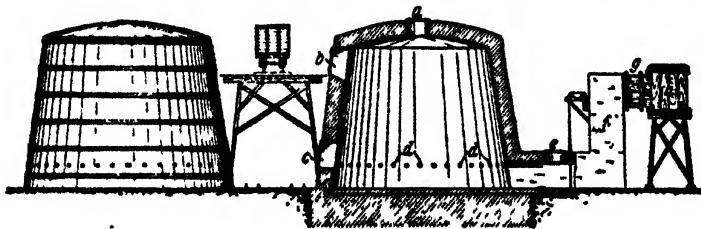


FIG. 1.

Brick wood-distilling apparatus for an 80-cord charge heated by burning a portion of the charge.

of hard wood than of pine wood (on account of the lower specific gravity of the latter), the efficiency of a distilling plant using hard wood is higher than one of the same size employing pine wood.

VARIOUS FORMS OF DISTILLING APPARATUS FOR CORD WOOD.

The number of forms of apparatus actually used for this purpose is large, and still larger is the number of designs which have been described in the literature or by patents taken out in different countries.

Only the most important types in practical use are given in what follows.

I. Distilling Apparatus made of Brick.

a. *Charring of the wood in brick kilns by fire gases which come directly in contact with the wood.*

1. *Fire gases generated inside the distilling apparatus by burning a part of the charge.*—To this type belongs the so-called 'American kiln,' seen in Fig. 1. This apparatus consists of a brick chamber, of about 15,000 cub. ft. capacity,

holding 80 cords of wood filled in by a top iron door *a*. There is a bottom iron door provided for discharging the charcoal. 4 ins. \times 4 ins. air inlet holes *d, d* are provided in the lower parts of the wall, and a couple of these kilns are connected by a brick goose neck *e* with the main smoke pipe, mostly built of wood. This main smoke pipe connects the kilns with the condenser plant *f g h*, and a fan is used for transporting the vapours and the gases from the kilns to the condensers and also for supplying the kilns with a certain amount of air, sufficient to generate the heat required for the destructive distillation of the wood by burning a certain amount of the wood, but avoiding any excess of air.

In the large plants at work in Michigan, often as many as 80 kilns are connected with condensers, using as much as 250 cords of wood per day, and condensing up to 50,000 gallons of crude pyroligneous acid. Unfortunately these kilns do not afford the proper amount of volatile by-products (acetic acid and wood alcohol) and about 50 p.c. of the possible yield is lost by being burnt to carbon dioxide and water. These kilns should only be used when wood is very

cheap and fuel and labour prices high and when there is not much demand for calcium acetate and wood alcohol. As these conditions seldom coexist, the kiln system must be considered wasteful and should be no longer used.

2. Fire gases are generated outside of the distilling apparatus by fuel (mostly wood) in a special fireplace and conducted from there to the wood — Fig. 2 represents such a type, originally known

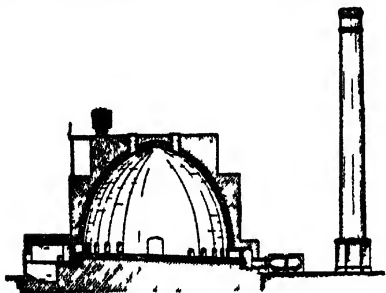


Fig. 2

Brick wood-distilling apparatus according to Schwartz heated by a special open fire

as the 'Schwartz kiln'. The Swedish kilns of Ljungberg and of Ottelinska are of a similar type.

b. Heating the wood in brick kilns by fire gas which, passed through radiators, transmits the heat by radiation to the wood

Inside a brick chamber, cast iron or steel radiators are provided, through which fire gases are passed, which transmit the heat by radiation to the wood surrounding these radiators

The oldest type of this kind of a wood distilling apparatus is represented by the 'Reichenbach kiln.'

Sweden developed a new form of this type called the 'Tube Oven,' seen in Fig. 3

These brick kilns do not permit the charcoal to be discharged immediately after the distillation is finished. In fact, every hole of the oven

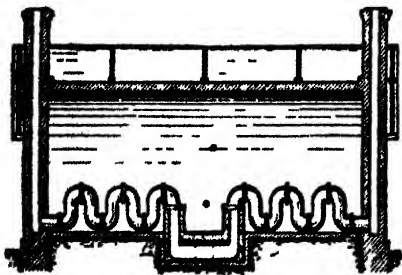


Fig. 3

Brick wood-distilling apparatus heated by steel coil radiators

has to be closed by bricks so as to allow the charcoal to cool with absolute exclusion of air. This cooling process requires, in the case of large sized kilns (50 cords or more), as much as eight days, and the efficiency is decreased correspondingly. In order to discharge the charcoal from kilns heated by radiators, immediately after the close of the distillation, the wood must

be loaded on iron cars capable of being pulled or pushed into the brick container. After the distillation is finished the cars, loaded with hot charcoal, are pulled out quickly and transferred to a steel chamber of the shape of the brick container, when cooling will not require more than 24 to 48 hours. After the cars are withdrawn, other cars, already loaded with new wood and ready for charging, will be put into the brick chamber, still hot by the previous operation

These brick kilns, heated by radiators, charged and discharged by iron cars, are the newest form of brick distilling apparatus.

A distilling apparatus built of brick is cheaper to build and possibly cheaper to maintain, but gives lower yields than steel apparatus as regards acetic acid and wood alcohol

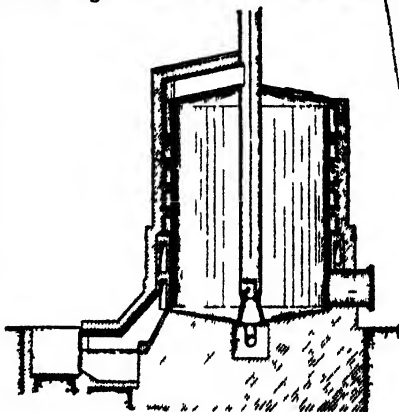


Fig. 4

Vertical steel wood distilling apparatus for large charges, heated by fire gases circulating around the steel container, called 'Carboven', used in Sweden

on account of the difficulty of preventing the brick walls from leaking

II. Steel Distilling Apparatus.

A. Intermittently operated apparatus.

The most important representative of this type is the Swedish 'Carboven,' shown in Fig. 4. This apparatus can be loaded with 100 cords of wood, and will require about three weeks for filling, distilling, cooling and discharging.

A couple of inner vertical heating tubes, instead of one large one, is the characteristic feature of the modern steel distilling apparatus,

B. Apparatus for discharging the charcoal immediately after the close of the distillation without cooling the charcoal before discharging.

1. Horizontal types — a. Apparatus for small charges. — To these belong the distilling apparatus, generally called 'retorts,' largely used in the past and still employed in Germany, Austria, Russia, Pennsylvania, and other countries or states. These retorts are about 30 ins. in diameter by 10 ft. in length, are round in section, and contain $\frac{1}{2}$ cord wood. But they are also built for one cord capacity. Usually, one set

of these retorts is heated by the same fireplace, the products of combustion being conducted around the horizontally placed steel cylinders. One side of the retort is provided with a cast-iron door, the other tight end with a nozzle which serves to connect the retort with a condenser (see Fig. 5).

The wood is loaded by hand into these retorts. Inside the retort there is a semi-circular scraper, which is pushed to the rear before the retort is loaded and is provided with a rod with a handle ending near the door. After

the distillation is finished, a steel container is placed underneath the front of the door. The door is opened, and by means of the scraper the hot and burning charcoal is quickly emptied into the steel container, the cover of which is then closed air tight. A new charge is loaded immediately after discharging. While the new charge is distilling, the charcoal cools inside the container, which is built of thin sheet steel.

As one of these 39 ins. \times 10 ft. retorts can handle only $\frac{1}{2}$ cord of wood in 24 hours, this type of distilling apparatus is not well adapted for

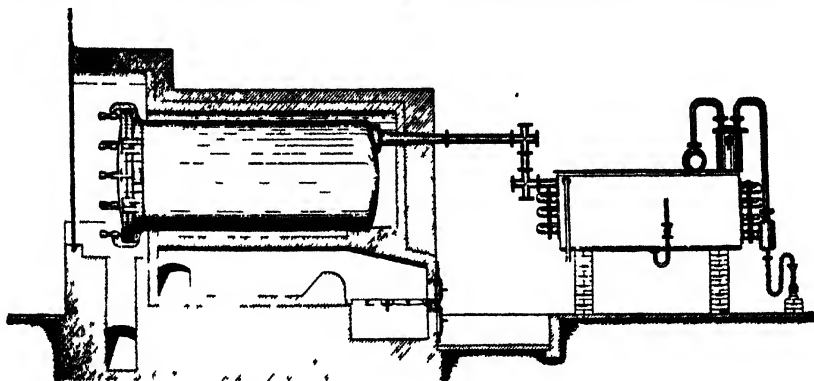


FIG. 5.

Horizontal steel retort for small charges; type, F. H. Meyer, Hanover-Hainholz.

the destructive distillation of wood on a large scale.

These small, horizontal retorts have the further disadvantage that the scraper used in discharging them causes much of the charcoal to be broken into small pieces. The charging of the retort by hand also requires many workmen, causing loss of time and decreasing the efficiency of the plant.

β. Wood distilling apparatus for large charges arranged for mechanically charging and discharging—The disadvantages above mentioned may

be avoided by employing retorts of large capacity, provided with mechanical contrivances for filling them with wood and also for discharging the charcoal. The distilling apparatus which meets these conditions best is the so called 'car retort.' A distilling apparatus of this kind consists of a horizontal steel retort, capable of working off a charge of 6 to 10 cords of wood (see Fig. 6). The wood is loaded on cars which are pulled or pushed into the retort; this has rails on the bottom and, according to its capacity, one or two doors for filling and

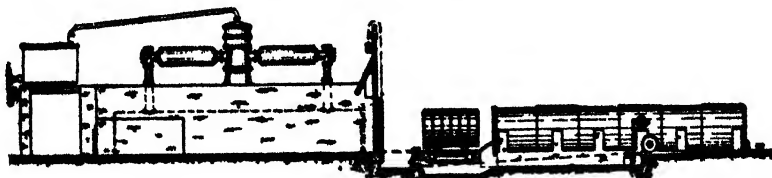


FIG. 6.

Horizontal steel retort, filled and discharged by cars; for charges up to 10 cords; type, F. H. Meyer, Hanover-Hainholz.

discharging. Each car, made of steel, contains usually two cords of wood. The retort is connected by necks with one or two condensers of the usual tube type. The heating of these retorts is mainly effected by an open wood or coal fire and, to some extent, also by burning the tar and the gases obtained in the destructive distillation of the wood. The combustion gases travel by flues round the retort and escape in a smoke stack. The heating by an open fire has lately been replaced by producer-gas, obtained either in the usual way, that is generated by gas producers, or as a by-product in

the destructive distillation of the wood. A gas-heated retort will last longer, will use less fuel, and will yield higher results. The question of the best kind of gas producer for this purpose is dealt with later. After the distillation is finished the doors of the retort are opened and the cars, containing the hot charcoal, withdrawn and transferred as soon as possible to a horizontal steel cylinder, exactly corresponding in shape with the retort and also provided with doors for filling and discharging. The withdrawal of the cars is mostly done by means of a locomotive or by means of transportable electric

or steam hoists, and has to be done quickly in order to avoid the combustion of the charcoal. After the cars containing the hot charcoal are transferred to the horizontal steel cylinder, placed opposite the retort, the doors of the cylinder are closed air tight and the charcoal allowed to cool with exclusion of air. The cooling requires, according to the weather and character of the wood, from 24 to 40 hours.

This kind of wood-distilling apparatus further allows of the preliminary heating of the wood before filling it into the retort, by means of the waste combustion gases, which escape from the last retort flue into the smoke stack. In order to utilise this waste heat, the cars loaded with the wood are placed in a brick channel located opposite the charging door of the retort. The waste combustion gases are driven over the wood by means of a fan.

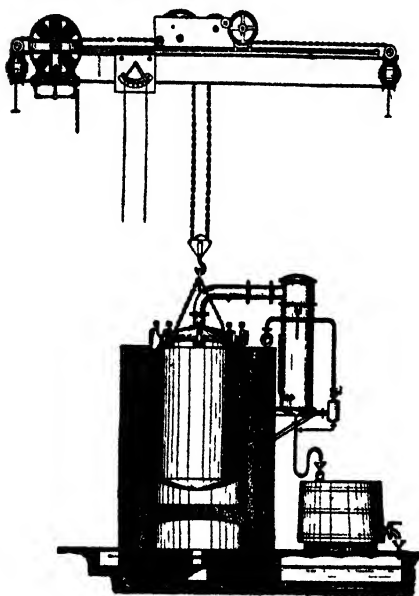


FIG. 7.

Vertical portable retort; type, F. H. Meyer, Hanover-Hainholz.

Fig. 6 shows a modern distilling apparatus, having a higher efficiency than any other wood-distilling apparatus in practical operation.

A charge of 10 cords of wood is worked off in 24 hours, including filling, distilling and discharging, and it requires also very few workmen to attend to the firing, charging and discharging. By discharging the charcoal in a cold state and without the use of scrapers, a better class charcoal is obtained with the production of only a very small amount of powder or small pieces.

A revolving retort of a capacity corresponding to a charge of 6 to 10 cords of wood has been tried but discarded on account of the difficulty of contriving proper outlets and of keeping these outlets tight. Moreover, revolving retorts gave, of course, large amounts of charcoal powder and small charcoal.

2. Vertical steel retorts.—Vertical steel retorts, either built stationary or transportable, are in use in Germany, Belgium, France, Italy,

and also in Russia. France, in particular, is the country of vertical retorts, which are almost always constructed as transportable ones. These retorts contain a charge of 1 to 1½ cords of wood and are heated by an open fire or by a gas fire from underneath (see Fig. 7). They are filled outside of the settings, after being placed in a horizontal position. After the retort is loaded and closed it is lifted, by means of a travelling crane, above the open space in the settings to which the retort belongs. Then the retort is lowered into its place and its cover connected, by means of a copper goose-neck, with the condenser. After the distillation is finished, this copper goose-neck is taken off, the goose-neck hole in the cover closed, and then the whole retort is lifted out of the settings by means of the crane and transported outside of the building, placed in a horizontal position and then allowed to cool down, which will require from 12 to 24 hours, according to the charge and the weather. These retorts give good yields and afford good charcoal, but their efficiency is not so good as that of the car retorts already described.

Sometimes these vertical retorts are constructed stationary and provided with a charcoal discharging door on the bottom. They are not as convenient as the transportable ones and do not give the same quality of charcoal, because the discharging is done by dumping, which causes breakages of the charcoal.

C. Continuously-working wood-distilling apparatus.

The distilling apparatus above described is either operated intermittently or only partly continuously.

But there are some types of distilling apparatus which are designed for continuous working as, for instance, the Swedish Groendal retort, which belongs to the type of the car retorts described on p. 493.

The Groendal retort consists of three main parts, namely:

1st. The drying chamber, built either of brick or of steel.

2nd. The distilling apparatus consisting of a horizontal steel retort.

3rd. The cooling apparatus for the charcoal, consisting of a steel cylinder of the shape of the retort.

These three parts are connected together but can be separated one from the other by means of vertical sliding doors of iron. The wood, loaded on cars, is filled in the drying chamber through which the exhaust combustion gases, escaping from the retort flues, are passed. After the drying is complete, the sliding doors between this drying chamber and the retort are lifted and the load transferred into the distilling zone of the system. This distilling apparatus is heated by any kind of heat generated by open fire or gas producers. The combustion gases travel around the steel shells, thus transmitting the heat to the wood inside the shell.

After the wood cars have passed the distilling part of the system, another slide door is opened and the cars with the finished charcoal are transferred into the charcoal cooling chamber, through which the cold non-condensable gases,

escaping from the condensers of the wood-distilling apparatus, are passed in order to do the cooling work and preheat the gases. A double sliding door at the other end of the system allows the cooled cars with the cooled charcoal to be continuously passed out.

Another continuously working wood-distilling apparatus which may be mentioned here is the wood-gas producer, which, however, does not yield any charcoal. This wood-gas producer is used for the generating of heating gas from second-class cord wood or wood refuse in order to heat boilers and retorts, but also to recover, at the same time, the by-products of the destructive distillation of wood, viz. acetic acid and wood alcohol. These gas producers (Fig. 8) consist of a vertical brick or brick-lined steel furnace provided on the top with a funnel with double doors for filling the gas producer with wood while in work. The bottom of this

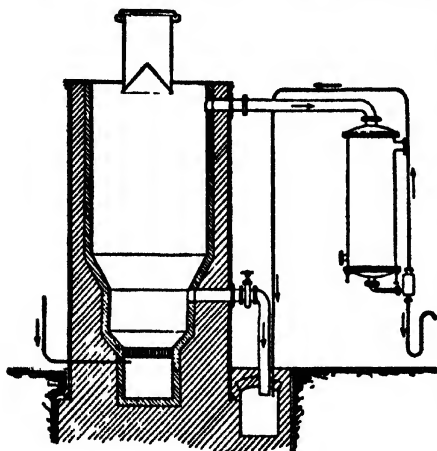


Fig. 8.

Wood-gas producers; type, F H Meyer, Hanover-Hainholz.

gas producer is provided with an iron grate through which a certain amount of air is allowed to enter. The upper part is connected with a condenser. In order to start the gas producers, charcoal has to be put upon the grate and allowed to become red hot. Then the filling in of the wood is started by means of the double-door funnel above-mentioned. The condenser, connected with this gas producer, communicates by means of a gas flue with the smoke stack of the boilers or the retorts, and by the natural draught of this smoke stack a certain amount of air enters through the grate into the gas producer, generating producer gas when coming in contact with the hot charcoal. This hot producer gas carbonizes the wood on the top of the charcoal zone on its way up to the outlet, and forms, at the same time, the products of the destructive distillation. These escape, together with the producer gas obtained by passing air through the hot charcoal layer, into the condenser, and while the non-condensable gases escape by the main gas flue, the vapours of pyroligneous acid and of tar are condensed and discharged by means of a siphon. In such a gas producer, there will be a hot charcoal zone on

the bottom, above this there will be wood in the distilling state, and above this zone there will be another zone of wood in the drying period, and on the top of this drying zone there will be the zone of the green wood, filled through the funnel.

These gas producers are not very efficient; they yield no charcoal and only 50 p.c. of the amount of acetic acid and wood alcohol obtainable from the same amount of wood when distilled in retorts. But considering that they produce heating gas and at the same time allow 50 p.c. of the acetic acid and the wood alcohol to be recovered, they are important and economical in working under favourable conditions.

Apparatus for the destructive distillation of pine wood, rich in turpentine and rosin.—As already mentioned, some varieties of pine wood contain, besides cellulose and lignin, large quantities of rosin and turpentine.

As it is the purpose of the pine wood distillation to separate the turpentine in its original state as much as possible before the destructive distillation of the cellulose, lignin and rosin sets in, the apparatus for the destructive distillation of pine wood of this kind must be provided by a heating system which allows a uniform transmission of heat to any and every part of the wood contained in the retort, or which at least allows the temperature to be under control.

It has been proposed to heat the retorts for this purpose by electricity instead of by an open fire or by superheated air or gases circulating around the retort; by oil or metal bath contained in a double jacket; or by superheated steam brought directly in contact with the wood.

These proposals are still in the experimental stage, but it would seem that these methods of heating are too expensive, inasmuch as a carefully designed gas-heating system, using gas, producer gas, or natural gas, will do the same work more economically.

Any one of the apparatus already described may in general be employed for pine wood distillation. But for recovering the turpentine in its original state, or at least not very much contaminated with the products of the destructive distillation of the wood and rosin, the smaller units (6 cords capacity) of ear retorts, heated by means of uniformly distributed gas burners, are most to be recommended.

DESTRUCTIVE DISTILLATION OF WASTE WOOD OR SPENT WOOD.

The splitting of the logs and cutting these into cord wood furnishes a large amount of small-sized wood waste. Also cutting the log into timber and working up the timber furnishes another class of waste wood known as slabs, edgings, shavings, sawdust, and so on.

As long as this wood waste consists of pieces large enough to furnish charcoal of the usual size, it can be handled just as cord wood in the standard retorts, and it will yield almost the same amount of charcoal, wood alcohol and calcium acetate as cord wood obtained from the same log, when these figures are referred to the weight and not to the volume of the wood, as a cord of slabs or edgings will weigh very much less than a cord of real cord wood.

With regard to the destructive distillation of

sawdust or shavings, this raw material is not capable of being distilled in any one of the standard apparatus previously described, on account of its voluminous character or by reason of the fact that there is not enough air space between the small, single wood pieces whereby the escape of the vapours and gases, formed on distillation, is rendered impossible. Back

pressure, and under unfavourable circumstances even an explosion, will be the consequence of trying to distill sawdust or other wood of this form in the standard wood distilling apparatus.

There have been numerous proposals to distill sawdust or other fine wood, and almost every one of these proposals is based either on the use of thin layers of sawdust or the use of stirring

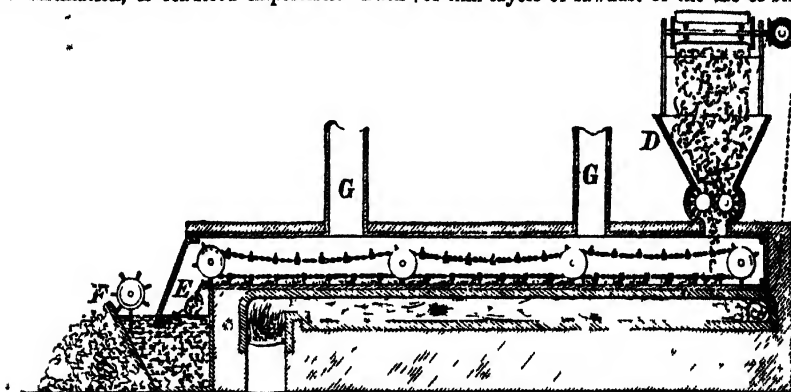


FIG. 9.

Retort for distilling small wood waste

contrivances, or of a combined system of thin sawdust layers and stirring contrivances or scrapers, or finally on the briquetting of the sawdust before it is distilled.

None of these apparatus has taken a practical form, at least on a large scale up to the

price, for the large quantities of charcoal powder produced.

Figs 9 and 10 show types of apparatus which are used for this purpose. The apparatus (Fig. 9) transfers the sawdust continuously by means of scrapers over fire heated steel plates, while in the apparatus in Fig. 10 the sawdust continuously drops down in thin layers by its own gravity between the space of the fire-heated shell of the vertical retort and the cast iron rings, which serve as outlets for the vapours and gases.

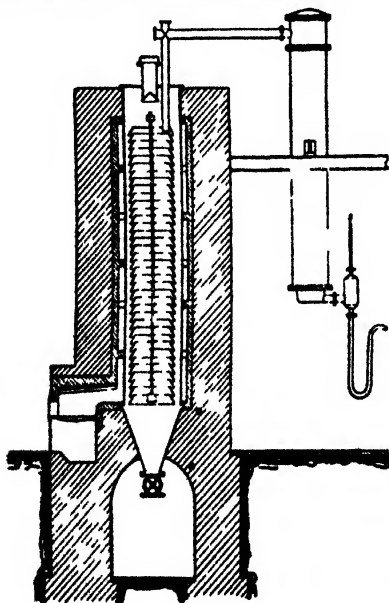


FIG. 10.

Vertical retort for the continuous distillation of small wood waste, type, F. H. Meyer

present time, neither small nor large plants which handle sawdust or a similar class of wood, are operated economically on account of the large initial outlay, which is out of proportion to the value of the output and on account of the fact that there is no market, at a sufficient

TREATING THE CRUDE PYROLIGNEOUS ACID.

Crude pyroligneous acid consists of a watery solution containing acetic acid, wood alcohol and its companions (aldehydes, ethers, ketones, allyl alcohol, phenols) and tarry matters in solution. This brown liquid is further mixed with tar in suspension.

Crude pyroligneous acid cannot be sold in large quantities, but acetate of lime and crude wood alcohol are in large demand.

The object of treating the crude pyroligneous acid is to separate the acetic acid and the wood alcohol from the water and the tarry materials.

First the tar, suspended in the liquid, is separated by allowing the liquor to stand. The tar will settle either on the top or on the bottom of the pyroligneous acid and is then drawn off.

But the remaining liquid still holds tar in solution and this dissolved tar must be separated in order to make marketable acetate of lime, which must contain at least 80 to 82 p.c. $(\text{CH}_3\text{COO})_2\text{Ca}$.

There are several methods employed in order to separate the tarry matters in solution or suspension from the crude pyroligneous acid. The oldest process, still in use in some plants, consists in a simple redistillation of the crude pyroligneous acid in copper stills, connected

with a condenser and heated either by an open fire or better by a steam coil (Fig. 11). The tar remains as a residue. The distillate is a more or less water-white liquid, which is now practically free from tar and contains principally water, acetic acid, wood alcohol and its associated products above mentioned.

This method of removing the dissolved tar by simple distillation requires about 50 p.c. of

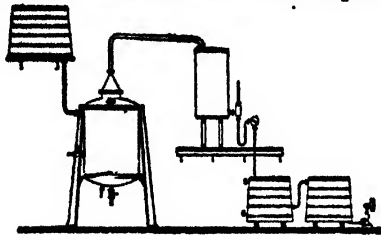


FIG. 11.

Apparatus for distilling crude pyroligneous acid; type, F. H. Meyer.

the total amount of fuel or steam generated in a wood-distilling plant.

The author of this article introduced new methods of distillation of the crude pyroligneous acid, and up to date the crude pyroligneous acid of about 1000 cords of wood is so treated.

This process is based on the principle of the multiple effect evaporators, originally used in the manufacture of sugar (Fig. 12). Two or

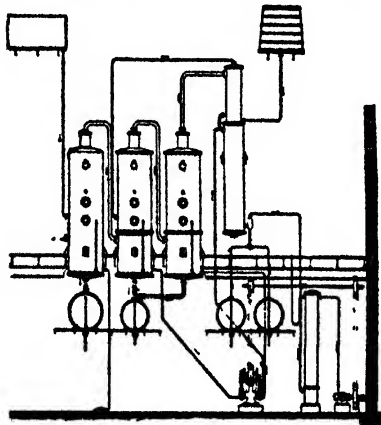


FIG. 12.

Apparatus for continuous distillation of crude pyroligneous acid in multiple effect distillers; type, F. H. Meyer.

more distilling stills are used, one connected with the other and provided with contrivances to maintain a different but gradually lowered boiling-point or a different but gradually lowered working pressure in each one of the stills. For instance, still 1 will be heated by steam of 15 lbs. pressure, using a steam coil or any other heating contrivance.

The liquor, surrounding this steam-heated contrivance, is kept under atmospheric pressure. The pyroligneous acid vapours, generated in still 1 by means of the heating effect of the steam, enter the heating contrivance of the second still, kept under a lower pressure by means of vacuum and therefore a lower

boiling-point of the liquid than in still 1. Therefore the pyroligneous acid vapours, escaping from the first still, heat and distil the crude pyroligneous acid in the second still. This system can be continued indefinitely theoretically, but a system of four combined stills is all that can be reached practically.

A distilling apparatus of this type requires only one-third of the amount of steam or fuel hitherto used for distilling the crude pyroligneous acid in simple distilling apparatus; or the saving may amount to 100 p.c. when sufficient exhaust steam is available. Fig. 12 shows such an installation, based on the multiple effect distilling system.

Besides these two processes, used for redistilling the crude pyroligneous acid, there is another, employed more particularly in German plants.

This process combines the distillation of the crude pyroligneous acid with the neutralisation of the tar-free distillate by means of milk of lime or soda ash and the separation of the wood alcohol from the acetate solution.

The pyroligneous acid is distilled in a copper still, heated by a steam coil. Instead of passing the vapours of pyroligneous acid into a condenser, they are forced through milk of lime or soda ash solution, contained in closed copper or iron tanks, which are connected with a condenser (Fig. 13). The acetic acid thus combines with the lime or the soda, forming acetate solutions, whilst the wood alcohol and water vapours escape to the condenser from which an aqueous solution of the alcohol is discharged containing 5 to 12 p.c. wood spirit.

All the processes described above for removing tarry matters before treating the pyroligneous acid with milk of lime or soda ash solution, are based on the *distillation principle* and handle the gross distillate discharged from the condensers connected with the wood distilling apparatus.

The writer has introduced another patented process which is not based on the redistillation of crude pyroligneous acid, but depends on separating the total amount of tarry matters from the vapours escaping from the wood-distilling apparatus *before* these vapours are condensed. This is effected by washing the vapours and gases by means of crude wood tar or a mixture of crude wood tar and pyroligneous acid in two or more gas washing apparatus, which are combined together, and maintaining in each one a gradually decreasing temperature.

For instance, in the tar washer 1, a temperature of about 300°F. may be maintained and in the last tar washer, or the washer next the condenser, a temperature of 212°F. may be maintained.

By the combined effect of the fractional condensation of the tar and of the absorbing affinity of the large amounts of tar used as a washing liquid, for the small amounts of tar contained in the form of vapours in the products, the pyroligneous acid discharged from the condenser will be practically free from tar and ready to be neutralised by milk of lime or soda ash.

This process is successfully used in many wood-distilling plants and saves entirely the expense of the redistillation of the crude product.

MANUFACTURE OF ACETATE OF LIME FROM CRUDE PYROLIGNEOUS ACID.

As already mentioned, grey acetate of lime, 80 to 82 p.c., is the product into which the acetic acid, contained in the pyroligneous acid, has to be transformed for the purposes of shipment.

The manufacture of grey acetate of lime starts with the tar-free distillate, obtained from the crude tar containing pyroligneous acid by one of the processes already described. This distillate is neutralised either by mixing it with milk of lime in a wooden tank, provided with a stirrer and cover, or by passing the vapours through layers of milk of lime.

The milk of lime combines with the acetic acid; it partly saponifies any methyl acetate; it transforms some of the aldehydes into insoluble resins; and it combines with phenols, forming insoluble lime compounds. After adding the milk of lime, the neutralised liquor is allowed to stand in order that the precipitates, formed by the neutralising processes, shall settle.

The next operation on the settled liquid, containing principally wood alcohol and its associates, acetate of lime and water, consists in separating the wood alcohol from the aqueous solution of the acetate of lime, either in form of a weak alcohol solution by means of a simple intermittently operated still, or in form of

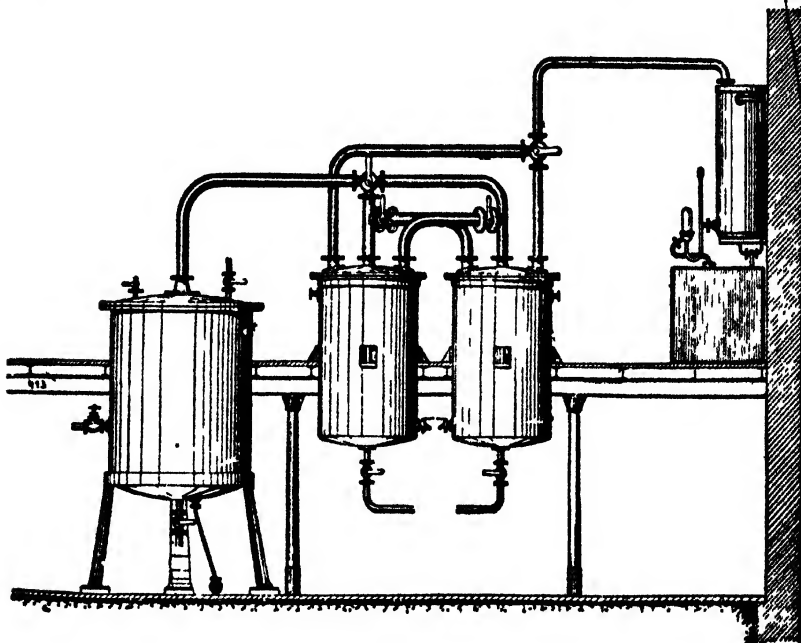


FIG. 13.

Apparatus for distilling crude pyroligneous acid by passing acid vapours through layers of milk of lime; type, F. H. Meyer.

concentrated wood alcohol by means of an intermittently or continuously operated rectifier.

The simple distilling still furnishes a weak wood alcohol solution, containing from 8 to 10 p.c. of wood alcohol, whilst the rectifier turns out by a single operation crude wood alcohol from 30 to 95 p.c., depending upon the design of the rectifier.

The simple still consists of a steel or copper still, provided with a copper heating coil and connected with a condenser.

The intermittently operated rectifier, shown in Fig. 14, is built of a steel or copper still with a copper heating coil, a copper column with rectifying sieve or bell plates, a separator and condenser. The working principle of these rectifiers is based on fractional distillation, and the 'columns' used for this purpose are very similar to those employed in manufacturing grain alcohol and known as the 'Savalle apparatus' from the name of the inventor. The

continuously working rectifiers, for separating the crude wood alcohol in a concentrated state from the neutralised liquor, are the most modern and most economically working apparatus for this purpose (Fig. 15). They have been introduced in the wood-distilling industry by the author of this article, and they furnish by a single operation the so-called 'crude wood alcohol' of 95 p.c. and separate at the same time the oils, originally contained in the neutralised liquor and also the acetone, if desired.

The continuously working apparatus are principally built of two columns; at the top of one column the neutralised liquor enters and the second column takes the wood-alcohol vapours escaping from the first column. The neutralised liquor travels in the first column downwards from plate to plate and meets on its way down the steam, entering into the bottom section. The wood alcohol, containing about 30 p.c. of wood alcohol and 70 p.c. of water,

escapes from the top section of the first column, while the acetate of lime solution freed from wood alcohol, is continuously discharged from the bottom section of this column. The 30 p.c. wood alcohol vapours enter the bottom part of second column, and on their way upwards from plate to plate they are concentrated by means of fractional distillation and discharged from

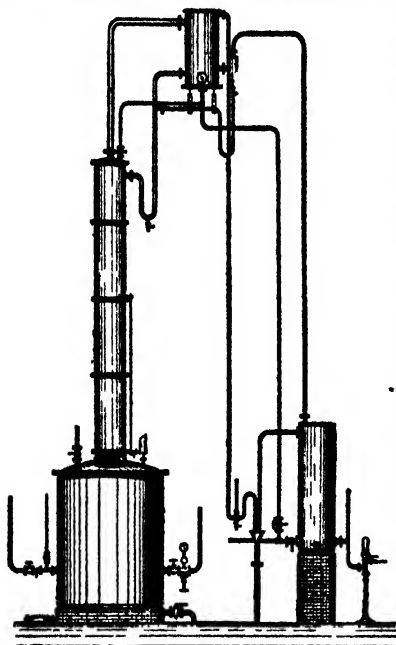


FIG. 14.

Intermittent-working rectifier for wood alcohol; type, F. H. Meyer.

the top section to a separator and from there to a final condenser, leaving the latter as a product containing up to 95 p.c. wood alcohol.

This product corresponds in chemical composition and physical characters with the so-called 'American Crude Wood Alcohol,' shipped in immense quantities from the United States to Europe. It still contains the total amount of acetone, aldehydes, ketones, esters, ammonia, amines, and allyl alcohol, originally contained in the neutralised liquor, and also some of the 'wood oils,' which always accompany the wood alcohol.

The average composition of this product may be given as follows:—

16 p.c. acetone and other ketones.

6 p.c. aldehydes, methyl acetate, amines, allyl alcohol and oils.

70 p. c. methyl alcohol.

8 p.c. water.

The following substances have also been found in 'wood spirit oil,' the residue left after the isolation of methyl alcohol from wood spirit: methyl ethyl ketone, methyl isopropyl ketone, dipropionyl-ethane, methyl oxide, trimethyl acetic aldehyde, isovaleric aldehyde, Δ^4 -hexene-3-one, cyclopentanone (Pringheim and Lebewitz, Ber. 1923, 56, [2] 2034; Chem. Soc. Abstr. 1923, 194, 1, 1052).

In order to manufacture 'pure' methyl alcohol from the crude wood alcohol, all these contaminating products have to be separated.

This is done by fractional distillation, carried out systematically by means of intermittently or continuously operated rectifiers, similar to those above described. The separation is usually assisted by adding chemicals—for instance, caustic soda and sulphuric acid—which destroy, polymerise, or saponify the products to be separated—for instance, aldehydes, esters, ketones, phenols, amines, and so on.

The separation of the acetone and the allyl alcohol, which are always associated with the methyl alcohol, is *entirely done* by a carefully repeated fractional distillation, which yields the concentrated acetone in form of 'head ends' and the allyl alcohol in form of 'tail ends.'

A mixture containing in specified proportion these head ends and tail ends represents the 'denaturing wood alcohol,' used practically everywhere for denaturing alcohol. This material must conform to certain specifications and tests prescribed by the different Governments.

The final product of such a repeated fractional

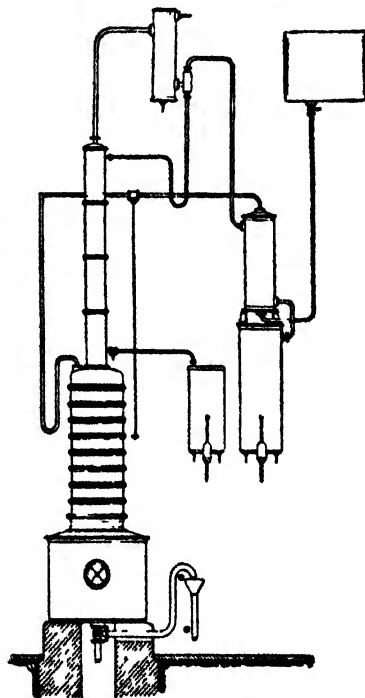


FIG. 15.

Continuous-working rectifier for wood alcohol; type, F. H. Meyer.

distillation, carried out either by intermittently working or continuously working rectifiers, represents the 'pure' methyl alcohol, which is free from acetone or contains only traces of it, and contains up to 99 p.c. real CH_3OH .

Besides this final product, free from acetone, and the 'denaturing wood alcohol' containing acetone, allyl alcohol, and other impurities, a

number of other wood alcohol grades are on the market; for instance, 'pure' methyl alcohol of 99½ p.c. with 0.1 to 1 p.c. of acetone and many other grades demanded by customers.

The pure grades are used for the manufacturing of aniline colours, of formaldehyde, of perfumes; the other grades for varnishes, as solvents, and the poorest grades for denaturing or burning.

The distillation of the neutralised liquor yields, as above shown, two products:

Wood alcohol, as a volatile product;

Acetate of lime solution as a non-volatile residue.

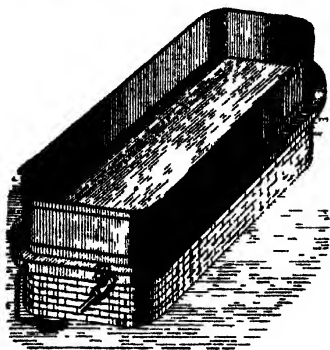


Fig. 16.

Open pan for evaporating acetate of lime solution.

This latter solution holds in suspension insoluble polymerised products, formed by a reaction between phenols and aldehydes with acetate of lime or traces of lime in excess, which must be settled by allowing the liquor to stand.

The settled solution contains varying quantities of acetate of lime, according to the nature of the original liquor and to the process used for distilling off the crude wood alcohol.

These quantities differ from 7 to 25 p.c.; this means, 100 lbs. acetate of lime solution may contain from 7 to 25 lbs. dry acetate of lime, 80-82 p.c. As it is impossible to recover the acetate of lime by a crystallising process on account of its equal solubility in cold and hot water, the solution must be boiled down until the salt is left in the solid state.

Up to the present this boiling was done in two steps. By the first step, the acetate of lime solution is evaporated in open, steam-heated, double-jacket pans (Fig. 16) just to the point at which the concentrated solution becomes solidified by crystallising. This point is reached when the acetate of lime solution contains about 35 to 40 p.c. of the dry salt. The crystallised magma is then spread out in thin layers upon an open drying floor, built of cast-iron plates or steel plates, heated by an open fire or by waste fire gases.

The operation of boiling down the acetate of lime solution to a magma of crystal requires very large amounts of steam on account of the coating of the heating surface by crystals and scales and by the immense reduction of the heat transmitting capacity.

Furthermore, the drying upon an open drying floor necessitates much hand work, as the material must be turned over and

gradually transferred from one end of the drying floor to the opposite one, whereby it travels with the current of the fire gases. This ensures that the wet acetate of lime, which can stand a high temperature, comes in contact with the hot fire gases, while the dried salt or partly dried salt comes only in contact with the fire gases of a lower temperature, in order to protect it against decomposition into acetone.

The author has introduced a drying process, in which the solution of acetate of lime will be continuously and mechanically evaporated and dried, doing away entirely with the steam-heated open pans and the high wages required by opening drying floors.

By this new process, already in successful operation in plants of all sizes from 30 cords up to 250 cords, the acetate of lime solution is continuously evaporated in specially designed multiple effect evaporating apparatus, operated on the same principle as above described for the multiple green liquor distillers.

The weak solution enters the first evaporator, travels from there to the second, and from the second to the third, leaving the same or the last one as a concentrated liquor, which contains up to 30 to 35 p.c. dry salt. This liquor will not crystallise when kept hot.

The liquor flows to a pan into which a rotary drum is dipping, heated inside by steam. This drum becomes coated with a thin layer of the concentrated solution.

While rotating, the thin layer dries quickly, and before the drum dips again into the concentrated solution the magma of crystals, which now coat the surface of the drum, is scraped off by means of knives, working on the surface of the drum (Fig. 17).

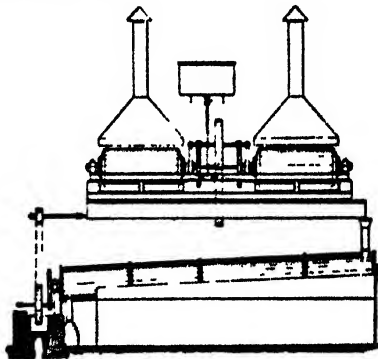


Fig. 17.

Continuous-working rotary evaporator for evaporating and drying acetate of lime; type, F. H. Meyer.

The magma of crystals then travels by means of a conveyor to a belt dryer, built of endless canvas belts or wire cloth belts, upon which the wet salt is transferred against a current of hot air or over pipe coils, heated by exhaust steam. This new type of apparatus for evaporating and drying acetate of lime does away with any kind of hand work; it obviates the disagreeable and unhealthy work of drying upon an open floor; and it saves almost all the wages hitherto spent for drying, and it saves, too, large amounts of fuel. Moreover, the acetate of lime obtained by this process, is of an even

form like peas; it does not contain much dust; it is of a brighter colour and is soft and voluminous, yielding on this account more acetic acid and acetone, when worked up into these products.

MANUFACTURE OF ACETATE OF SODA.

Next to acetate of lime, acetate of soda is the most important salt of acetic acid manufactured in wood-distilling factories.

In order to produce sodium acetate in a crystallised state, the distillate of pyroligneous acid, obtained by one of the processes already described, is neutralised by soda ash. The acetate of soda solution is then freed from wood alcohol by the methods before mentioned, and boiled down by open double-jacket pans, or by

modern multiple effect evaporating apparatus, until the crystallising point is reached. By the next step the condensed solution is completely dried in cast-iron, fire-heated pans, provided with scrapers, and the heating is continued until the whole of the water is driven off and the anhydrous sodium acetate is completely melted, when the liquid mass will have a temperature of about 320° . At this temperature, sodium acetate is not decomposed, but sodium propionate and butyrate, as well as tarry or resinous matters present in the original product, will be destroyed and converted into insoluble matters.

After melting, the mass is dissolved in water to form a concentrated solution and the charred matter separated by filtering the solution,

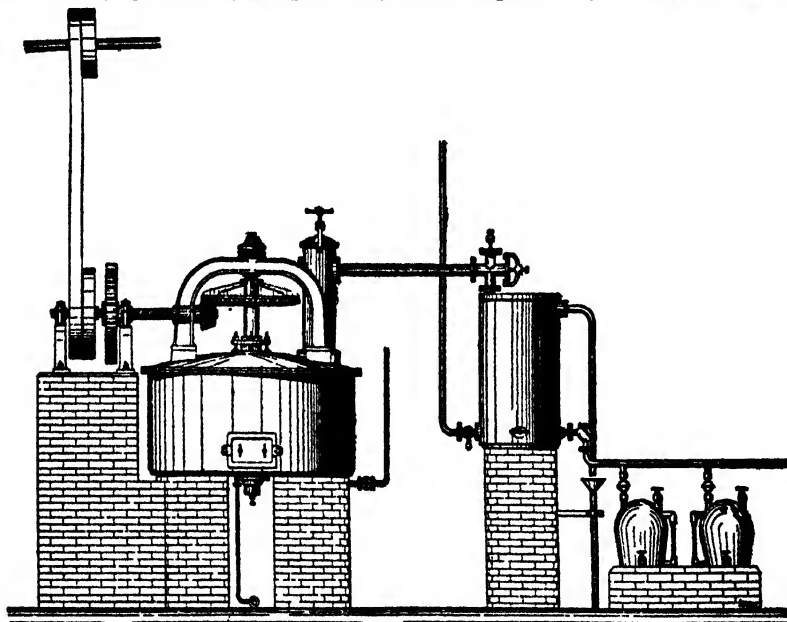


FIG. 18.

Cast-iron still for decomposing acetate of lime by sulphuric acid; type, F. H. Meyer, Hanover-Hainholz.

usually by a filter press. The filtrate is transferred to crystallising vessels and the crystals and mother liquor separated by a centrifugal machine. The crystals are recrystallised and the mother lees returned to the evaporating pans.

TREATING OF THE PRIMARY MARKETABLE PRODUCTS RESULTING FROM THE DESTRUCTIVE DISTILLATION OF WOOD.

The first products resulting from the destructive distillation of wood are: charcoal, crude pyroligneous acid, tar, when hard wood is distilled; or charcoal, crude pyroligneous acid, crude turpentine, crude pine oil and crude pine tar, when pine wood, containing turpentine and resin, is employed. Of these, the charcoal only is ready for sale. The other products must be further treated in order to convert them into marketable commodities.

From the crude pyroligneous acid acetate of lime, acetate of soda and crude wood alcohol

are obtained, and from the latter the 'pure' methyl alcohol, the refined wood alcohol, and the denaturing alcohol as above described.

Many of the wood distilling factories work up the acetate of lime into acetic acid or acetone and the methyl alcohol into formaldehyde.

Manufacture of acetic acid.—In order to manufacture acetic acid, only acetate of lime, 80–82 p.c., is used nowadays as raw material. This is mixed with sulphuric acid of 92 to 98 p.c. in a closed cast-iron still, provided with stirrer and scrapers and heated by high-pressure steam (Fig. 18). After the mixing process is finished the acetic acid is distilled off, a vacuum being maintained in the still during the process of distilling. The crude acetic acid, resulting from the process, contains about 80 p.c. acetic acid (propionic and butyric acid included), traces of sulphur dioxide, and is of a yellow colour. This acid can be used for many purposes in the arts, as, for instance, manufacturing white lead, amyl acetate, &c.

In order to produce 'pure' glacial acetic acid of 96 to 99½ p.c., the crude 80 p.c. acetic acid, obtained by the action of sulphuric acid on acetate of lime, must be rectified in a copper rectifier (Fig. 19).

First a weak acetic acid is obtained containing propionic and butyric acid; then the distillate becomes gradually stronger and after distilling over 40 to 50 p.c. of the original charge, glacial acetic acid distills over: this has a melting-point of 14°-16° and contains 99 to 99½ p.c. CH₃·COOH. At the end of the process the melting-point again falls, and with it the content of acetic acid owing to the presence of propionic and butyric acids.

In order to manufacture 'pure' acetic acid, 99½ p.c., corresponding to the requirements of the pharmacopœas of different countries, the glacial acetic acid, obtained from the first rectification of the crude 80 p.c. acetic acid, will be oxidised and then redistilled by use of a simple still connected with a silver condenser.

Manufacture of acetone.—Acetone is manufactured by the dry or destructive distillation of

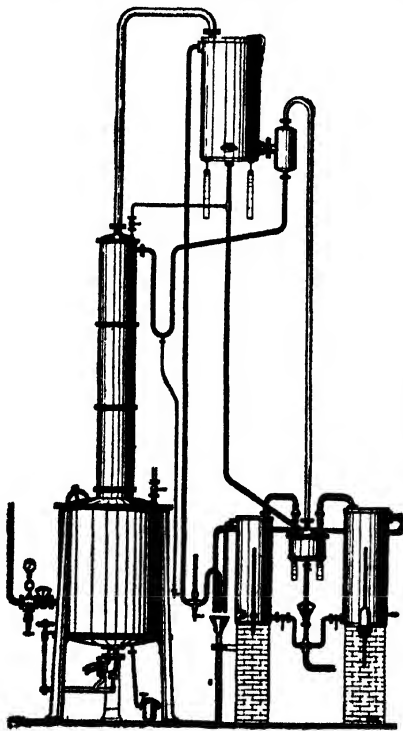
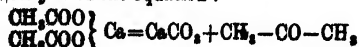


Fig. 19.

Apparatus for rectifying crude acetic acid in order to manufacture glacial acetic acid; type, F. H. Meyer.

calcium acetate. The process corresponds theoretically with the equation:



According to the author's patented process, used in most of the existing acetone factories, acetate of lime is spread out in thin layers on steel plates, to be placed one above the other upon platforms on steel cars, allowing sufficient

clearance from platform to platform (Fig. 20). These cars are pushed into horizontal steel retorts, heated by fire gases. The retorts are capable of treating from 3000 to 15,000 lbs. of

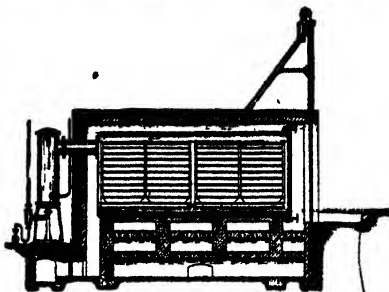


Fig. 20.

Retort for decomposing calcium acetate; type, F. H. Meyer.

calcium acetate in 24 hours and are connected with a condenser. The destructive distillation sets in at about 300°. After the charge is charred, the cars are withdrawn and other cars, already loaded, charged into the retort.

By the older acetone process, calcium acetate was distilled in charges not exceeding 1000 lbs. by means of fire-heated, closed, cast-iron pans, provided with a stirrer and scrapers. But these forms of apparatus yielded only 17 lbs. 'pure' acetone from 100 lbs. of calcium acetate instead of from 20 to 21 lbs. as obtained by the process above described.

There is a third process used, based on the distillation of calcium acetate by means of a stream of superheated steam which is brought directly in contact with the acetate.

The crude acetone obtained by one or other processes contains, besides the acetone, tarry matters, formic and acetic acids, aldehydes, ketones formed by the propionic acid and butyric acid originally contained in the crude material, hydrocarbons, and other products.

By means of repeated fractional distillation, assisted by the use of small amounts of caustic soda and sulphuric acid, acetone of 99½ p.c. is obtained, whilst the tarry matters remain in the residue. The acids are fixed by the alkalis, which destroy the aldehydes, and the foreign ketones and hydrocarbons are obtained as 'tail ends' from the rectifier, from the fact that their boiling-point is considerably higher than that of acetone.

FORMALDEHYDE.

This important disinfectant is obtained from the 'pure' methyl alcohol by oxidising it by the oxygen of the air under the influence of catalytic agents: $2\text{CH}_3\cdot\text{OH} + 2\text{O} = 2\text{CH}_2\text{O} + 2\text{H}_2\text{O}$. The manufacturing process differs in some respects from the theoretical equation, as side reactions set in whereby a part of this formaldehyde is broken up into carbon monoxide and hydrogen, according to the equation $\text{CH}_2\text{O} = \text{CO} + 2\text{H}$.

The excess of oxygen under the influence of the red hot catalytic material combines with the carbon monoxide as well as the hydrogen:

